

SMC Bulletin

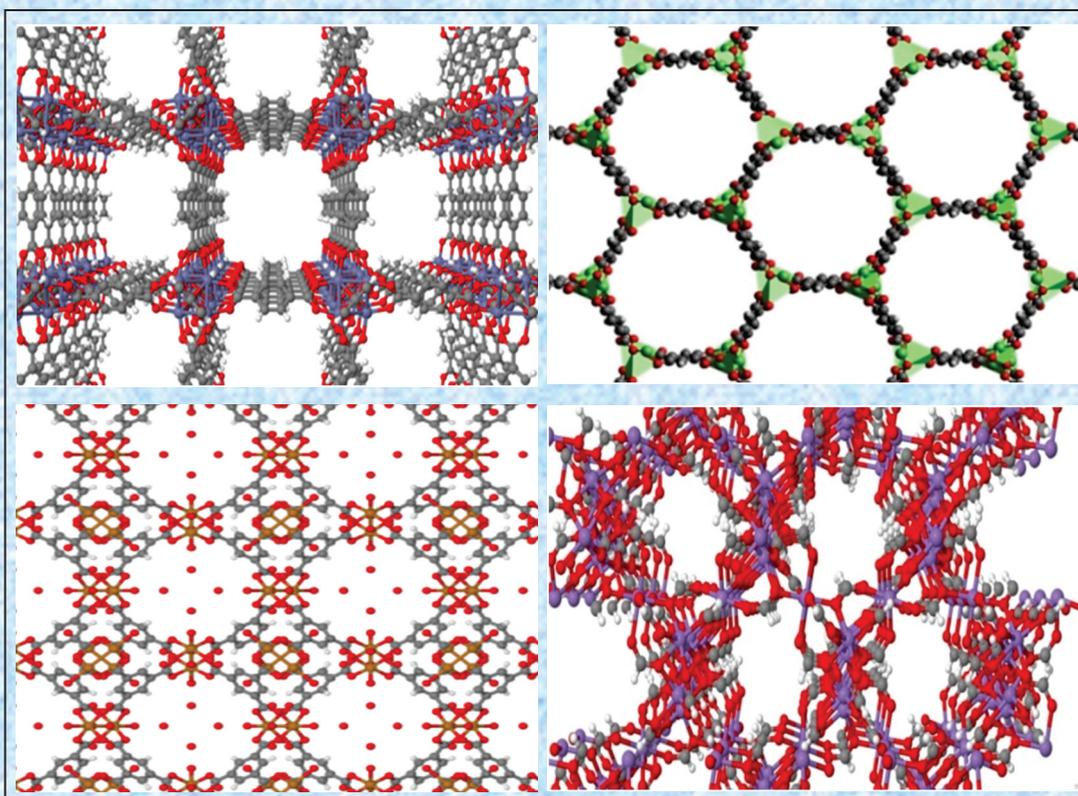
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Volume 7

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August & December 2016



Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

- (a) to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,
- (b) to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,
- (c) to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.
- (d) to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,
- (e) to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.
- (f) to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,
- (g) to undertake and execute all other acts as mentioned in the constitution of SMC.

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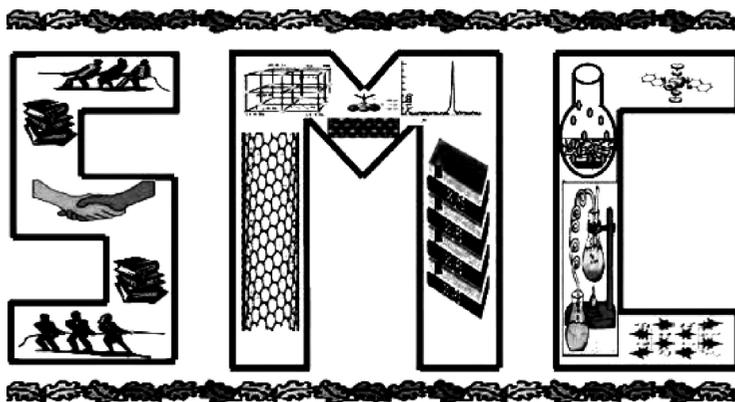
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*Please note that the authors of the paper are alone responsible for the technical contents of papers and references cited therein.
Front cover shows different metal organic frameworks used for Xe and Kr storage and separation.*

Guest Editorial



Dr. D. Das



Dr. B.N. Jagatap

Operation of a nuclear reactor involves a large number of safety measures. This special issue of the SMC bulletin is devoted to various aspects of nuclear safety that are based on chemical sciences, specifically focussing to PWR/PHWR/AHWR technologies. The issue includes six articles covering wide spectrum of safety measures, namely, (1) Specifying water chemistry for safe operation of nuclear power plants, (2) Chemistry of iodine in nuclear reactor containment and mitigation methods, (3) Materials for entrapment of radioactive gases (Xe and Kr), (4) Catalysts for hydrogen mitigation by passive autocatalytic recombiner, (5) Material chemistry issues in managing severe accidents in nuclear reactors, and (6) Corium containment methodology for AHWR: High temperature chemistry of thoria based systems. The articles are written by the experts in the respective fields and cover the very recent advances in the field of nuclear safety. Each article is complete in terms of the technical needs for safety, the details of measures being practiced with their merits and the persistent issues that are currently being examined. The role of material chemists in establishing the safety measures is immense and their involvement in solving and standardizing the safety aspects will be evident in these articles. On behalf of SMC and on our own behalf, we thank all the authors for their scholarly contributions. We are sure that the information presented here will provide up to date knowledge of the chemical safeties to our valued readers.

From the desks of the President and Secretary



Dr. V.K. Jain
President



Dr. P. A. Hassan
Secretary

Dear Readers,

Considering the ever increasing demands for advanced safety features in nuclear power plants, tremendous progress has been made in the area of materials chemistry in developing new materials for improving the operational safety of nuclear reactors. Moreover, new generation reactors such as Advanced Heavy Water Reactor, Compact High Temperature Reactor, Molten Salt Reactors, Accelerator Driven sub-critical systems, etc. require new materials and technologies to incorporate advanced safety features. Increase in the capacity for building of nuclear installations at a given geographical location also puts additional constraints with regard to nuclear safety. Keeping in view of these developments in Nuclear Industry and the pivotal role played by materials chemistry, this issue of SMC Bulletin is dedicated to the theme, "*Chemistry in Nuclear Safety*".

The coolant water chemistry is extremely important in mitigating the corrosion and activity build-up of primary and secondary heat transport system of pressurised heavy water reactors (PHWRs). New developments and current practices in this area are being discussed in this issue. Another important aspect related to safe operation of nuclear power plants is to incorporate suitable hydrogen mitigation systems in the containment building. Development of new catalysts for hydrogen mitigation is of prime importance in nuclear industry and development of passive catalytic recombination devices (PCRD) using advanced catalysts are undertaken in India. Technological advancements in this area have taken a big leap in recent years and have led to the installation of indigenously developed PCRD in Indian nuclear reactors.

Containment of volatile fission products in reactors and reprocessing plants requires effective sorbents and filtration system. Development of materials that can capture volatile fission products in normal operating conditions as well during accidental conditions has become a frontier research area in reactor materials. Generation of thermo-physical/chemical data with respect to high temperature chemistry and phase behavior of new core-catcher materials are also of paramount importance. The present issue brings together articles from experts working in these diverse areas relevant to nuclear safety.

We are extremely thankful to all contributing authors for sharing their knowledge and highlighting the recent advances in this area. We put on record our sincere thanks and appreciation to our Guest Editors, Dr. D. Das and Dr. B. N. Jagatap for sparing their valuable time in bringing out this issue. We are sure our readers will find it extremely valuable and will motivate them to contribute immensely in the years to come. We express our gratitude to each and every members of SMC for their continued cooperation in the growth of the Society.

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Specifying Water Chemistry for Safe Operation of Nuclear Power Plants

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Abstract

Most of the unplanned shut downs in nuclear power plants are attributed to corrosion of structural materials of the water coolant systems. Hence, chemistry specifications of water coolant systems are important from the point of safe operation and maintenance of the nuclear power plants. The chemistry of the water coolant such as pH, dissolved oxygen and the impurities such as chloride, sodium etc., are specified in such a way that the corrosion of structural materials are kept to a minimum and the radiation field is kept under control. While specifying the coolant chemistry consideration is also given for localized corrosion of materials such as corrosion cracking and flow accelerated corrosion which can lead to failure of components. The specification of chemistry of the coolant also takes into account the operating experience of the nuclear power plants and the knowledge gained through research and development. The present R&D in this regard is also mentioned in this report.

1. Introduction

Nuclear power plants are constructed with materials whose performance has been well tested through experiments carried out under simulated conditions. Metals and alloys are used as structural materials of various reactor systems. Fuel cladding, calandria, primary heat transport system, steam generators, condensers are components of nuclear power plants which are constructed of metals and alloys. These metals and alloys are specially prepared to match the requirement of nuclear grade materials. Zircaloy, an alloy of zirconium is used as fuel clad and coolant channel and calandria tube. Various steels including carbon steel and stainless steel are used as structural materials of calandria, primary/reactor coolant systems [1], secondary, tertiary and process water systems. Nickel containing alloys such as Monel-400, Inconels and Incoly-800 are used as steam generator tube materials. Condenser tubes in nuclear power plants are made of alloys such as cupro-nickel, brass, stainless steel or titanium. Even though these materials are nuclear grade and known to be of high quality, undergo corrosion in water because of thermodynamic instability in the medium especially at higher temperatures. Temperatures of the reactor coolant system are in the range 40 – 325° C. As an electrochemical phenomenon, the overall reaction involved in the corrosion is constituted of anodic and cathodic processes. The corrosion rate is decided by the kinetics involved in the electrochemical steps. The water medium, in which the corrosion reaction takes place, plays an important role in deciding the kinetics of the reaction. The level of water impurities such as ionic impurities, dissolved oxygen and also the pH are the factors that control the corrosion.

2. Corrosion in nuclear power plants

i) General corrosion

Corrosion manifests in several forms. General or uniform corrosion is common in most of the reactor structural materials. Corrosion of structural materials in reactor coolant system, followed by the transportation of the corrosion products and their activation by the neutron flux in the core of the reactor result in the formation of radioactive isotopes such as ⁵⁸Co and ⁶⁰Co causing radiation field build up in the nuclear power plants [2]. As a result of general corrosion, metal loss or wall thinning of pipes/tubes also take place. However, the loss of wall thickness due to general corrosion can be taken care of at the design stage itself by adequately giving corrosion allowance. Whereas localized corrosion of materials of nuclear coolant systems is important from the point of safety.

ii) Localized corrosion

Pitting, stress corrosion cracking, nodular corrosion, denting, galvanic corrosion, erosion and flow accelerated corrosion are important forms of localized corrosion observed in nuclear power plants. Among the localized corrosion, flow accelerated corrosion (FAC) is assuming importance in view of its high rate of corrosion and due to its non-compliance to leak before break [3]. Pipe rupture can take place in the FAC affected regions leading to loss of coolant (LOCA). Failure due to FAC has taken place in Surrey (USA), Mihama in Japan and in small scale in several other countries including India [4].

Stress corrosion cracking (SCC) both in inter granular and transgranular modes is also of concern. It is more common in boiling water reactors and in steam generators

of pressurized water reactors and in condenser tubes. Cracking in steam generator tubes is of concern for Pressurized Heavy Water Reactors (PHWRs) as it can lead to heavy water (D₂O) coolant leaking and mixing with the secondary coolant.

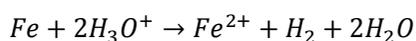
Pitting and under deposit attack are another common form of corrosion failure in nuclear industry.

Failures due to localized corrosion lead to shut down and hence loss of production. Significant number of unplanned shut down of the plants is attributed to localized corrosion. As the temperature and pressure of the water coolant systems in nuclear power plant is high (coolant temperature up to 325°C in water cooled reactors pressure of 125 bar, coolant system failure can result in safety related consequences. Hence, all efforts should be made to prevent such failures. In this regard, the chemistry of the water coolant plays an important role in minimizing such failures and also in controlling the radiation field build-up in the nuclear power plants.

2.1 Controlling the radiation field

Radiation field in the nuclear power plants is attributed to the formation of corrosion products followed by their transportation to the core of the reactor and their neutron activation and re-transportation and deposition in the out-of-core surfaces. Thus, corrosion of out-of-core materials plays an important role in the build-up of radiation field. Controlling the corrosion, the release and the deposition of corrosion products can be achieved by controlling the chemistry of the water coolant.

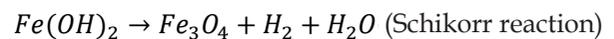
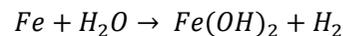
Corrosion rate of any material is dependent on several chemistry parameters, such as the pH, temperature, dissolved oxygen concentration and conductivity which in turn depend on the presence of several impurities. The pH of the water coolant is an important parameter that can be used for not only controlling the corrosion, but also in minimizing the deposition of the corrosion products in the core of the reactor. In a water coolant system where dissolved oxygen is controlled to < 5 ppb and other impurities are kept under control, the rate of corrosion of structural materials such as carbon steel is controlled mainly by the pH of the coolant. The corrosion reaction in the absence of oxygen is written by equation



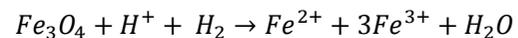
Thus, under acidic condition, the rate of corrosion of carbon steel is high and as the pH increases, the rate decreases. However, under highly alkaline condition the corrosion rate increases again because of the formation of soluble Fe₂O₄²⁻ species. Thus, the pH vs corrosion rate is an inverted bell shaped curve reaching a minimum and

then increasing with further increase in pH. At normal temperatures, the minimum is reached at about pH 9.0 and the rate remains low up to pH 11 and thereafter the rate of corrosion further increases.

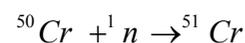
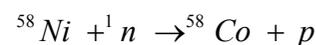
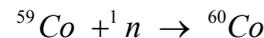
Thus, the pH of the coolant has to be kept above 9.0 but below 11. Another important consideration in specifying the coolant is the transportation and deposition of corrosion products in the core of the reactor. The major coolant channel surfaces to consider are carbon steel and nickel alloys in light-water cooled reactors, and in CANDU reactors. Under primary coolant conditions, these materials form a variety of oxides when they corrode. The solubility of the oxide formed by the corrosion reaction is an important consideration. The magnetite (oxide) over the carbon steel is formed by



The magnetite (Fe₃O₄) thus formed undergoes dissolution



and the dissolved products get transported to the core of the reactor. Depositions of the products in the core lead to the formation of radioactivity build up by the neutron activation



If deposition of the corrosion products in the core is prevented, significant reduction in radiation field can be achieved. Thus, attempts were made elsewhere to understand the process of deposition in the core of the reactor. As the temperature of the water coolant increases as it traverses along the core from the inlet to the outlet (250 - 300°C), the solubility of the corrosion products (Fe₃O₄) as a function of temperature (t) was measured at different pHs. It was observed that the solubility co-efficient (dS/dt) in the temperature range 250 - 300°C [5]

(dS/dt) is +ve if pH of the coolant is > 10

(dS/dt) is -ve if the pH of the coolant is < 10

This indicated that at pH > 10, the solubility of the oxide would increase as the coolant traverses across the core and hence, deposition of corrosion product oxides would not occur. As against this, at pH < 10 because of the negative temperature co-efficient of solubility the deposition in the core is facilitated. This important observation made all the reactor operators to specify the primary coolant system pH to > 10 even though the requirement of pH for corrosion

control is > 9.0 . In Pressurized Water Reactors (PWRs), the corresponding high temperature pH ($\sim 7.2 - 7.4$) is maintained.

In PHWRs, taking advantage of increasing solubility with increase in pH, the observed pH of the heavy water (pHa) coolant is being maintained in the range 10.2 – 10.5 [6]. Some of the reactors, the pH was maintained as high as 10.7 with the hope of maintaining crud free core and achieving low radiation field. However, the observation of excessive wall thinning in certain locations of the carbon steel feeder pipe led to rethinking on the upper value of pH.

2.2 Flow Accelerated (assisted) Corrosion and water chemistry

As flow accelerated corrosion (FAC) observed in certain locations of the carbon steel pipes has resulted in wall thinning which is more than the corrosion allowance assumed during design, it has emerged as a cause of concern for the operators of the nuclear plants. Detailed studies carried out on the chemistry parameters affecting the rate of FAC indicated that pH of the water coolant is one of the important factor. Increase in pH from the neutral condition resulted in decrease in the rate of FAC. However, the rate of FAC after reaching a minimum at about 9.8, started increasing with further increase in pHa. Thus, an optimum pHa is to be specified taking into consideration the radiation field build-up and the FAC. The build-up of radiation field, as stated earlier, depends very much on the quantity of crud deposited in the core (fuel bundles and pressure tubes in the case of PHWRs). The quantity of crud deposited in the core decreases with increase in pHa from 9.5 as the solubility co-efficient assumes positive values after this pHa value. Hence, higher pHa of the heavy water coolant ensures clean core and thereby resulting in lower activation and radiation field. Currently, all the PHWRs are operated at a pHa of 10.2 – 10.5. Detailed studies are required to fine tune the pHa so as to have minimum FAC without compromising on the low radiation field achieved by maintaining pH > 10.2 .

2.2.1 Possibility of controlling radiation field and FAC in PHWRs with metal ion passivation

Boiling Water Reactors (BWRs) achieved radiation field reduction by injecting zinc ion at a few ppb concentrations (2 – 5 ppb). Radiation field was reduced by a factor of two to five in the BWRs that followed the zinc ion passivation (ZIP) technique. In Pressurized Water Reactors (PWRs) also, this technique was adopted and it is claimed that radiation field reduction up to a factor of two was achieved. It is believed that zinc ion gets incorporated in the chromium containing oxide film of the reactor coolant system surfaces and helps to form thin and tenacious

oxide layer. Formation of thinner and tenacious oxide film on the structural materials result in low inventory and low release of corrosion products there by resulting in low radiation field in the out-of-core surfaces of BWRs [7]. Also, it is explained that zinc ion has a preference for the tetrahedral sites of the normal spinels such as chromites ($M_xFe_yCr_2O_4$), thereby pre-empting the pick-up of active ions such as Co^{2+} (^{60}Co , ^{58}Co etc.). The zinc ion has high tetrahedral site preference energy as compared to cobalt. Hence, zinc ion is preferentially picked up on the chromite oxide lattice. The cobalt ions that are not picked-up by the chromites are removed by the purification system.

Attempts to evaluate the usefulness of zinc ion passivation (ZIP) in PHWRs indicated that under the alkaline pH condition prevailing in the primary coolant system, the zinc ion is expected to be in zincate (ZnO_2^{2-}) form. Also, the dominant oxide in PHWRs is magnetite (Fe_3O_4) which is a ferrite having inverse spinel structure. Magnetite is formed in the carbon steel (CS) feeders and headers. The surface area of carbon steel feeders and headers is quite high (1500 m^2 for 220 MWe PHWRs). As the corrosion rate of carbon steel is higher than stainless steel, the thickness of oxide formed over the CS surface ($10 - 40\ \mu\text{m}$ over a period of 10 years) and the release rate of oxide is quite high. Hence, deposition of ferrites takes place on steam generator tubes (surface area 9000 m^2 for 220 MWe PHWRs) which are made of either Monel-400 (Cu-Ni alloy) or Incoloy-800 (Fe-Cr-Ni alloy) and to some extent on core zircaloy surfaces. Thus, even though the Incoloy-800 steam generator tubes contain significant amount of chromium and has chromium containing oxide film, the deposited oxide which is mostly iron oxide with incorporated nickel dominates the oxide film over its surface. These nickel containing iron oxides (ferrites) also have inverse spinel structure. The divalent Zn^{2+} incorporation in the octahedral site of the inverse spinel is not facilitated. Thus, considering the fact that zinc exists mostly in the form of zincate ion and the incorporation of zinc ion in the ferrite is not facilitated, zinc ion at ppb level concentration is not expected to significantly influence the corrosion kinetics of carbon steel and the cobalt activity pick-up on its oxide surface. Hence, alternate ions were evaluated for their suitability to serve as passivators for the ferrites dominated primary heat transport system of PHWRs and magnesium ion emerged as a possible alternative.

2.2.1.1 Magnesium ion as passivator

Magnesium and zinc are divalent and has a diagonal relationship in the periodic table of elements and hence have similar properties. The following are the characteristics of magnesium ion:

- i) Magnesium ion exists as Mg^{2+} or $Mg(OH)^+$, the latter can easily dissociate to Mg^{2+} .
- ii) Mg^{2+} when incorporated into the ferrite lattice forms a stable $MgFe_2O_4$.
- iii) Under the alkaline condition (pHa 10.2 – 10.5) and high temperature (300°C) prevailing in the primary coolant system of PHWRs, it has significant solubility (about 10 ppb).

Considering all these aspects, attempts were made to investigate its suitability as passivator for the structural materials of primary coolant system [8]. Repeated experiments indicated the following:

- i) The corrosion rates of carbon steel at ~ 300°C and under pH 10.0 decreased by a factor of two
- ii) The oxide thickness and corrosion release rate were found to be less when the carbon steel was exposed to magnesium containing solution
- iii) Inconel-800 also showed lower corrosion rate
- iv) Zircaloy was found to be compatible with magnesium in the absence of silicates

Considering the above, magnesium ion can be a passivator under PHWR conditions. However, it has to be tested under reactor conditions for ascertaining its usefulness in reducing the radiation field in the primary coolant system of PHWRs.

As, magnesium ion modifies the oxide film on carbon steel, the magnesium incorporated magnetite ($Mg_xFe_{2-x}O_4$) is expected to have lower solubility as compared to magnetite (Fe_3O_4). As flow accelerated corrosion (FAC) depends on the solubility of the oxide over the carbon steel surface, passivation with magnesium ion is also expected to have beneficial effect. Efforts are on to experimentally prove the beneficial effect of magnesium in controlling the FAC.

In addition, attempts are being made to ascertain the beneficial effect of forming film that contains nano sized magnetite particle in reducing the radiation field and flow accelerated corrosion in the PHT system of PHWRs [9].

2.3 Secondary coolant system chemistry

The secondary coolant system of PHWRs employs light water as coolant and it is a two phase system. The heat transferred from the primary coolant system converts the water into steam. The steam at about 250°C runs the turbine to generate electricity. The steam after running the turbine is condensed in the condenser and sent back to the steam generator for raising the steam. Part of the steam after running the turbine is extracted to re-heat the water that goes from the condenser to the steam generator.

The chemistry specification of the system is framed in such a way that the entire system is protected from corrosion and deposition in the steam generator tubes and turbine internals. The pH is maintained in the range 8.8 – 9.5 and the dissolved oxygen is controlled by the de-aerator and by adding hydrazine.

The pH of the secondary coolant is maintained by adding all volatile amines. Several amines can be added to maintain the pH [10]. The following amines are used:

- i) Ammonia
- ii) Morpholine
- iii) Ethanolamine

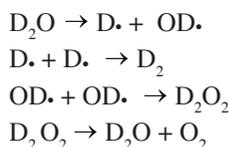
At present in Indian nuclear plants Ethanolamine (ETA) is used. The main consideration in the choice of amines for the control of pH in the secondary system is its distribution between water and steam. The distribution co-efficient (steam / water) should be such that as the steam condenses, the water phase of the two phase mixture should contain sufficient amine to protect the carbon steel/low alloy steels used in the system. In this respect, ammonia is limited by its tendency to remain in the steam phase. Whereas morpholine and ethanolamine fares better as they stay in the water phase.

2.3.1 Controlling flow accelerated corrosion in secondary coolant system

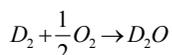
After flow accelerated corrosion (FAC) became a cause of concern, more importance was given for the distribution co-efficient and in maintaining higher pH in all parts of the secondary system. Rate of FAC decreases with increase in pH (for the range of pH 8.5 – 9.5 maintained in the secondary system). Hence, attempts are made to maintain higher pH in all parts of the secondary coolant system. The two phase regions such as steam extract lines and the lines that carry water from the condenser up to steam generators are prone to FAC. The two phase lines can be protected by choosing an amine whose distribution co-efficient is < 1. The amine should also have appropriate pK values so that higher pH can be ensured even with low concentration of added amine. In this regard, ethanolamine is considered to be better as compared to morpholine and ammonia.

2.4 Safety measures in the operation of moderator system

The PHWRs has a separate moderator system. High purity heavy water (D_2O) moderates the neutrons formed in the fission reaction. The neutrons and the accompanying γ -photons radiolyse the heavy water to form deuterium (D_2) and oxygen (O_2).



The deuterium and oxygen thus formed in the moderator moves to the moderator cover gas (Helium). The cover gas containing the deuterium and oxygen is continuously passed through a Recombiner Unit (RU) that contains palladium catalyst and forms into heavy water



The deuterium (Isotope of Hydrogen) in combination with oxygen can form an explosive mixture. Hence, its concentration has to be controlled in the moderator cover gas so that it never exceeds the 8% limit set for preventing explosion. Normally deuterium (D_2) is maintained below 2% V/V concentration. Both deuterium and oxygen are expected to be formed in stoichiometric concentrations. But, very often non stoichiometry is observed due to the consumption of hydrogen peroxide (precursor to oxygen) by the organics released by the ion exchange resin kept in the purification system. The excess deuterium released does not undergo recombination as there is paucity of oxygen. Hence, deuterium concentrations can build-up. This is taken care of by purging the cover gas with Helium. An attempt is being made to evolve fuel cell based hydrogen (Deuterium) burner so that the excess deuterium is also converted to D_2O and recovered back.

Conclusion

Thus, utmost care is taken in framing the chemistry specifications of water coolant systems of nuclear power reactors so that safety of the plant is ensured. In this regard, the PHWR water coolant systems' specifications are optimized taking into account the experience of operating the systems and the observations made out of the R&D carried out world over. Work is being continued

to modify/introduce new chemistry features such as metal ion passivation/nano coating so that further improvement in the performance of the system is ensured.

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Since 1985, **Dr. S. Velmurugan** has been carrying out R&D activities in the field of water chemistry as relevant to Pressurized Heavy Water Reactors (PHWRs). His main research objectives are to control the radiation field build-up in the reactor coolant systems of Indian nuclear reactors. He has carried out extensive works to understand and optimize chemical processes for the decontamination of reactor coolant systems of PHWRs. These include studies on oxide/oxide film dissolution, ion exchange studies with metal ions, activities and complexant pick-up on ion exchange resins, studies on corrosion behaviour of reactor structural materials in the chemical formulations used for the decontamination, chemical cleaning etc. The chemical process thus evaluated has been applied several times to decontaminate the Indian PHWRs. He has also carried out research on corrosion of reactor structural materials, evaluation of high temperature dispersants, radiolysis of gadolinium nitrate and chemistry specifications of Advanced Heavy Water Reactors (AHWRs) etc. As Chairman of the Committee on Steam and Water Chemistry (COSWAC) of nuclear power plants he advises on various chemistry issues. In addition, he is serving as Professor in Homi Bhabha National Institute, Mumbai and in guiding PhD students. He has about 58 journal papers to his credit. Presently, he is heading the Water and steam Chemistry Division of Chemistry Group located at BARCF, Kalpakkam.

Chemistry of Iodine in Nuclear Reactor Containment and Mitigation Methods

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Abstract

Radioiodine has been identified to be a major contributor to the potential source term for radiological impact assessment under certain postulated nuclear accident scenarios. Various phenomena governing iodine speciation, partitioning and subsequent release, under conditions expected to prevail in a reactor containment during an accident, have been investigated through several large, intermediate and small scale experimental programmes, namely PHEBUS-FP programme, Thermal Hydraulic and Iodine experiments (THAI), Programme on Air Radiolysis Iodine and Surface Interactions (PARIS) and Behaviour of Iodine Project (BIP). An updated review of the existing literature on iodine chemistry in the containment and the recent advances in mitigation methods is presented here. A few unresolved issues pertaining to the chemical forms of iodine (elemental, molecular, aerosol, or organic) in the reactor containment, which need further investigations for realistic estimation of the source term as well as for designing appropriate techniques for management of radioactive releases are highlighted.

1. Introduction

The inability to remove heat produced by the reactor core, as in a typical loss of coolant accident (LOCA), leads to overheating of the reactor fuel followed by rupture of fuel cladding and subsequent release of fission products. These fission products are transported through the reactor coolant system (RCS) into the reactor containment in the form of gases or aerosols along with substantial release of steam and non-condensable gases such as H₂. This leads to excessive pressure build-up in the containment. In order to ensure containment integrity, it may be necessary to release the high temperature, high pressure gas, from the containment to the outside. The type, quantity and chemical nature of the released material, which can act as the sources of potential for exposure to radioactivity is called "source term" and this must be assessed as realistically as possible to determine the immediate and long-term health and environmental effects, and to devise management strategies. Plant assessments for a range of accident scenarios have shown that iodine contributes significantly to the source term. During normal operation of a nuclear power plant, the amount of iodine created inside the fuel is relatively small compared to other fission products. For example, in a PWR 900 core, at its equilibrium, the total iodine mass constitutes a small fraction (~12kg) of the FPs (~2000 kg); about ten times less than that of cesium. Iodine has many short half-life isotopes: ¹³¹I (8 days), ¹³²I (2.3 hrs), ¹³³I (20.8 hrs), ¹³⁴I (0.9 hr) and ¹³⁵I (6.6 hrs). Therefore total iodine activity is one of the most important among other fission products (around ten times more than cesium), over the

first few tens of hours from the core shutdown. During the Fukushima Daiichi nuclear power plant (FDNPP) accident (11th March, 2011), ~ 160 PBq of ¹³¹I, in addition to 18 PBq and 15 PBq, respectively of ¹³⁴Cs and ¹³⁷Cs, as well as other radionuclides were emitted into the atmosphere [1].

Assessment of radioiodine emissions incorporate large uncertainties due to different chemical forms in which iodine can exist such as inorganic iodine (I₂ and IO_x) and volatile organic iodine (methyl iodide). Most of the airborne ¹³¹I from Chernobyl that reached Japan was found to be a mixture of I₂ (5%), HOI (6%), aerosols (19%), and organic compounds (70%) [2]. A recent analysis of the extent of reactor core damage and the releases of radioactive material from the Fukushima Daiichi accident suggested that a significant amount of the radioactive iodine was released in elemental and organic forms [3]. Gaseous molecular iodine can also be oxidized by air radiolysis products (generated under high radiation fields inside the containment) into aerosol borne iodine-oxygen-nitrogen compounds. Organic iodides (RI, R=CH₃ for example) are a particularly volatile form of the fission product iodine that are difficult to retain by post-accident filtration systems and pose a serious radiological risk to health. Iodine is biologically active and in mammals it accumulates readily in the thyroid. Exposure to high levels of radioactive iodine may increase the risk of radiogenic thyroid cancer in later life. It is therefore important to build sufficient knowledge base in respect of iodine behavior in the containment in order to evaluate its possible release after LOCA condition and to establish

the impact of iodine mitigation measures to prevent or minimize iodine release to the environment. To this end, experimental and modeling efforts on iodine behaviour under severe accident conditions were initiated by Institut de Radioprotection et de Sûreté Nucléaire" (IRSN), the Nuclear Energy Agency (NEA) of the Organization for Economic Cooperation and Development (OECD), Canadian Nuclear Laboratories (CNL, formerly AECL) and other agencies. In this review, we have attempted to present the insights gained on iodine chemistry in the containment from concerted programmes of the international iodine community. This review is organized as follows:

Section 2 briefly introduces the main experimental results on iodine and cesium chemistry, carried out after the Three Mile Island -2 accident. Section 3 discusses the Phebus fission product experiments designed to understand main phenomena occurring during a severe accident in light water reactors (LWR), with focus on degradation of fuel rod bundle, behaviour of fission products as well as structural and control rod materials released via primary coolant circuit into the containment. Section 4 presents the insight gained on formation and destruction of air radiolysis products (ARP) in severe accident containment atmospheres and the impact of ARP on conversion of iodine to iodine oxides. Section 5 describes the studies pertaining to characterization of iodine oxides and their adsorption and re-vaporization behaviour. Studies on radiolytic oxidation of organic iodine, and iodine-paint interaction are discussed in section 6 followed by some new insight obtained on the effect of beta radiation on iodine speciation (section 7). Iodine chemistry in the aqueous phase is briefly discussed in section 8. Recent advances in iodine mitigation strategies are discussed in section 9. Finally, in Section 10, the specific issues that need focused attention are highlighted.

2. Status of knowledge on iodine and cesium chemistry from assessment of Three Mile Island (TMI) Unit -2 meltdown

Preliminary studies performed after the TMI-2 reactor meltdown (March 28, 1979) suggested that iodine is mostly transported in the RCS as cesium iodide (CsI) and partly emitted in volatile form in the containment [4, 5]. This scenario is based on the rationale that during normal operation of a nuclear power plant, the fission products are almost completely retained in the fuel pellets barring a small fraction (<1atom%) which escapes into the gap between the fuel pellet and metallic cladding and to the free volume on top of the fuel column [6]. This fraction mostly comprises of noble gases Xe and Kr and some volatile elements (I, Br, Cs, Te). However during a loss of

coolant accident in a nuclear power plant, the temperature of the reactor core rises rapidly and the fuel loses its ability to retain the fission products. The enhanced mobility of fission products in the lattice facilitates reaction between them at the grain boundaries leading to formation of mixed compounds such as CsI or Cs₂Te. In the event of a tube break, these species are released into the containment atmosphere both in gaseous and particulate forms. The particulates are expected to be removed from the gas phase of the containment by engineered safety systems such as sprays and suppression pools as well as by natural aerosol processes like settling and diffusiophoresis. However, the CsI aerosol particles when released into the containment are likely to settle in the sump, where they instantaneously dissociate into Cs⁺ and I⁻. Gaseous elemental iodine can hydrolyse in water or steam. Iodine aqueous chemistry is very complicated as it can assume different oxidation states. Acidification of water due to formation of nitric acid as well as other radiolytic processes promote partitioning of molecular iodine back to the atmosphere. It might also lead to formation of volatile organic iodides. Elemental iodine in gas phase can react with radiolysis products such as ozone to form iodine oxides (IO_x) aerosols. Both IO_x and CsI aerosols could alternatively condense and undergo interactions with the containment surface materials and may form new iodine species of less volatility which might reduce the volatile source term. The probable transport flow path of iodine activity in reactor containment under severe accident conditions is schematically shown in Fig.1.

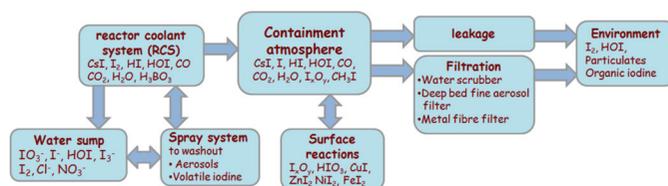


Fig. 1 Flow chart showing transport of iodine activity in reactor containment under severe accident conditions

With partitioning taking place between the gaseous, aerosol, aqueous and condensed phases, the various physicochemical processes can eventually affect retention probability in the reactor containment. A thorough understanding of the reactor containment chemistry is therefore crucial for predicting the source term as realistically as possible. To this end, several large, intermediate and small scale experimental programmes namely, PHEBUS FP programme, Thermal Hydraulic and Iodine experiments (THAI), Programme on Air Radiolysis, Iodine and Surface Interactions (PARIS) were launched to study the nuclear power plant reactor core degradation, the transport of fission products and their release into the

reactor containment volume. The key results from these programmes are discussed in the following sections.

3. Main phenomena occurring during a severe accident in light water reactors (LWR)

The International Phebus Fission Product (Phébus FP) programme, initiated by the French Institut de Radioprotection et de Sûreté Nucléaire (IRSN) in cooperation with European Commission in the early 90s, provided the opportunity to study iodine behaviour during core meltdown accident conditions, using realistic configuration and chemical environment. These tests carried out in a scaled down model of a PWR reactor (reduced scale 1/5000 vs. 900 MW Pressurized Water Reactor), were designed to study degradation of fuel rod bundle, behaviour of fission products as well as structural and control rod materials released via primary coolant circuit into the containment. These experiments established the fact that iodine is formed in multiple forms, thus confirming the complex iodine chemistry during such an event. The data from the first two Phebus tests FPT0 and FPT1 indicated a significant fraction of iodine (~2-4% of bundle inventory) reached the containment in vapour form. This suggested the occurrence of non-equilibrium reactions in the primary circuit. The Phebus tests also revealed organic iodine to be the predominant gaseous iodine species in the long term containment atmosphere; hence any severe accident measure to reduce iodine source term to the environment needs to consider this iodine speciation. In a surprising revelation, all the Phebus FP tests showed a steady state concentration of iodine vapour in the containment atmosphere for days, unaffected by temperature or pH of sump waters. Another highlight was the importance of modeling the Ag-In-Cd control rod degradation. Silver (Ag) released into the containment as a result of control rod melting was observed to play a key role in the sump chemistry. Silver, in excess quantities, as compared to iodine in sump water, precipitated as silver iodide, thus efficiently suppressing the volatilization of gaseous iodine from the sump. However, the chemical and physical form of Ag reacting with iodine could not be ascertained. The Phebus results were analyzed using engineering software code packages such as ASTEC30 and MELCOR31 which are based on phenomenological descriptions of the physical and chemical processes. The rate of release of iodine and aerosol sedimentation rate were consistent with current severe accident modelling. The depletion of gaseous iodine from the atmosphere was much faster than expected in the early phase of the tests. Although the Phebus results confirmed numerous assumptions made in model systems, they

have put a premium on acquiring a detailed mechanistic understanding of the following issues:

1. Influence of radiolytic processes on conversion of gas phase molecular iodine and organic iodide to iodine oxides, iodine nitrooxide particles [7].
2. Contribution of painted surfaces and steel walls towards gas phase iodine species concentration

4. Air radiolysis and iodine sorption studies in severe accident containment atmosphere

With a view to generate sufficient database on air radiolysis products (ARP) formation and destruction in severe accident containment atmospheres, study the impact of ARP on conversion of I_2 to IO_x and to develop new or validate existing kinetic models of formation and destruction of iodine oxides, IRSN in collaboration with AREVA NP initiated the two phase small scale experimental Programme on air radiolysis and iodine sorption (PARIS) in 2002.

4.1 ARP formation and destruction in the presence of structural containment surfaces

The non-iodine tests of PARIS-1 project [8] were aimed at determining the rates of formation and destruction of air radiolysis products in the presence of both structural containment surfaces (decontamination coating "paint" and stainless steel), aerosol particles such as silver particles (from control rods) in boundary conditions representative for LWR or PHEBUS facility containments. The ARP concentration was observed to increase with dose and approach saturation levels at doses higher than about 1kGy. This behaviour was more evident in oxygen/steam atmospheres, producing ozone, than in air/30% (v/v) steam atmospheres; the latter favouring the model-predicted ongoing production of nitrogen dioxide even at very high doses (Table-1). The results obtained in oxygen/steam atmospheres could be explained by a simple empirical model, based on zero-order production and a first-order destruction of air radiolysis products. The PARIS data did not show any influence of temperature on ARP concentrations for the experiments carried out at 80 and at 130° C in air/steam, air/steam/hydrogen and oxygen/steam atmospheres. The behaviour in air/steam atmosphere seemed to contradict Funke's observation [9]. It is quite possible that any small temperature effect could have been masked by appreciable scattering of the experimental air radiolysis product concentrations and too few data points. Therefore, PARIS data did not confirm or improve current approaches for the temperature dependencies.

Table-1: Evolution of O₃ concentration versus dose at 130 °C in an oxygen/30 % (v/v) steam atmosphere, comparison of data and empirical model [8]

Dose (kGy)	[ARP] Exptl. (mol / L)	[ARP] Model (mol / L)	% deviation
0.1	4.12 E-8	1.12 E-8	267.8
1.5	1.46E-7	1.07 E-7	36.4
23.8	8.1 E-8	1.78 E-7	54.5
37.5	6.8 E-8	1.78 E-7	61.8

Furthermore, the inserted surface coupons (stainless steel, epoxy paint and silver) having representative surface/volume ratios did not exhibit significant effects on the air radiolysis product concentrations. The fact that small effects could be hidden behind appreciable scattering of data could not be ruled out. Hence no definitive conclusions on model rate constants of ARP or ozone destruction at surfaces could be formulated from the PARIS database. The PARIS-1 results thus stressed the need for refining the ARP concentration measurements and speciation.

4.2 Radiolytic conversion of iodine to iodine oxides

An extensive experimental database on radiolytic conversion of molecular iodine into iodine oxides at different boundary conditions relevant to severe accident containment atmospheres was generated in the second phase of the PARIS project. The iodine tests were performed at very low, realistic iodine concentrations. The formation of IO_x species was considerably reduced in H₂ atmosphere as the later decreased the oxidation potential of the irradiated atmosphere. Temperature variation from 80 to 130 °C did not exert significant impact on the IO_x formation. In the PARIS tests, the evolution of I₂/IO_x conversion was measured only at two limited dose ranges, hence development of a quantitative model for IO_x formation kinetics could not be taken up.

In order to understand the influence of steel, paint and silver surfaces on iodine radiochemistry, coupons with surface to volume ratios representative of LWR and PHEBUS-FP containments were used. Studies with silver surfaces were aimed at simulating a conceivable effect of aerosols containing silver on the radiolytic I₂/IO_x conversion.

Painted surfaces proved to be efficient traps for I₂. In an air/steam atmosphere at initial I₂ concentrations below 1 × 10⁻⁷ mol L⁻¹, the radiolytic oxidation of iodine in the gaseous phase is largely suppressed. Only at higher

initial I₂ concentrations, radiolytic IO_x formation seemed to compete with I₂ adsorption. Contrary to the experimental data, the model predicted dominant IO_x formation at higher doses. Efforts are underway to develop a new model of release of organic iodides from painted surfaces under irradiation. Fig.2 summarizes the main phenomena considered relevant for the interaction of iodine and steel (left) and epoxy paint (right).

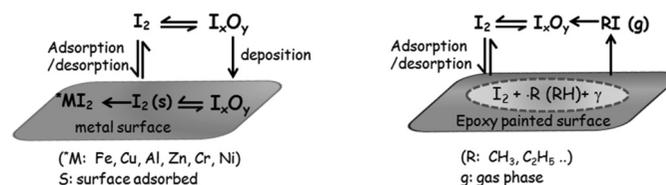
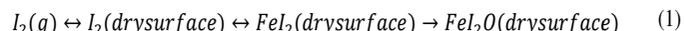


Fig.2 Phenomenon considered relevant for the interaction of iodine with metal (left) and epoxy painted surface (right) [10]

Stainless steel turned out to be no efficient trap for iodine, and so the majority of the iodine was converted into iodine oxides in these tests. These experimental results were well reproduced by empirical, reversible iodine adsorption model. However, some recent updates on the mechanism highlight the fact that some iodine is definitively trapped on the stainless surface in oxidized form. The proposed model considers two reversible steps leading to adsorption of iodine under I₂ and FeI₂ forms, followed by an irreversible step that involves chemical trapping of an oxidized species (FeI₂O).



Using this new kinetic model which has recently been updated in ASTEC V2.1, the interaction between iodine and steel surface can be predicted better.

Silver surfaces also presented an effective I₂ trap in the PARIS tests. Unlike the painted surfaces, the model calculation successfully reproduced the experimental iodine partitioning between gaseous phase and surface [10].

A large number of irradiated iodine tests were performed in the PARIS project. However, the numerous experimental parameters involved did not allow sufficient number of repetitions, which otherwise would have reduced the large data scattering. The impact of silver on iodine radiochemistry can be quantified in a better way by using more representative conditions such as replacing the silver foils in the PARIS project with multi-component aerosols containing silver.

5. Behaviour of iodine oxides (I_xO_y) - characterization, adsorption and re-vaporization

The behaviour of iodine oxides and their characteristics were investigated in the intermediate scale Thermal

Hydraulic and Iodine (THAI) tests Iod-13 and Iod-14. The THAI facility did not have provision for ionizing radiation sources. Conditions for radiolytic oxidation of molecular iodine were simulated by directly injecting O_3 from an ozone generator in order to oxidize gaseous I_2 . The tests performed at temperatures of about 100°C and relative humidity of about 60–70% revealed a substantial production of iodine oxides [11]. The observed iodine oxides had mean volume-related diameters of ~ 0.35 micron and showed low deposition rates in the tests performed in the absence of other nuclear aerosols, the later condition being necessary so as to mimic the early accident scenario in LWR containment. Further studies are being conducted to get a better estimation of their size, composition and behaviour under different conditions within the objective to better consider their behaviour in severe accident codes. The THAI test did not provide any evidence for gaseous I_xO_y suggesting that formation of iodine aerosols from gaseous precursors, i.e., iodine and ozone, is fast as compared to their chemical interaction. The radiolytic stability of I_xO_y was not addressed in the THAI tests; this aspect is currently being investigated in the Experimental Programme on Iodine Chemistry Under Radiation (EPICUR) project.

Aerosol particles containing iodine deposited on various surfaces may act as a source for volatile elemental iodine. To this end, preliminary studies on adsorption and re-vaporization behaviour of iodine oxide aerosols deposited on containment surface materials in LWR were initiated at VTT Technical Research Centre, Finland. The containment surface materials chosen for this study include Teknopox Aqua VA epoxy paint, stainless steel (SS 316), copper, zinc, aluminium, platinum and palladium). Raman and X-ray photoelectron spectroscopy (XPS) analysis did not reveal any chemical bond between iodine oxides and stainless steel, paint or Al surfaces. Raman spectrum indicated iodine to be in a partially hydrated form of $I_2O_5 \cdot HIO_3$ on painted and SS surfaces. Peaks corresponding to solid HIO_3 were detected in the Raman spectra of copper and zinc samples. Further, XPS analyses suggested possible reactions between iodine oxide aerosols and copper and zinc surfaces, CuI and ZnI_2 being the probable reaction products. Peaks of molecular iodine (I_2) were detected in the Raman spectra of all samples, which would have resulted from the decomposition of I_2O_4 and I_4O_9 particles on the surfaces [12].

The influence of temperature, humidity and radiation fields on iodine chemistry in a post- accident containment was also investigated. Humidity in the air was found to be the major parameter for the decomposition of iodine

oxide aerosols generated at a temperature of 120 °C. Pre-irradiation and pre-heating were found to have influence the ability of the paint to chemisorb iodine. Irradiation can cleave C-C bonds and thus remove groups which may be required for chemisorption. The aerosol deposited on Pt and Pd was easily re-vaporized by humidity, heating and low dose of gamma rays thereby suggesting that the functionality of recombiners will not be seriously affected by these aerosols. The deposited aerosols could be the main source of inorganic iodine and may influence iodine volatility in the long term. Hence determining their radiolytic decomposition kinetics is very crucial for reliable iodine source term estimation.

6. Radiolytic oxidation of organic iodine or iodine-paint interaction

The Behavior of Iodine Project (BIP) [13] was initiated to investigate various aspects of iodine-containment paint interaction such as iodine sorption behaviour and the subsequent formation of organic iodides. BIP tests were focused on epoxy paint, which are commonly used surface coatings within containment buildings. The results suggested the strong influence of relative humidity on the rate of iodine deposition on epoxy paints. The deposition velocities on different epoxy paints were also different. Experiments investigating the formation of methyl iodide from irradiated paint showed that CH_3I concentration, determined by a balance between fast formation and destruction, exhibited time dependent behaviour during irradiation. The presence of residual water affected the CH_3I production rate. Tests using coupons loaded with iodine by contact with aqueous solution showed higher org-I formation rates compared to gas-loaded coupons. These observations suggest that water may mobilize paint solvents trapped within the paint matrix or maybe required for an aqueous phase process within the paint pores.

Investigations on radiolytic oxidation of organic iodine were carried out in the NROI-2 and NROI-3 project (2009-2014) at VTT Technical Research Centre, Finland and Chalmers University of Technology, Sweden as a part of the Nordic collaboration NKS-R programs. Previous studies have shown that along with CH_3I , various short chain RI such as CH_2I_2 , C_2H_5I , $n-C_3H_7I$ and $iso-C_3H_7I$ are formed under irradiation from various building surfaces of the reactor containment area [13]. In order to avoid experimental complexities, only methyl iodide was used in the containment experiments.

Studies on the effect of ozone / UV and gamma radiation (~20 kGy/h) on methyl iodide (CH_3I) in dry and humid conditions showed a decrease in CH_3I concentration in the facility with increase in temperature and UV-

radiation intensity. Similar behaviour was observed when ozone was present in the system. The organic species formed during the decomposition of methyl iodide were identified to be formaldehyde and methanol. At elevated temperatures ($\geq 90^\circ\text{C}$), other reaction products such as formic acid and methyl formate were also formed. A "new" reaction product iodoform (CHI_3) was detected in these experiments [14]. The particle formation was instant and extensive when CH_3I was exposed to ozone and/or radiation at all temperatures. The SEM-EDX analyses of the particles suggested that these were some kind of iodine oxides (I_xO_y). The exact speciation of the formed particles could not be ascertained as the particles melted and fused together under the electron beam. The mass concentration of aerosols seemed to increase with rise in temperature. This was partly attributed to the more efficient decomposition of gaseous CH_3I and subsequent aerosol formation with ozone. The gaseous reaction products were formed very efficiently despite the short residence time of the flow inside the facility (~ 7 sec), thereby suggesting a significant contribution from thermal decomposition reactions towards formation of reaction products.

7. Effect of beta radiation on iodine speciation

So far, the estimated effect of radiation dose on the radiolysis reactions of fission product species has been widely studied with gamma radiation. However, beta radiation constitutes a very significant fraction of the radiation dose during a severe accident. In the simulation study of Phébus FPT1 test, it was found that after ~ 5 hrs from the initiation of FPs release to the model containment, $\sim 70\%$ of the radiation dose rate in the containment gas phase originated from beta radiation. Experiments with beta irradiation at BESSEL facility [15] have shown the effectiveness of beta radiation on the production of aerosol species (most likely iodine oxide particles) from methyl iodide, in oxygen atmosphere. The exact stoichiometry of these species could not be established by SEM since these particles reacted with air humidity and were volatile under the electron beam of SEM.

The airborne concentration of these particles as well as gaseous CH_3I decreased very slowly with increasing irradiation time, suggesting attainment of equilibrium between gas phase iodine compounds and iodine species deposited on wall surfaces after long irradiation period. Under such equilibrium conditions, the rate of formation of new particle was low. When the facility was purged, a fraction of the methyl iodide was observed to desorb from the surfaces. With increase in irradiation time, the extent of desorption decreased and the onset of desorption was delayed. Particle nucleation rate increased during the

oxygen purge flow, thus suggesting that the radiolysis reaction products were limiting the particle formation within the facility. Ozone was needed for the nucleation to take place, as particle formation was not observed without irradiation or in pure nitrogen atmosphere. Carbon dioxide was the only observed gaseous reaction product observed. These results could partially explain the constant concentration of iodine, which was observed in the gas phase of containment at the end of every Phébus FP test. Detailed investigations are warranted to fully understand the impact of beta decay on the speciation of fission products and on the possible source term.

8. Iodine chemistry in aqueous phase

The chemistry of iodine in the aqueous phase is very complex; the chemical reactions and products are strongly influenced by water radiolysis products (WRP), which in turn depend on competing reactions from dissolved impurities in containment water [16, 17]. The dissolved oxygen reacts with hydrated electron very effectively and lowers its concentration, which would result in lowering $\cdot\text{OH}$ and $\cdot\text{H}$ while increasing H_2O_2 , H_2 and O_2^- . These changes could have a significant impact on the I_2 production rate. Metal ions, even at a trace level, can significantly affect water radiolysis product concentrations by catalytic consumption and could considerably affect iodine volatility. Nitrate/nitrite ions, formed by the radiolysis of humid air could alter the pH of containment sump and react with water radiolysis products. They consume the reducing species, e_{aq}^- and $\cdot\text{H}$, to form compounds that are successively lower in oxygen content and more reduced than their precursors. The chloride ions, generated mostly by radiolysis or pyrolysis of cable insulations such as chlorosulfonated polyethylene, as well as HCl generated in the containment, could lower the sump pH and also provides chloride ions well in excess of iodide. Chloride ions could also react with WRP producing chlorine radicals. Recent results obtained from Paul-Scherrer-Institute, Switzerland also show an increase in the iodine volatility under weakly alkaline conditions. Organic impurities (RH) dissolved in water would react with water radiolysis products to form organic radicals ($\cdot\text{R}$), which either react with I_2 to form organic iodides (RI), or react with dissolved oxygen and decompose eventually to CO_2 . The effect of CO/CO_2 , which is also formed from concrete-corium interactions or from boron carbide oxidation, on the iodine sump chemistry and in turn on the iodine inventory in the containment is not well known and hence also requires further study.

The iodine inventory in the containment depends on the complex chemical equilibrium between gaseous organic

and inorganic iodine compounds, adsorption of iodine on surfaces (such as paint) and the formation of iodine oxides and metallic aerosols. The discussions presented in the preceding sections have shown that inorganic gaseous molecular iodine (I_2) and volatile organic iodide (mostly CH_3I) react with the products of air radiolysis to form iodine oxide particles. The radiolytic gas-to-particle conversion could be an important factor in determining the fate of gaseous iodine injected into the atmosphere from the reactor coolant system or evolving from surfaces within the containment. Fig.3 outlines the probable scheme of events related to gas phase oxidation of iodine. The cycle begins with iodide, which is believed to be the predominant species of iodine at the start of a hypothetical reactor accident. Iodide is oxidized by water radiolysis products to I_2 which then partitions to the gas phase. I_2 in the gas phase undergoes radiolytic oxidation to form iodine oxides that are non-volatile at containment temperatures. These oxides form aerosols that eventually settle down on containment surfaces. These oxides are decomposed by the action of heat and/or radiation to re-release gaseous iodine species, or yield iodate when dissolved in water.

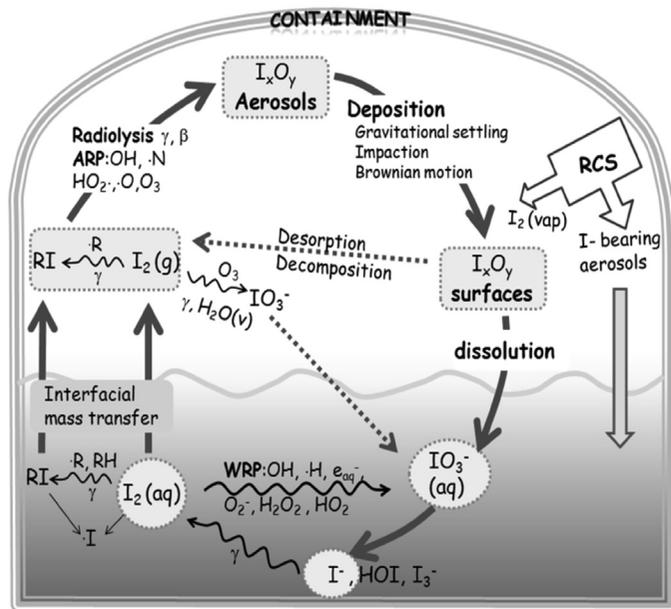


Fig.3 Schematic of iodine transformations within the containment

The aqueous iodate is easily converted to iodide upon irradiation. The reformation of iodide completes the cycle [18]. Although only some of the possible iodine reactions are mentioned, the very existence of the cycle suggests that gas-particle conversion will not be effective in decreasing total gas phase iodine concentration in containment.

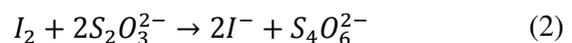
9. Iodine mitigation strategies

As discussed in the introduction, in the event of a severe accident in a nuclear power plant, the containment pressure can exceed the allowable maximum pressure. Venting the containment building as an essential accident management measure, can prevent loss of structural integrity. The subsequent radionuclide release to the environment can be minimized by incorporating efficient source term mitigation systems such as the filtered containment venting system (FCVS). These venting systems are designed to retain a certain fraction of aerosol distribution thus limiting the release of radioactive species to the environment. The performance of these filtration systems as measured by the decontamination factor, will vary for different species. Besides fission product aerosols, the vented gas flow contains gaseous iodine in both elemental and organic forms that need to be efficiently retained by the FCVS. It is therefore necessary to identify the type, form and quantity of different species to be vented. This section discusses the progress made in development / optimization of filtered containment venting devices, leading to potential improvement in mitigation.

9.1. Wet scrubber and Dry Filter based FCVS

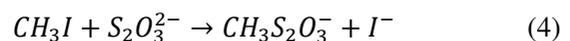
Two different FCVS products; a wet scrubber system referred to as "SVEN" (Safety Venting system) and a dry filter system, referred to as "DFM" (Dry Filter Method) have been recently developed by Westinghouse.

(i) **SVEN wet scrubber system:** This venting system, based on a combination of wet scrubbing and sintered metal fibre filter separation technique [19], filters aerosol and retains gaseous elemental and organic iodine. The scrubber liquid consists of sodium thiosulfate ($Na_2S_2O_3$) and sodium hydroxide (NaOH) dissolved in demineralized water. Elemental iodine is removed from the gas bubbles by chemical reaction with thiosulfate solution.



This reaction is very fast and effective. Organic iodide compounds will react in the scrubbing solution with OH^- and $S_2O_3^{2-}$ by nucleophilic displacement reactions [20].

For Ex., in case of CH_3I , which is the most dominant volatile organic iodide present in relevant accident conditions, the decomposition reactions is given as:



However, the kinetics of methyl iodide decomposition reaction is not fast enough to achieve complete conversion under representative venting conditions. Due to limited

residence time of venting gas, the retention of organic iodide is limited. A demister installed above the scrubber liquid, removes moisture from the vent flow. Aerosol retention efficiencies in the integrated system are higher than 99.99 % (DF > 10,000) [19]. Typical elemental iodine retention efficiency is larger than 99.9 % [19]. Organic iodine retention in the bubbling phase is moderate, about 50% (DF≈2). In order to improve the retention efficiency for organic iodine, the vent flow is routed through a molecular sieve consisting of beds of silver doped zeolite beads. The filtering mechanism inside the zeolite filter is based on the chemical reaction between iodine (both, elemental and organic) and the silver doping.

(ii) DFM Dry Filter Method: It comprises of two different types of filter modules, connected in series, to filter aerosols and retain gaseous iodine. In the first stage, aerosols are filtered from the venting gas flow using a specially designed deep bed metal fibre filter. The later consists of a multistage design containing metal fibres which decrease in diameter over the depth of the filter.

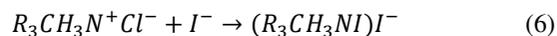
The efficiency of this system for removal of fission product aerosols was tested using an aerosol mixture consisted of CsI, CsOH, and MnO. Decontamination factors up to 3,000,000 were obtained for Cs. In the second stage, located downstream of the aerosol filter, both elemental and organic gaseous iodine are retained in a silver-doped zeolite molecular sieve. For a typically designed iodine filter of the DFM type, decontamination factors for elemental iodine and organic iodine were 1,000 and 50 respectively.

9.2. Novel Process for Efficient Retention of Volatile Iodine Species

A novel process developed at PSI, enables fast and efficient decomposition of volatile iodine species (molecular and organic iodine) in aqueous solution into non-volatile ions, thus suppressing the release of gaseous iodine species from aqueous solution [21]. The chemical scheme is based on the use of a phase transfer catalyst (Aliquat 336; a quaternary long chain ammonium salt) as a co-additive to Na₂S₂O₃ which is widely used in water pools of FCV systems.

The phase transfer catalyst functions by clustering both reactants, i.e. THS ions and the CH₃I molecules are brought together to accelerate their interaction. Thus the decomposition of CH₃I is enhanced. Aliquat 336 also contains chloride anion which acts as anion exchange for iodide ions and thus prevents their radiolytic oxidation into I₂. The ion exchange takes place as a concurrent reaction to the nucleophilic reduction by a covalent reaction with an

exchange of iodide ion for the chloride ion to form a tertiary amine Eq.(5) and quaternary long chain ammonium salt Eq.(6).



The lab scale experiments under different conditions (including the influence of pH, temperature, impurities) have established the right combination of Na₂S₂O₃ and Aliquat 336. Preliminary experiments in a dynamic system of small lab scale liquid scrubber column have shown promising decontamination factors (~ 2600 at 75° C). In order to assess the performance under prototypical conditions present during containment venting, a full height, reduced diameter test facility (VEFITA) has been erected and analytical work to characterize important FCVS thermal hydraulics variables is underway.

9.3. Innovative systems for larger source term attenuation

Experimental studies on innovative systems which may achieve larger source term attenuation such as acoustic agglomeration systems; high pressure spray agglomeration systems; electric filtration systems improved zeolite filtration systems; combined filtration systems, have been initiated in the PASSAM (Passive and Active Systems on Severe Accident source term Mitigation) project launched by the European Commission (2013-2016). Some of these systems are discussed below:

(i) Acoustic agglomeration systems

Enhancement of particle agglomeration would significantly improve mitigation. Agglomeration of sub-micron particles in the containment building would result in larger particles that would be depleted at a faster rate by sedimentation. The filtration devices containing wet/dry containment filter systems show a minimum efficiency for particles in the range of 0.1 to 0.3 microns. Agglomeration of particles (hence enlarged particles) in the venting line would enhance the performance of the filtration devices. In order to study the feasibility of potential application of acoustic agglomeration systems in nuclear severe accident conditions, preliminary tests under the anticipated working conditions during a severe accident have been initiated with an Acoustic Agglomerator (21 KHz, 300W/unit) at CIEMAT facility (Spain).

(ii) Electrostatic precipitators (ESP)

An ESP removes aerosols from gas flow due to forces induced by strong electric fields [22]. Although electric filtration systems such as ESP, air ionizers and ion wind devices, are being used for reduction of many industrial

emissions, including coal and oil fired power plants, salt cake collection from black liquor boilers in pulp mills, and catalyst collection from fluidized bed catalytic cracker units in oil refineries, their potential application in a nuclear severe accident condition such as radiation and high temperatures ($> 90^{\circ}\text{C}$), and pressures (>1 bar) for filtration of iodine volatile species including organic iodides is being evaluated currently at VTT, Finland.

(iii) Improved zeolites

Several zeolite families such as Mordenite, Ferrierite, Faujasite are presently being used for different industrial Processes. Silver doped zeolites seem to give the best results for iodine retention. Two types of silver-containing solids silver mordenite (AgZ) and silver faujasite (AgX) have emerged as better candidates for iodine trapping. Faujasite Ag-X adsorbents showed high decontamination factors (DF) for both molecular iodine and organic iodides, but their efficiency depends on presence of steam and nitrous oxides. In case of Mordenite, I_2 chemisorption is enhanced in the presence of metallic silver [23]; high humidity affects reduces organic iodide trapping; silver zeolites are robust and can withstand high temperature, humidity and radiation conditions.

Future experiments in the PASSAM project are aimed towards optimization of the nature of the zeolite in order to avoid poisoning effects and to obtain high iodine DFs; identifying optimal active sites for the trapping of iodine and organic iodides, providing extensive data on the effect of expected severe accident working conditions including influence of chemical effects (steam and gas contaminants) and potential irradiation effects on iodine trapping capacity.

10. Conclusion and Newly emerged issues

The detailed parametric studies in multi-component environments, performed in various intermediate scale, large scale and small experimental facilities have revealed new synergistic phenomenon affecting iodine volatility in the containment. The new information on iodine chemistry have been utilized in the development of new models for iodine (I_2 and CH_3I) - paint interaction under irradiation; formation and radiolytic decomposition of iodine oxides aerosols; adsorption of I_2 on aerosols. The model of I_2 interaction with steel has been refined and a preliminary model of gaseous conversion of I_2 into CH_3I through volatile organic compounds has been developed. These models have been recently updated or added in ASTEC code. Despite the significant progress made in modeling some of the key phenomena responsible for iodine volatility, there are a few remaining uncertainties in iodine source term estimation. These issues are:

1. The stable ARP concentrations are relatively low, hence very sensitive methods with low detection limits (e.g. Raman spectroscopy, flash photolysis) have to be used for unambiguous identification and quantitative determination of stable ARPs. This could provide useful information to validate the models describing the formation of ARP.
2. Mass spectrometric techniques could be employed for the determination of chemically more stable compounds (e.g. N_2O , $\text{NO}_2/\text{N}_2\text{O}_4$). The new data could serve as a basis to simplify the mechanistic model.
3. The influence of control rod materials on ARP formation and destruction needs more elaborate investigation with corresponding aerosols (and not surface coupons) as the basis.
4. The various paint "ageing" mechanisms, during normal operation as well as during the course of an accident, and their impact on iodine volatility need to be studied.
5. In order to evaluate the contribution from radiolytic decomposition of iodine oxides towards iodine volatility, the influence of temperature, humidity, presence of CO need to be investigated.
6. The radiolytic oxidation of multi-component iodine aerosols have to be studied to estimate the amount of volatile iodine that could be released under irradiation from iodine aerosols deposited on dry surfaces. Iodine adsorption on those aerosols should also be investigated.
7. The very small aerosols in the submicron range released from a boiling pool (as indicated by the THAI tests) might remain airborne for a long time. These fine particles cannot be removed by water sprays and metal fiber filters, and may therefore pose a challenge in providing high decontamination factors. In the wake of Fukushima, as passive operation of filtered containment venting systems (FCVS) is desired for > 24 hours [24], information on aerosol types (soluble, insoluble, or hygroscopic), mass concentration and particle size distribution at the time of venting will be vital for performance testing of FCVS in order to ensure reliable attenuation of fission product source term to the environment.
8. Despite the observation that relative yields of the different alkyl iodides formed from alkanes depend on the structure of the hydrocarbon, the organic iodine fraction in containment is usually represented by methyl iodide. The sampling or mitigation system designed to retain the radioactive methyl iodide may

not be effective for other organic iodine compounds. This issue must be factored into the sampling and mitigation systems.

9. The Fukushima accident has highlighted modification of the iodine speciation in the environment during its transport in the atmosphere. Iodine reactivity in the atmosphere is likely to be influenced by photolysis, atmospheric conditions and presence of pollutants. Quantifying these atmospheric modifications is very crucial for iodine source term estimation.

It is hoped that concerted efforts of the international iodine community in the above discussed areas will enhance the predictive capabilities of safety analysis tools and bring closure to the iodine issue.

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Materials for Entrapments of Radioactive Gases (Xe and Kr)

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Abstract

Entrapment of radioactive noble gases (Xe and Kr) released from nuclear fission reactors and spent nuclear fuel reprocessing plants is of major concern for nuclear safety. These gases are volatile and special attention should be taken to avoid their release to the environment. Currently, cryogenic distillation is widely employed to capture noble gas which is a very cost demanding process. Adsorption of Xe and Kr on porous materials is an alternative cost effective method for the capture of noble gases. Noble gases generally do not form conventional bonds due to completely filled valence shell which make them difficult to trap in materials. Porous materials like charcoal, alumina, and zeolites have been studied extensively for the entrapment of gases including Xe and Kr. These materials lack high selectivity and uptake capacity. After the discovery of new class of crystalline materials known as Metal-organic Frameworks (MOFs), new records have been reported in surface area, intake capacity and selectivity. Recent reports show that MOFs have superior properties in adsorption and separation of noble gases compared to other porous materials. MOFs are versatile such that their chemical and structural properties can be tuned by changing the central metal atom or the connecting organic linkers. The use of MOFs for entrapment of Xe and Kr is an emerging area. In the current review article, we narrate the recent developments in the capture of Xe and Kr using MOFs.

1. Introduction

The energy demand in India is going to increase drastically due to developing economy and campaign like 'Make in India'. India's economic growth significantly depends upon the sufficient generation of energy for both industrial and human resources development. The energy production from coal, oil and natural gas are restricted due to their limited supply and emission of greenhouse gases. Nuclear energy is clean (without carbon emissions), efficient and can play vital role in India's energy demand. According to International Energy Agency (IEA), India is planning to boost its nuclear power generation by three times from the current capacity by 2024. For the adequate expansion of nuclear power production, the safety and environmental issues related to nuclear energy such as entrapment and storage of radioactive elements should be properly addressed. In the context of nuclear safety, radioactive fission gases such as Xenon and Krypton released from spent nuclear fuel reprocessing plants and nuclear reactors need special attention. The entrapment of these volatile radionuclides is necessary for safety, nuclear waste management and clean environment.

The noble gases Xe and Kr are extremely rare in the atmosphere with concentrations of 0.09 ppm and 1.1 ppm respectively. In general, cryogenic distillation process is employed for the industrial production of Xe

and Kr from air and their capture from off-gas streams of nuclear plants. Cryogenic distillation requires high capital investment due to very low temperatures and high pressure working conditions. Thus, there is a demand for an efficient inexpensive technology for the entrapment of noble gases. Physisorption based separation of noble gases using porous materials is a viable alternative to expensive cryogenic distillation. The adsorption of Xe and Kr on these materials is performed at ambient conditions which reduces the production costs. Activated alumina, charcoal, activated carbon, zeolites and metal-organic frameworks are the extensively used porous materials for separation of gas mixtures. Noble gases pose difficult problem for separation since they generally do not make chemical bonds with the substrate. Xe and Kr are physisorbed on these porous materials by attractive van der Waals interactions. Among the porous materials, MOFs have high intake capacity, superior selectivity and can tune structural/chemical properties for desired application [1]. This makes them superior candidate in separation and storage of gases compared to other porous materials.

The isotopes of xenon released aftermath of nuclear fission and Spent Nuclear Fuel (SNF) reprocessing facilities are rather shorter lived compared to isotopes of krypton. During SNF reprocessing, ¹²⁷Xe with a half-life of 36.3 days and ⁸⁵Kr with a longer half-life of 10.8 years are produced [1].

The volume of Xe produced is roughly ten times larger than the Kr. Thus, separation of Xe from Kr significantly reduces the storage of nuclear waste for longer time period. Xenon has various industrial applications and used in lamps, anesthesia, MRI scanning, NMR spectroscopy and lasers. Other volatile radionuclides such as $^3\text{H}_2\text{O}$, $^{14}\text{CO}_2$ and ^{129}I are also produced from nuclear fission and reprocessing plants [2]. The mitigation of these species is also a challenging task in the domain of nuclear safety. In the current review, we focus on the current status of entrapment of Xe and Kr using various metal-organic frameworks investigated by both experimental and computational techniques.

2. Metal-Organic Frameworks

MOFs are connected through metal atom clusters with organic linkers generating extended porous structures [3].³ Depending up on the nature of central metal atom and organic moiety, MOFs show different pore diameters and topology. MOFs have reported very high surface area, free volume (> 90%) and superior adsorption characteristics. A comparison of surface area of MOFs with other conventional porous materials like zeolites, silica and carbons are shown in Figure 1 [1, 4-7]. These unique properties make MOFs the preferred material for storage, separation, catalysis and biomedical imaging [3,8]. The under-coordinated metal atoms, polarizable ligands [9], pore size [10], surface area and accessible free volume [7] play significant role in MOFs for gas adsorption and separation. MOFs are synthesized by mechanochemical, microwave, electrochemical, and ultrasonic methods [11,12]. The industrial production of MOFs is still limited. The gram-scale production of only a few MOFs has been reported such as HKUST-1 and MOF-5 [12].

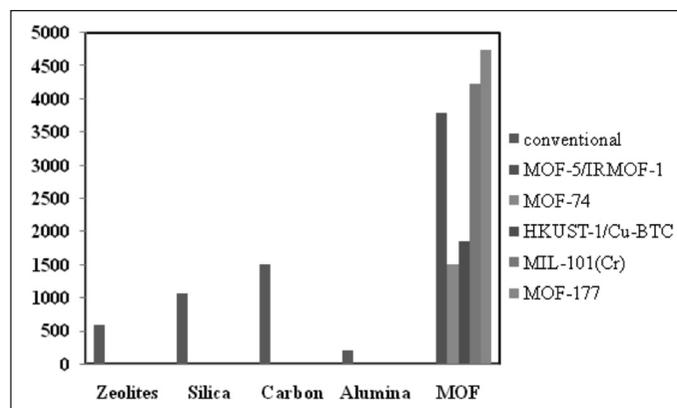


Fig. 1 Comparison of surface area of MOFs with other porous materials.

3. Experimental Studies

Thallapally and co-workers have done extensive studies on Xe/Kr separation properties of different porous

materials. In this regard, the Xe/Kr separation properties of Ni-MOF-74 and MOF-5 are compared with traditionally used activated carbon [13]. The xenon uptake capacity of Ni-MOF-74 is roughly double than the MOF-5(IRMOF-1). The uptake selectivity of Ni-MOF-74 is 5-6 which is higher than 3.8 obtained for charcoal [13]. These experiments are performed at standard temperature and pressure. The Cu-BTC(HKUST-1) MOF have been tested for Xe/Kr adsorption and adsorbed wt % was twice compared to the uptake of high surface area carbon [14]. Similarly, the noble gases (Ar, Kr, Xe) are found to adsorb more in metal-organic framework filled steel containers. The MOF-5 filled containers showed more uptake capacity compared to empty cylinders. The enhancement is directly related to polarizability of noble gases. Thus, Xe adsorption has the highest impact followed by Kr and least for Ar [14]. The dynamic breakthrough experiments are carried out for the noble gas separation properties of Ni-MOF-74 and HKUST-1 from air containing 400ppm Xe and 40 ppm Kr (78% N_2 , 21% O_2 , 0.9% Ar, 0.03% CO_2) [15]. Both Ni-MOF-74 and HKUST-1 have open metal sites, Ni(II) and Cu(II) respectively. The presence of open metal sites would enhance the adsorption of Xe and Kr in MOFs. The experiments are performed at low concentrations of Xe and Kr to match the actual scenario in applications (air purification and SNF reprocessing plant off gas streams). Both MOFs have shown affinity to adsorb more Xe compared to Kr. This is due to the larger polarizability of Xe compared to Kr. This trend remained same even for different composition of Xe:Kr mixtures that Xe was preferentially adsorbed over Kr. The capacity to adsorb Xe was highest for Ni-MOF-74 followed by activated carbon and HKUST-1. The dynamic capacity for Kr was following a different order, activated carbon > HKUST-1 > Ni-MOF-74. Thus, Ni-MOF-74 has the highest selectivity compared to activated carbon and HKUST-1. Another interesting fact from these experiments is that there is no direct relation between the uptake capacity and surface area of these three materials [15]. The higher uptake capacity of Ni-MOF-74 is due to the presence of six open metal sites in each pore. Apart from that the uniform pore structure may also help to enhance the Xe/Kr selectivity [15]. For the composition of 400 ppm Xe and 40 ppm Kr in air, the selectivity as high as 7.3 [15]. Some of the widely used MOFs for Xe/Kr separation are shown in Figure 2.

Another MOF which has been studied experimentally for Xe/Kr separation was FMOFCu and FMOFZn [16]. The FMOF has a V-shaped structure connecting the organic linker with two zinc atoms. These units are repeated forming 3D structures of interconnected tetrazinc clusters and (carboxyphenyl)-hexafluoropropane molecules. The

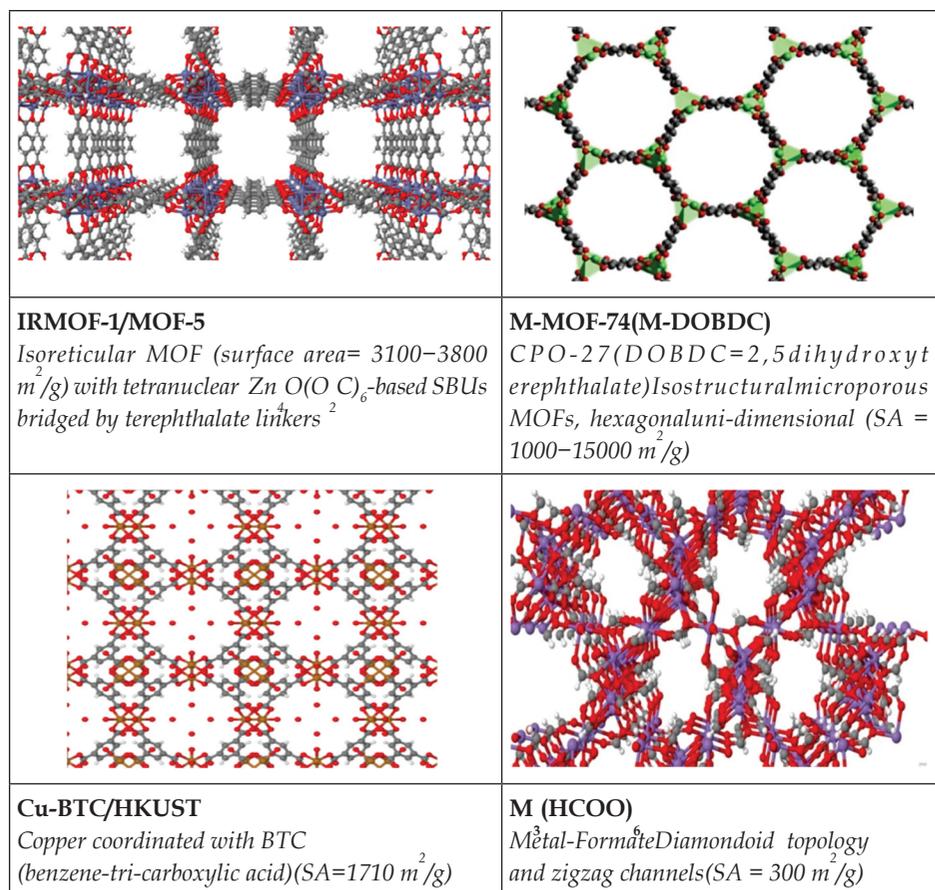


Fig. 2 Different MOFs employed for Xe and Kr storage and separation.

peculiar fact about FMOFZn that it forms two kinds of cavities with tubular cavities of size 4.67 Å X 4.78 Å and pore with 5.53 Å diameter. The FMOFCu has a different pore structure with ordered 1D channels of Cu paddle wheels. Here the tubular cavities are slightly larger in size 5.1 Å X 5.1 Å while pore opening diameter 3.5 Å X 3.2 Å is slightly smaller compared to FMOFZn [16]. Since the pore dimensions in FMOFCu are in the range of kinetic diameters of Kr (3.60 Å) and Xe (3.96 Å), they can selectively permit the diffusion Kr compared to Xe. Here FMOFCu shows reverse selectivity for Kr below 0°C. Generally, MOFs show affinity towards Xe due to larger polarizability of Xe atom. Above 0°C, the reverse selectivity for Kr vanishes [16]. Surprisingly, FMOFZn doesn't show such temperature dependent selectivity. This might be due to larger pore size (after contraction) of FMOFZn even at lower temperatures compared to FMOFCu. For FMOFCu, the experimentally reported Kr/Xe selectivity is 36 at low temperatures (203 K).

Wang et al. investigated the Xe/Kr separation properties of Co₃(HCOO)₆ using both experimental and computational techniques [6]. This particular MOF has one dimensional zig-zag channels with a pore diameter of ~5

Å. The heats of adsorption obtained for this metal formate MOF was higher than the other widely studied MOFs. Apart from that the IAST calculations predicted very high selectivity of 12 to 22 for different composition of Xe/Kr mixtures. The adsorption characteristic for Xe and Kr are different at 1 bar and near room temperatures. The Xe and Kr show type I and linear adsorption isotherm respectively. The Xe uptake was 3 times higher than that of Kr. The calculated Henry's constant and isosteric heats of adsorption values are higher for Xe compared Kr.

Recently, Thallapally and co-workers studied Xe/Kr adsorption properties of SBMOF-2 through experimental and computational breakthrough techniques [17]. This MOF shows Xe/Kr selectivity of about 10 at standard temperature and pressure. The SBMOF-2 has calcium metal centre connected with 1,2,4,5-tetrakis(4-carboxyphenyl)-benzene. It has two types of channels (one with phenolic -OH groups). SBMOF-2 shows a selectivity of 10 at 298 K with Xe capacity of 27 %.

4. Computational modeling studies

The Xe/Kr adsorption properties MOFs are generally modeled by Grand Canonical Monte Carlo (GCMC) methods using Universal Force Fields (FF) [7,9,18-20]. The computational studies on separation properties of MOFs are performed on the experimentally determined crystal structure or on a computationally optimized structure. The van der Waals interactions between the Ng atoms and MOF network are accounted by Lennard-Jones potential. During the simulations, MOF atom positions are fixed at their equilibrium geometry. The flexible force field parameters for MOFs are very rare. Sikora *et.al* investigated the Xe/Kr selectivity for more than 137000 hypothetical MOF structures [18]. The adsorption characteristics are analyzed for different pressure ranges (1-10 bar) at 273K based on MOF properties such as pore diameter, and accessible free volume. The MOFs with pore diameter close to Ng atom size and uniform pore structure showed better Xe/Kr separation [18]. Keskin *et.al* [21,22] employed GCMC and equilibrium molecular dynamics simulations to understand the adsorption and diffusion of noble

gases (Xe, Kr and Ar) in several MOFs. The adsorption isotherms and diffusion constants are calculated for ten different MOFs. Specifically, Xe/Kr entrapment efficiencies are investigated for BioMOF-11, Cu-BTC, Ni-MOF-74, Co-MOF-74, IRMOF-1, ZIF-1, ZIF-2, ZIF-3, ZIF-10 and Zn(bdc)(ted)_{0.5} [22]. Among these MOFs, ZIF-1, ZIF-2, BioMOF-11 and Zn(bdc)(ted)_{0.5} showed better adsorption selectivity for Xe/Kr separation. In contrast, the working capacity is higher for different MOFs such as IRMOF-1. The adsorption selectivity is higher for narrow pore MOFs while working capacity (diffusion permeability) is higher for larger pore materials [22]. In general, separation properties of MOFs are better than zeolites. Perry *et. al* calculated adsorption isotherms for Xe/Kr in MOF-74 and nbo-MOF series [7]. In MOF-74 series, different central metal atoms are considered such as Mg-MOF-74, Co-MOF-74, Ni-MOF-74 and Zn-MOF-74. Among nbo-MOF series, NOTT-100, NOTT-101, NOTT-102, NOTT-103, and PCN-14 are considered for the adsorption studies. The focus was on comparing MOFs with same pore topology (in the same MOF series) and same metal sites (in different MOF series) [7]. The results showed that in MOF-74 series, the charges on metal atoms change very little in different MOFs. Thus, the effect of central metal atom on Xe/Kr adsorption was not significant. For nbo-MOF series, the intake capacity and Henry's constant were increased with decrease in the pore size [7]. The adsorption affinity for noble gases is directly related to their atomic polarizability. Some of the results from Ref.7 were contradictory to experimental findings which might originated from neglect of noble gas polarizability and frozen lattice approximation. The force field parameters for Xe/Kr treat them as neutral spheres but in reality the interaction between Ng atoms and MOF atoms are charge-induced dipole interactions [7].

The microscopic understanding of adsorption mechanism is difficult since force field parameters available for MOFs could not accurately account the Xe/Kr interactions with MOF atoms. The first principle based computations can effectively describe Ng-MOF interactions at the molecular level. Density functional theory based calculations can give accurate results and computations are possible for materials of our interest (eg: MOFs). These electronic structure calculations can provide insight to structural, mechanical and adsorption properties of wide range of materials. The recent developments in first principle based calculations are described in the next section.

5. Recent Developments

Even though many MOFs were studied using computer simulations, a molecular level picture of noble gas

adsorption on MOFs is lacking. Recently, Thallapally and coworkers investigated the adsorption mechanism of Xe and Kr in Ni-MOF-74 using XRD experiments and first principle based DFT simulations [23]. Unfortunately, this study was limited to only one MOF (Ni-MOF-74). Very recently, our group investigated the Xe/Kr adsorption properties of many M-MOF-74s which include all the experimentally reported M-MOF-74s (M= Mg, Mn, Fe, Co, Ni, Cu and Zn) and early transition metal (yet to synthesize) M-MOF-74s (M=Ti, V, Cr) [24]. The adsorption of Xe/Kr on variety of MOFs (here 10 different MOF-74s) investigated by density functional based calculations are reported for the first time to best of our knowledge. Especially, the effect of central metal atom for Xe/Kr binding in various M-MOF-74s was never been studied for wide range of metal atoms. We employed accurate first-principle based DFT calculations to understand the nature of different adsorption sites and relevant interactions for noble gas adsorption in MOFs. The DFT based calculations can rectify the shortcomings of generally employed force field potentials. Our calculations are performed by incorporation of dispersion interactions and correct electronic characteristics of transition metals in DFT calculations. In this regard, we have employed Grimme's semiempirical D2vdW [25] corrections to the PBE [26] exchange-correlation functional to account dispersion and Hubbard U corrections to treat correct orbital occupancies of open shell d-electrons in metal atoms. All DFT simulations are performed using a plane wave basis with all-electron Projected Augmented Wave [27] potentials implemented in the VASP5.3 [28] program. The computed lattice parameters for M-MOF-74s from our study are identical with the reported experimental and computational data [29]. Since the uptake capacity of MOFs is a crucial factor, we have considered different number of Ng atoms adsorbed inside each MOF pore. There are six Xe(Kr) atoms binding to six open metal sites (6Ng + M-MOF-74) and an additional Xe(Kr) atom adsorbed at the center of the pore (7Ng + M-MOF-74) in our study. The crystal structures of bare M-MOF-74 and Ng adsorbed M-MOF-74 (with six and seven Ng atoms in each pore) are shown in Figure 3. Xe binds stronger than Kr in all M-MOF-74s at all uptake capacities. Comparing the binding energies in 6 Xe/Kr +M-MOF-74 systems, MOF-74s with Ti and Ni show highest adsorption energies while Mn and Cu have the least adsorption energies. The adsorption energy for Xe follows this trend Ti > Ni > Co > Zn > Cr > Fe > V > Mg > Mn > Cu among various metal atoms studied in M-MOF-74s for a uptake capacity of six. The Zn-MOF-74 expected to show lower binding strength due to larger screening of incoming Ng atom electron cloud by completely filled Zn d-orbitals as compared to

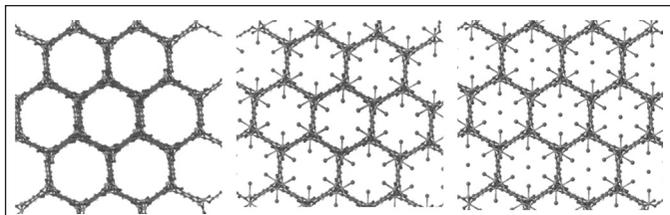


Fig.3 The left panel show the M-MOF-74 before noble gas adsorption. The central panel shows an uptake capacity of six that Ng atoms are adsorbed on the metal atoms in M-MOF-74. The right panel shows that total of seven Ng atoms are adsorbed with six on the metal atoms and one at the center of the pore.

Co and Ni metals [7]. Similar behavior is noticed from our simulations that Xe and Kr binding energy is higher for both Ni and Co MOF-74s as compared to Zn-MOF-74. The heats of adsorption obtained from experiments for Xe are greater than Kr [7, 23, 30]. Our calculations as well as experiments predict that open metal sites are the strongest binding sites for Xe/Kr adsorption in MOFs.

The atomic distances between Ng and metal atoms are reported in the range of sum of their vdW radii. The vdW interactions (attractive) between Ng atoms and MOF atoms decrease the Ng-M distance [23]. To further understand the noble gas binding mechanism in different M-MOF-74s, Bader charge analysis [31] is performed on bare M-MOF-74 and 6 Xe + M-MOF-74. The charge density analysis shows that the central metal atom and linker atoms in the MOF showed only slight change in electronic charge after the Xe adsorption. The charge on Xe atom (+0.02 e to +0.04 e) is very small which conveys that van der Waals interactions are weak.

Our calculations report highest adsorption strength for Ti-MOF-74 compared to all the other MOF-74s. The 3d transition metals show different electron screening effects depending upon their orbital occupations. This screening influences the interaction with incoming Ng atoms and changes the adsorption strength for different metal atoms. The higher adsorption strength of Xe compared to Kr in MOFs originates from the larger atomic polarizability of Xe than Kr. Due to larger distance from the MOF atoms, the binding energy is roughly constant for Ng atoms adsorbed at the center of the pore, irrespective of the central metal atom. The GCMC simulations are generally performed on experimentally reported MOF structures which restrict its relevance for prediction of new MOFs for gas separations.

6. Conclusions and Future Work

In summary, the computational modeling can provide relevant information in designing efficient materials for

the storage/separation of radioactive noble gases. The working efficiency of MOFs are influenced by many factors such as uncoordinated metal sites, accessible volume, pore diameter, pore structure and diffusivity of adsorbed gas. The MOFs with open-metal sites have larger uptake capacity but highly sensitive to water [17]. MOFs with pore diameters close to Kr will show larger selectivity by hindering the diffusion of Xe. The presence of polarizable atoms/group in the pore channels enhances the noble gas adsorption in MOFs due to attractive van der Waals interactions. Another challenging problem for MOF based technologies is that only a few MOFs have been produced at the industrial scale. Large scale production of MOFs is still a difficult task. Many MOFs are reported for gas separations and experimental realization of their efficiencies for noble separation/storage is a costly and time consuming task. Computational study on experimentally synthesized and similarly structured MOFs will be the optimal solution for finding efficient materials for entrapment of noble gases. Later, experimental synthesis and Xe/Kr adsorption studies can be carried out on selected candidates obtained from accurate modeling studies. The authors of the current article have already initiated accurate first principle based modeling of MOF materials for the efficient trapping of Xe and Kr [24]. The extension of this study to more diverse class of porous materials and properties are under development.

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Catalysts for Hydrogen Mitigation by Passive Autocatalytic Recombiner

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Abstract

Hydrogen released in nuclear reactor containment from clad/fuel – steam interaction under severe accident scenario poses threat to containment and hence can lead to release of radioactivity. Regulating of hydrogen concentration by catalytic recombination is a viable solution to this problem. Various supported platinum, Platinum-ruthenium and platinum-palladium catalysts, with stainless steel or cordierite supports have been developed for this purpose. The catalysts prepared have been characterised for the loading of noble metal, phase purity, surface morphology and surface composition. The catalysts have been evaluated for recombination of varying concentrations of hydrogen with oxygen in ambient and moist air. The performances of these catalysts in presence of various poisons like moisture, CO₂, CO and hydrocarbons provide data about use of these catalysts under the actual scenario. While, SS wire-gauze supported catalysts are found to perform better in presence of humidity and condensed moisture and within limited CO concentrations, the cordierite based catalysts exhibit poor performance in presence of condensed moisture though have enhanced resistance to carbon monoxide.

1. Introduction

Under loss of coolant accident condition (LOCA) large amount of hydrogen can accumulate in nuclear reactor following failure of emergency core cooling system (ECCS). This is invariably so in PWR where zircaloy clad fuel pins are used. Once this hydrogen leaks out of the structurally failed parts of the containment vessel and its concentration surpasses the flammability limit in air (4%) it could create adverse impact on environment as there can be chances of radioactivity to fallout [1]. Three Mile Island (USA) and Fukushima (Japan) accidents have highlighted the threat due to hydrogen explosion in nuclear reactors [2]. To avoid this kind of situation lots of efforts have been put by concerned nuclear organizations worldwide [3, 4]. Several alternatives have been proposed for dealing with this issue, viz. the uses of pre and post inerting, deliberate ignition system, dilute venting, and passive autocatalytic recombinder. Passive autocatalytic recombinder (PAR) is one of the most suitable candidates to deal with this situation. Because it has an inherent advantages over others that it can be auto initiated, cannot depend on external power supply, it can be placed at any location in containment and it can be operate by remote handling also [5]. Various types of catalysts such as Pt/Al₂O₃, Pt/SnO₂, Pt/Polyester, etc. have been reported so far for meeting the specification of PAR [6, 7]. Considering the imminent technological importance, our department stressed upon the need of indigenous development of PAR. Herein, our group developed various wire-gauze and cordierite ceramic supported Pt, Pt-Pd, Pt-Ru catalysts [8-10]. Catalytic activity study compared for various H₂ concentrations in air and for various probable

poisons like CO₂, CH₄, CO, and effects of relative humidity and condensed water.

2. Experimental

Here, for this purpose SS wire-gauze and cordierite plates with dimensions of 5 cm X 16 cm were exploited as supports. Using suitable precursors of the noble metals with the reducing agents, wire-gauze and cordierite based catalysts have been prepared. Electroless deposition route has been attempted for the synthesis of Pt, Pt-Pd, Pt-Ru/ wire-gauze based catalysts whereas chemical reduction route has been employed for the synthesis of Pt, Pt-Pd/ Cordierite based catalysts. All prepared samples have been characterized for their noble metal contents by NAA, phase purity using XRD, surface area by BET, surface morphology by using FEG-SEM, elemental distribution by EDS and surface composition by XPS.

3. Result and Discussion

Fig.1 shows the SEM images for wire-gauze (WG) and cordierite (Cord) supports before and after deposition of noble metals. SEM images reveal the difference in morphology and in particle size for all the samples. Fig. 1a) and 1b) show the SEM images of wire-gauze and cordierite supports before the coating. Fig.1 c) shows the SEM image of Pt-Pd/WG sample. Particles are observed with dimension of ~ 0.1 to 0.5 micron. Fig. 1d) shows the SEM image of Pt-Pd/Cord sample. The observed particle size is in the range of 3.5 to 5 nm. Fig.2 (a) & (b) shows the variation in $t_{1/2}$ and T_{max} for Pt-Pd/cord catalysts when exposed with different hydrogen concentrations.

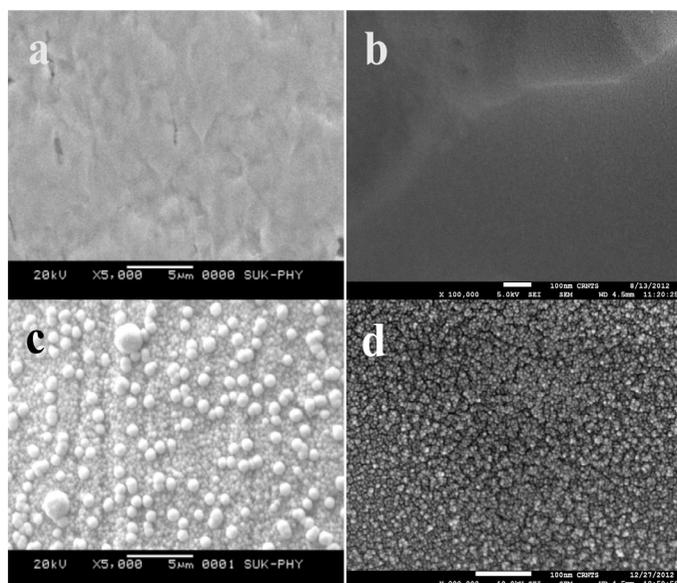


Fig. 1 SEM images of (a) Blank wire-gauze, (b) blank cordierite, (c) Pt-Pd wire-gauze and (d) Pt-Pd cordierite

It has been observed that with increase in hydrogen concentration, time required for completion of half of the reaction ($t_{1/2}$) has decreased and maximum temperature rise on the catalyst surface (T_{max}) has increased. Maximum temperature (T_{max}) rise observed for various hydrogen concentrations is in the range of 65 to 193 °C.

Table 1 shows the comparable study of catalytic activities for wire-gauze and cordierite based catalysts. Here it depicts that Pt and Pt-Pd/WG based catalysts show better catalytic activity in presence of condensed moisture whereas Pt, Pt-Pd/Cordierite based catalysts performs better in presence of carbon monoxide. In case of CO poisoning better performance of Pt-Ru/WG based catalysts was found compared to Pt-Pd/WG but the performance is not as good as cordierite based catalysts.

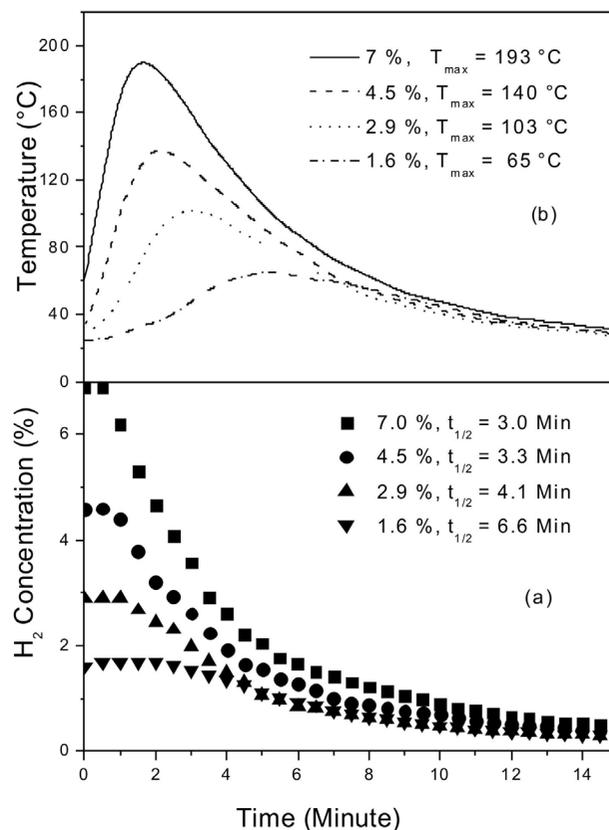


Fig. 2 Catalytic activity details for Pt-Pd/Cord catalyst in terms of change in (a) H₂ concentration & (b) Temperature rise.

4. Conclusion

Wire-gauze and cordierite supported Pt, Pt-Ru and Pt-Pd catalysts were successfully prepared by electroless deposition and chemical reduction route method. It has been observed that Pt, Pt-Pd/WG supported catalysts perform better in presence of condensed water whereas Pt, Pt-Pd/Cordierite catalysts show better catalytic activity in presence of carbon monoxide.

Table-1: Catalytic activity details of catalysts in presence and absence of poisons

S. No.	Catalysts	NM Wt. gain (%)	$t_{1/2}$ (min)	T_{max} (°C)	$t_{1/2}$ (min)					$t_{1/2}$ after flushing (min)
					CH ₄ (0.5%)	CO ₂ (0.5%)	CO	Rel. Humidity (100 %)	Condensed Water	
1.	Pt/Wg	0.83	2.0	207	2.0	1.8	5.0 ^a	3.8	-	2.1
2.	PtPd/Wg	0.83	1.8	233	1.9	2.1	2.3 ^b	2.6	-	2.1
3.	PtRu/Wg	0.90	2.0	268	2.2	2.3	3.7 ^c	2.5	5.6	2.1
4.	Pt/Cord	0.20	3.3	148	3.4	3.5	4.7 ^d	3.6	24.3	3.4
5.	Pt+Pd/Cord	0.20	3.3	140	3.5	3.8	3.9 ^e	3.4	9.5	3.3

Superscripts of $t_{1/2}$ (min): $t_{1/2}^{a\&b} = 50$ ppm of CO, $t_{1/2}^c = 400$ ppm of CO, $t_{1/2}^d = 2000$ ppm of CO, and $t_{1/2}^e = 1000$ ppm of CO

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Material Chemistry Issues in Managing Severe Accidents in Nuclear Reactors

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Abstract

A severe accident occurs in a nuclear reactor when multiple safety systems fail leading to complete loss of heat sink, which leads to fuel melting and ultimately the core melt is relocated into the containment cavity if not cooled inside the reactor vessel. This melt reacts with the concrete basemat causing its ablation and generates gases like CO, CO₂, H₂ which is a threat to containment integrity. The hydrogen generated has a potential danger of explosion. Besides, if basemat melt-through occurs, there is a potential danger of ground and water contamination by radiological contamination. In addition, during the progression of accident, failure of fuel rod claddings and heating up of the fuel leads to volatilization of fission products and activation products from the fuel, core structural material and control rod materials. In order to prevent the progression of severe accident, severe accident management strategies have been incorporated in new reactors and they are being retrofitted in existing reactors. These strategies include core catcher for managing core melt, containment filtered venting system for retaining fission products and passive autocatalytic recombiners for hydrogen mitigation. In order to design a robust severe accident management system, understanding of physical, chemical phenomena during progression of core melt accident is needed. While most of the research is carried out on typical uranium fuelled reactors, no data is available for thorium based reactors. In this manuscript, the material chemistry issues of thorium fuelled reactor systems for coolability and stabilization of core melt and retention of fission products using filtered venting system are discussed. The importance of determination of corium composition and properties, molten core sacrificial material (SM) interaction, chemistry issues in fission product generation in thorium fuels and their retention are discussed.

1. Introduction

In the entire history of commercial nuclear power, three major accidents leading to melting of reactor core have taken place so far, i.e. at Three Mile Island (1979), Chernobyl (1986) and recent Fukushima (2011). In the case of the Three Mile Island accident, even though the core had melted, there was no radiation exposure to any plant operator or any member of the public in spite of a series of human errors. The Chernobyl accident was a consequence of several design errors compounded by a series of human errors. The recent Fukushima accident has been a concern for public since it happened especially with regard to design safety of nuclear power plants. The accident in Fukushima occurred mainly due to extreme events such as earthquake of magnitude of 9.1 followed by gigantic tsunami of height 14-15 m. These resulted in prolonged station blackout conditions ultimately leading to core melt down and hydrogen explosion.

These accidents have reinforced the necessity to further improve safety in the nuclear power plant design. New reactor designs have incorporated measures for managing severe accident and existing reactors are being retrofitted

with several new measures. A severe accident is said to be terminated when

- the molten core has been quenched and stabilized for prolonged period;
- hydrogen concentration in the containment is in non-flammable limits;
- containment pressure is within design limits, and the
- fission products released are retained without exposing the public/plant personnel beyond allowable limits.

In order to provide mitigation strategies for severe accidents, it is very important to understand the phenomenology of severe accident progression in nuclear reactors.

2. Phenomenology of severe accidents

A severe accident occurs mainly due to failure of multiple safety systems leading to imbalance between the heat production rate and heat removal rate, which ultimately may result in significant degradation of reactor core. This may happen in pressurised state in a light water reactor for example in a prolonged unmitigated station

blackout (SBO), or at low pressure for example in case of a LOCA without availability of ECCS. The reactivity induced accidents leading to severe accident is eliminated by design. However, in both the former cases, core uncover occurs. The fuel heats up releasing the radioactive fission products, and large amount of hydrogen is produced due to steam-zircaloy reaction. The rods may eventually melt and form a molten mass.

In vessel type reactors, this mass can be relocated at the lower head of the vessel keeping the pressure boundary intact giving rise to an in-vessel scenario. This was the case in TMI2 where tonnes of molten core was relocated inside the RPV. One of the easiest ways to arrest the progression of the accident is to flood the entire core with water inside the vessel. Sufficient flooding will ensure the coolability of the melt inside vessel. However, if the cooling arrangement is not sufficient, the vessel may fail and the melt may be ejected into the containment cavity on the base material. This is an ex-vessel scenario. To avoid the high pressure melt ejection, the light water reactors have engineered safety systems to depressurise the vessel in case of such accidents. If water is already present in the cavity, the molten mass may breakup in a heat generating debris bed. If the debris bed is not quenched, it will again remelt due to the decay heat. The melt starts attacking the concrete base which is termed as the molten coolant- concrete interaction (MCCI). The heat transfer from the hot melt to the concrete causes ablation of the concrete. Further, the melt starts reacting with the water vapour and may release Hydrogen. This has manifold impacts as the chemical reactions add a lot of heat into the system and generate a lot of non-condensable gases because of concrete decomposition (i.e. CO, CO₂, H₂ and water vapour) and pose a threat because of containment pressurization. The hydrogen generated has a potential danger of explosion. Besides, if basemat melt-through occurs, there is a potential danger of ground and water contamination by radiological waste. The final barrier is the containment, which in any case, should not be breached for which design provisions have been made in new and existing designs by incorporation of filtered venting systems.

Failure of fuel rod claddings and heating of the fuel leads to volatilization of fission products and release of activation products from the fuel, core structural material and control rod materials. The release of fission products to the containment occurs in phases associated with the degree of fuel melting and relocation, reactor pressure vessel integrity, and, due to interaction of melt with concrete below the reactor cavity by MCCI. The radionuclide release occurs in several phases, for example, (i)

Coolant Activity Release, (ii) Gap Activity Release, (iii) Early In-Vessel Release, (iv) Ex-Vessel Release, (v) Late In-Vessel Release, etc.. On the basis of similarity in chemical behaviour, 8 radionuclide groups are defined as reported in Table 1[1].

Table-1: Classification of fission products

Noble gases	Xe, Kr
Halogens	I, Br
Alkali metals	Cs, Rb
Tellurium group	Te, Sb, Se
Barium, Strontium	Ba, Sr
Noble metals	Ru, Rh, Pd, Mo, Tc, Co
Lanthanides	La, Zr, Nd, Eu, Nb, Pm, Pr, Sm, Y, Cm, Am
Cerium group	Ce, Pu, Np

An earlier study reported on BWRs, relates the correspondence of these fission products with the phases of radio-nuclide release [1]. The summary of the same is given in Table 2 along with the fractional release to the containment. Further the chemical compositions of existence in the containment atmosphere for each fission product are given in Table 3.

Table-2: release fraction to the containment

	Gap Re-lease	Early In-Vessel	Ex-Vessel	Late In-Vessel
Duration (Hours)	0.5	1.5	3	10
Noble Gases	0.05	0.95	0	0
Halogens	0.05	0.25	0.3	0.01
Alkali Metals	0.05	0.2	0.35	0.01
Tellurium group	0	0.05	0.25	0.005
Barium, Strontium	0	0.02	0.1	0
Noble Metals	0	0.0025	0.0025	0
Cerium group	0	0.0005	0.005	0
Lanthanides	0	0.0002	0.005	0

As shown in Table 2, noble gases (Kr, Xe), volatile fission products (Cs, I) and relatively less volatile fission products (Sr, Sb, Te, Ba, Ru, Zr) in form of aerosols form the radioactive inventory inside the containment. Due to oxidization of Iodide ions generated due to dissolved aerosol particles, a large amount of Iodine gets re-entrained resulting in an increased release of gaseous elemental Iodine [2]. Iodine-paint reactions as well as the reaction of iodine with organic residuals in sump water are the main mechanisms for the generation of high volatile organic Iodides [2].

Table-3: Chemical composition and forms of existence

Element	Chemical State during normal operation	Released as aerosol
Xe, Kr	No chemical reactions, gaseous form	-
I, Br	Single phase halide solution CsI, I, I ₂	> 80%
Cs, Rb	Will form compounds with most other elements in the fuel. Alkali metal halides, compounds with uranates and Cs ₂ MoO ₄	> 80%
Te, Se	Mainly elemental form. Other possible forms are single phase chalcogenide solution (Cs ₂ Te) and products from reactions with Zircaloy	20 - 90% (influenced by reactions with Zircaloy and by oxidation potential in the melt)
Ba, Sr	Oxides which can dissolve to some extent in the fuel and form separate phases BaO, Ba ₂ (Zr-U-Pu)O ₃	2 - 40 % (influenced by reactions with Zircaloy and by oxidation potential in the melt)
Mo, Tc, Ru, Rh, Pd	Single phase metallic alloy	< 5% (influenced by reactions with Zircaloy and by oxidation potential in the melt)
La, Y, Zr, Nb, Lanthanides	Oxides which dissolve in fuel	-

Of the fission products listed in Table 1, volatile radioactive iodine, especially the I-131 isotope has a half-life of 8 days, which poses a health hazard if present in high concentrations due to easy and almost irreversible transport to the human thyroid gland, where it can locally induce malicious cell growth leading to cancer. Apart from Iodine, Cs-137 is another fission product which needs mitigation. The main problem with cesium-137, which is present in the form of salts, is its high water solubility. Cesium-137 ions are readily distributed in the body, and especially in the muscle tissues. The biological half-life is 110 days. This means that half of the cesium-137 has been excreted again after 110 days.

Based on long term land contamination and Thyroid dose to public, Cs-137 and I-131 are the most important radioactivity which needs high decontamination. Therefore, it is evident to seek for engineered safety systems to contain them so as to mitigate its consequences.

3. Mitigation of severe accidents Features and issues therein

In order to prevent the progression of severe accident, severe accident management strategies have been incorporated in new reactors and they are being retrofitted in existing reactor. These strategies include

- 1) Cooling and stabilization of molten corium in a dedicated core catcher (New reactors)
- 2) Introduction of water into pressure vessel and flooding of containment cavity (existing reactors)

- 3) Containment filtered venting system for retention of fission products and preventing containment overpressurization
- 4) Management of hydrogen using Passive Autocatalytic Recombiners

In this manuscript, the material chemistry issues for coolability and stabilization of core melt and retention of fission products using CFVS are discussed.

3.1 Core Catcher

In the event of severe accident, the molten corium is retained and cooled by a dedicated core catcher in new reactor designs. The objectives of core catcher are

- to contain the melt inside the core catcher
- to prevent re-criticality
- to cool and stabilize the melt inside core catcher for sufficiently long time (several months)

3.2 Chemistry issues in coolability of melt

a) Melt composition

The core of a typical water cooled reactor mostly consists of uranium dioxide fuel, zirconium cladding and steel as structural material. At high temperatures, zirconium is oxidized by water vapour forming zirconium dioxide, so the main constituents of core-melt, or corium, are UO₂, ZrO₂, unreacted Zr, Fe, Cr and Ni. The melting point of the pure oxides is around 2700 °C, while the metals melt at 1350 -1900 °C. Mixtures of different species do not have single melting points. Instead, they change from solid

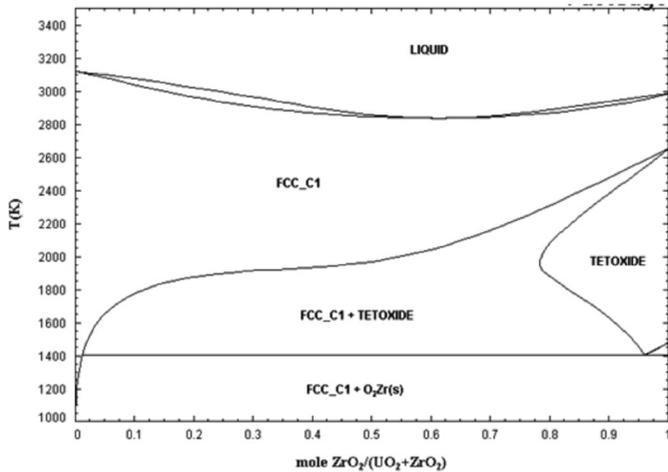


Fig. 1 UO_2 - ZrO_2 phase diagram

to liquid over a range of temperatures, between so-called solidus and liquidus temperatures. A typical $UO_2 - ZrO_2$ phase diagram is given in Fig 1 [3].

This figure is valid for typical LWRs having UO_2 as a fuel. However, in Thorium based fuel systems, the fuel composition is substantially different as compared to common LWRs. While, for typical LWRs, the corium typically consists of 76% UO_2 +9% ZrO_2 +15% Zr , the properties and phase equilibria are well understood. On the contrary, for Thorium based fuel systems, the fuel composition is (Th:Pu:U) O_2 : (95.8 : 2.64 : 1.56). In order to determine the composition of corium in Thorium based fuel systems, ternary system of $ThO_2 - PuO_2 - ZrO_2$ needs to be determined. ThO_2 , having high melting point (~3400 °C) experimental determination of phase diagram poses a challenge.

b) Corium properties

Application of heat transfer correlations for heat transfer from molten corium to surrounding structures, sacrificial material etc. requires values for various physical properties of the corium like density, thermal conductivity, thermal diffusivity, strength, viscosity etc. For typical LWR fuel corium, literature is available for estimation of most of these properties [4]. However, Thorium based fuel systems contain major component as ThO_2 , which is having higher thermal conductivity, higher melting temperature, lower density with respect to UO_2 . Hence, the properties of thorium fuel are substantially different than conventional fuel. Such data needs to be generated for Thoria based core melt.

c) Molten core sacrificial material (SM) interaction

In design of any core catcher, a sacrificial material is always put on the core catcher which directly sees the corium and avoids damage to the structure core catcher.

Besides, it reduces the thermal intensity of molten corium by preferential ablation. Mixing of sacrificial material with corium brings down its melting temperature and alters various properties like density, viscosity, solidus, liquidus temperature, which assists the mixture spreading on large surface area. Melting of SM reduces the specific volumetric heat release. Endothermic interaction between corium and sacrificial matrix brings down the overall temperature of final melt.

The oxides in corium and SM are miscible with each other, but the metallic species are immiscible with the oxides. Because the metals are lighter than the corium oxides, a metallic layer may be formed on the surface of the oxidic pool. When SM oxides are added to the melt, its density decreases eventually below the density of the metals. After this, the metallic layer may relocate to the bottom of the pool.

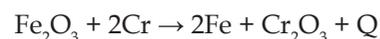
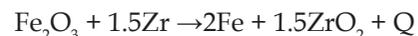
After the desired ablation has taken place, the coolant is flooded on the corium SM mixture to achieve the coolability.

In the entire process, it is very essential to understand the thermochemical reactions taking place during corium-SM interaction as the coolability strongly depends upon the extent of reactions.

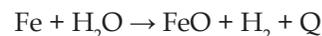
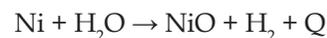
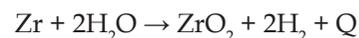
In a typical LWR having UO_2 - ZrO_2 - Zr - Fe - Ni - Cr as a fuel and is Fe_2O_3 (65 - 70%), Al_2O_3 (28 - 30%), SiO_2 (~ 7%) as sacrificial material, following reactions are known to be occurring.

Stage -I: When first molten metal layer falls on the SM

- Oxidation of metals by SM



- Reaction of metals with steam present in environment (Exothermic)



Stage -II: Mixing of corium material with mixed oxides (endothermic)



This mixture of mixed oxide has lower density than metallic fuel which causes it to float at the top. Water is then added on the top to cool this heat generating oxide layer. The rate constants of these reactions at high temperature are not known.

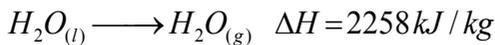
Generation of data for corium –SM interaction is vital for demonstration of core catcher performance. For Thorium based fuel systems, very few information is available on this aspect. The sacrificial material composition of Thorium based fuel systems is as given in Table 4.

Table 4: Thorium based fuel systems sacrificial material composition

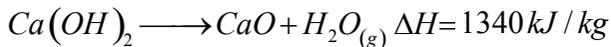
SiO ₂	40-45 %
Fe ₂ O ₃	30-35 %
Al ₂ O ₃	2-3 %
Binder material	Balance

Since the SM contains small amount of cement as binder, some of the reactions taking place during thermal decomposition of cement concrete, may take place. Typical reactions are as follows [5]

- At T > 100 °C: Loss of evaporable water



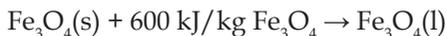
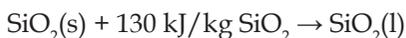
- T ~ 500 - 600 °C: Dehydration of Ca(OH)₂



- Dehydration of binder (T ~ 300 - 800 °C)



- Thermal decomposition of aggregates (endothermic)



It is important to understand the reactions taking place between ThO₂-ZrO₂ melt with SiO₂/Fe₂O₃ SM, and their rate constants, resulting phase equilibria of the components needs to be understood.

d) Change in corium properties as a result of corium – SM reactions

During mixing of sacrificial material with corium, the properties of the mixture change drastically. Fig. 2 shows the change in solidus and liquidus temperature with addition of sacrificial material (here, concretes of different types). It can be seen that, with addition of only 20 % by weight of sacrificial material, the solidus temperature drops to 1200 °C from 2500 °C. Such interaction of Thorium based

specific corium with sacrificial material is not understood fully. Besides solidus and liquidus temperature, change in properties like, heat of fusion, thermal conductivity, thermal diffusivity, density, strength, viscosity etc due to addition of increasing weight percentage of sacrificial material are not known for Thorium based fuel systems.

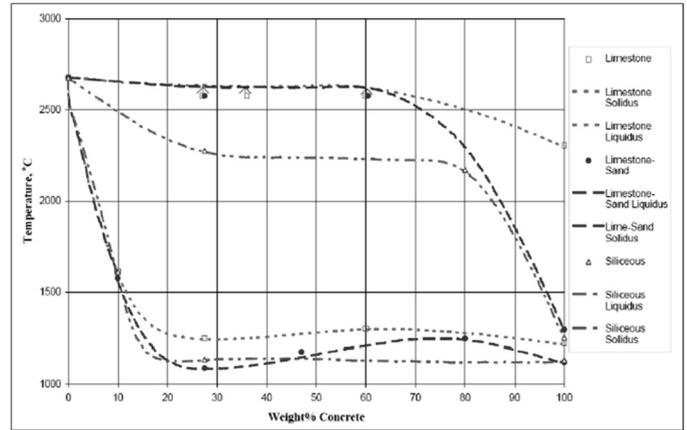


Fig. 2 Change in solidus and liquidus temperature with addition of sacrificial material

3.3 Containment Filtered Venting System (CFVS)

As said before, the containment is the last barrier to retain the fission products released from fuel from exposing them to public. For prevention of containment over-pressurisation and retention of radioactive fission products, most of the new reactors are designed with Containment Filtered Venting System (CFVS) and existing reactors are being retrofitted with them. The function of the CFVS is to release the pressure from primary containment to atmosphere by venting and also to reduce the level of radioactive release to the public within allowable limits by using efficient scrubbing systems. Most of the CFVS employs a two stage filtration process to meet the above functional requirements comprising of a wet scrubber followed by a demister and a metal fibre filter.

With actuation of the CFVS, the gases from the containment are released through the scrubber tank having a venturi manifold. While passing through the throat of the venturi-nozzle, the gas velocity increases resulting in reduction of pressure at the throat. The alkaline solution from the scrubber pool enters the throat through the holes due to pressure difference existing between water pool and the throat of the venturi scrubber. The gas, owing to its high velocities in the throat section shears the liquid spray, producing enormous number of tiny alkaline droplets. Particle and gas removal occur in the throat section as the stream interacts with the entrained droplets by inertial capture. The capture efficiency depends on the relative velocity between the gas and droplets, liquid loading and

the liquid flux distribution (important for molecular iodine capture) in the throat section of the venturi scrubber. Due to this scrubbing action, volatile radio-active materials such as Iodine, Cesium, and Tellurium get dissolved in the water droplets and hence get retained in the scrubber pool. The mixture exiting the venturi scrubber forms large air bubbles, which passes through the bulk water in the tank, where further dissolution and scrubbing takes place. When the gas bubble rise to the free water surface of the scrubber tank, the bubble breaker ensures breakage of large bubbles and further downstream the demister arrests the fine entrained droplets carried along with the gas flow. In addition to the demister pad, a metal fiber filter is employed to retain very fine aerosol particulates present in the gas stream. Following the two stage filtration process in the scrubber tank, air-steam mixture along with FPNGs is discharged through the stack into the environment.

3.4 Chemistry issues in mitigating fission product release

Aerosols and other gaseous fission products contribute to the radio-active inventory of the CFVS. Fission product aerosols are expected to dominate the filter load for early venting scenarios, and mostly non-active aerosols formed by core-SM interaction dominate the late (a few days) stage venting. A couple of 10s of kilograms to several 100 kilograms may envelope the aerosol load for a typical PWR type reactor. In containments, aerosols may be characterized by agglomerates composed of different fission product and inactive materials [6]. The composition may change depending on the accident progression and timing of the venting. The size of the particles, based on many research results, may cover a wide range. The most typical size entering the containment from the reactor primary coolant system is considered to be 1-2 μm . In the containment, the particles grow due to their hygroscopicity, agglomeration, and coagulation. However, the existence of particles smaller than 1 μm cannot be excluded. Such particle mixtures could be present in dry super-heated condition as well as under saturated condition and contain water droplets. Apart from the uncertainty regarding aerosol size distribution, the composition of these aerosol particles also governs the overall decontamination achieved by the CFVS.

In Indian context, the fission product evolution, following a severe accident in a Thoria based core, is yet to be established. This includes both, the evaluation of the aerosol inventory along with the composition and the size distribution of the particles generated during such elevated temperature and pressure conditions of accident progression.

Along with aerosols, Iodine (both in elemental form and organic form) also contributes largely to the decontamination requirement. There are many factors affecting the generation and release of gas phase iodine in the containment. These include the type of the reactor, timing and speciation of the iodine release into the containment from the reactor coolant system, radiation and thermal chemistry in containment sump (PWRs and PHWRs) or pressure suppression pools (BWRs), as well as surface reactions with the painted surfaces, to name a few. Paint and gas phase (containment air) reactions may significantly change the level of airborne iodine concentration and its speciation. The timing of the venting initiation will determine the amount of iodine load and its characteristics [6]. Thus, the total iodine load to the CFVS may be as small as a few grams or as high as one kilogram depending on the factors mentioned above.

Therefore, from the CFVS design point of view, the amount of iodine release along with the mass fraction of its existence governs the efficiency of the system. Following similar lines of justification, the estimation of Iodine speciation and inventory calculation for Thorium based reactors is of utmost importance.

4. Summary

A severe accident in nuclear reactor leads to melting of fuel and release of radioactive fission products in the containment. In order to limit the progression of accident, a dedicated core catcher has been provided for cooling and stabilization of molten corium in many new reactors and suitable flooding techniques is being retrofitted in existing reactors. In addition, containment filtered venting system is provided for retention of fission products and depressurise the containment in such conditions. Cooling of corium involves complex thermochemical and thermophysical interaction amongst fuel, cladding, structural material and sacrificial material of the core catcher. It is important to know the composition of corium, its properties, thermochemical reactions with sacrificial material, their thermodynamics and kinetics in order to establish the cooling strategy.

The release of fission products depends on the extent of fuel melting and relocation, reactor pressure vessel integrity and on the interaction of the molten core materials with the concrete below the reactor cavity. Depending on the accident progression, the radioactive inventory along with the chemical composition of the released fission products serve as the basis for designing efficient scrubbing system which not only prevents the containment from over pressurisation but also retains the radio nuclides. Thus,

understanding the composition of the released fission products plays a vital role in meeting the decontamination limits by the scrubbing system.

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Corium Containment Methodology for AHWR: High Temperature Chemistry of Thoria Based Systems

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Abstract

In this article, we briefly present some basic studies with the aim of development of sacrificial materials for futuristic nuclear reactors, like AHWR, IPWR, etc. using oxide fuel system. We have attempted to conclude the phase behavior of the fuel system and sacrificial materials with temperature. The studies indicate that the fluorite type phases will be dominating in the fuel system while ZrO_2 contribution in some cases appears as monoclinic or tetragonal ZrO_2 . Also formation of phase with silica and composites like red-mud are also presented.

1. Introduction

The development of Advanced Heavy Water Reactor (AHWR) is an important step towards thorium utilization for power generation. It is one of the safest reactor systems with many passive safety features. However, in a remote event of severe accident (such as LOCA), the decay heat removal system may fail, leading to core meltdown. As part of post-Fukushima design modifications in AHWR, a core catcher and containment filtered venting system (CFVS) has been incorporated in AHWR design for stabilization of core melt and mitigation of fission products released. The main functions of core-catcher are to efficiently reduce the molten core (corium) temperature and volume of liquid as well as to minimize release of fission products and hydrogen generation from metal water reaction. In this context, it is important to study the high temperature solid state chemistry using various sacrificial materials and interaction of corium and sacrificial materials. Some of the results of our studies on high temperature behaviors of complex oxides containing various elements of fuel or sacrificial materials are discussed in this article. The results will find applications in validating the conditions required for the design of core-catcher.

2. Experimental

CeO_2 , ZrO_2 , ThO_2 , Gd_2O_3 and SiO_2 (all 99.9 %) were used as the starting materials and more than 200 compositions in CeO_2 - ThO_2 - ZrO_2 , CeO_2 - Gd_2O_3 - ZrO_2 , CeO_2 - Gd_2O_3 - ThO_2 systems were investigated. Ceria was used as a surrogate for plutonia. The stoichiometric amounts of reactants were weighed for each nominal composition. The mixtures were grounded well, pelletized and subjected to multi-step heating at 1473 K, 1573 K and 1673 K with intermittent grinds and pelletizing. All the products were analyzed by systematic XRD diffraction

studies at different temperatures, and Electron probe for micro-analysis (EPMA). Red mud produced from NALCO (National Aluminum Company Limited) is used for high temperature studies. The thermogravimetry and XRD were used to characterize the Red-mud processed at different temperatures.

3. Results and discussion

The salient results of the studies carried out in simulated fuel system in the absence and presence of sacrificial materials taking note of the reaction products are explained below.

(a) CeO_2 - ThO_2 - ZrO_2 system

In this system, phase relations studies were performed on three binary series ThO_2 - CeO_2 , CeO_2 - ZrO_2 and ThO_2 - ZrO_2 . The ThO_2 - CeO_2 system showed the formation of solid solution in the complete homogeneity range. In ThO_2 - ZrO_2 series, only about 5 mol % of zirconia could be dissolved in the lattice of the ThO_2 whereas thoria did not have any solubility in zirconia lattice. This can be well explained based on relative ionic sizes of Th^{4+} and Zr^{4+} . In $Ce_{1-x}Zr_xO_2$ series, about 20 mol % ZrO_2 could be incorporated to ceria retaining the fluorite structures which are in agreement with literatures. In pseudo-ternary systems, ZrO_2 - $Th_{0.5}Ce_{0.5}O_2$, CeO_2 - $Th_{0.5}Zr_{0.5}O_2$ and ThO_2 - $Zr_{0.5}Ce_{0.5}O_2$ and the corresponding opposite species were chosen as the end members. Only 10 mol % zirconia was found to get incorporated in the lattice of $Th_{0.5}Ce_{0.5}O_2$ in the ZrO_2 - $Th_{0.5}Ce_{0.5}O_2$ system. The CeO_2 - $Th_{0.5}Zr_{0.5}O_2$ system revealed a two-phase region, viz. cubic solid solution of ceria in thoria and m- ZrO_2 . Beyond 30 mol% CeO_2 , presence of small amount of t- ZrO_2 is also observed and thus the system turns to be triphasic. The ceria-rich region (70 mol% CeO_2 onwards) however depicted single-phasic fluorite

structure. In $\text{ThO}_2\text{-Zr}_{0.5}\text{Ce}_{0.5}\text{O}_2$ system, the end member $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$, consists of a cubic solid solution and t-ZrO_2 . In the compositions between $\text{Ce}_{0.40}\text{Zr}_{0.40}\text{Th}_{0.20}\text{O}_2$ and to $\text{Ce}_{0.15}\text{Zr}_{0.15}\text{Th}_{0.70}\text{O}_2$, the segregation of m-ZrO_2 phase is also noticed. The cubic fluorite-type phase was observed in the compositions containing more than 75 mol% ThO_2 .

Several specimens of $\text{CeO}_2\text{-ThO}_2\text{-ZrO}_2$ systems were quenched from 1400°C and were subjected to detailed electron probe microanalysis (EPMA). Based on the volume fractions of both the phases and microstructural evidences in these bulk compositions and phase relations in the $\text{CeO}_2\text{-ThO}_2\text{-ZrO}_2$ system were established. Also, a number of single phasic compositions with fluorite-type structure were identified and their lattice thermal expansion was investigated in the temperature range 293 to 1473 K by High Temperature XRD.

(b) $\text{CeO}_2\text{-Gd}_2\text{O}_3\text{-ThO}_2$ system

The ternary phase relations in $\text{CeO}_2\text{-Gd}_2\text{O}_3\text{-ThO}_2$ system were established. In this system XRD data revealed the presence of different phase regions namely, cubic fluorite-type solid solution, C-type solid solution, and the biphasic regions containing C and F-type solid solutions and two F-type solid solutions. The phase relation with Gd_2O_3 was found to be different with CeO_2 and ThO_2 , despite the fact that both have fluorite structure. In case of $\text{CeO}_2\text{-Gd}_2\text{O}_3$ system a monophasic F-type or C-type phase field is present throughout whereas in case of $\text{ThO}_2\text{-Gd}_2\text{O}_3$ systems an F-type phase field is present up to 70 mol% ThO_2 and thereafter a biphasic F+C phase field is observed. Both ThO_2 and CeO_2 are able to stabilize cubic gadolinia up to 1400°C. In $(\text{Gd}_{0.5}\text{Th}_{0.5})_{1-x}\text{Ce}_x\text{O}_{1.75+x/4}$ system, $(\text{Gd}_{0.5}\text{Th}_{0.5})\text{O}_{1.75}$ and CeO_2 are soluble throughout the entire range. In $(\text{Ce}_{0.5}\text{Th}_{0.5})_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ system, $\text{GdO}_{1.5}$ dissolves up to 40 mol% in $(\text{Ce}_{0.5}\text{Th}_{0.5})\text{O}_2$ lattice giving an F-type lattice and beyond the phase splits into an F-type phase and a C-type phase. The phase fraction of F and C-type depend on the $\text{GdO}_{1.5}$ content and the amount of F-type phase decreases with increasing $\text{GdO}_{1.5}$. The $(\text{Ce}_{0.5}\text{Gd}_{0.5})_{1-x}\text{Th}_x\text{O}_{1.75+x/4}$ system also depicted a biphasic phase field consisting of two fluorite-type phases in compositions with $x = 0.6$ to 0.8, the compositions in rest of the system adopt single-phasic fluorite type structure. On comparing the system $\text{CeO}_2\text{-ThO}_2\text{-Gd}_2\text{O}_3$ with $\text{CeO}_2\text{-ThO}_2\text{-ZrO}_2$ system, it was observed that former depicts a wider range of cubic phase field as compared to the system containing zirconia.

(c) $\text{CeO}_2\text{-ThO}_2\text{-YSZ}$ (Yttria stabilized zirconia)

Ternary phase relations were also established in $\text{CeO}_2\text{-ThO}_2\text{-YSZ}$ ($\text{Zr}_{0.75}\text{Y}_{0.25}\text{O}_{1.875}$) system. It was found that the $\text{CeO}_2\text{-YSZ}$ system shows the formation of a cubic solid

solution throughout the homogeneity range whereas $\text{ThO}_2\text{-YSZ}$ system was bi-phasic throughout the range. The lattice parameter of the cubic solid solution in $\text{CeO}_2\text{-YSZ}$ system decreases linearly on going from CeO_2 to YSZ end member. $\text{CeO}_2\text{-ThO}_2$ was also found to be completely miscible throughout the range with lattice parameters following Vegard's law. The ternary system $\text{ThO}_2\text{-(Ce}_{0.5}\text{YSZ}_{0.5})\text{O}_{2.6}$ was biphasic consisting of two fluorite type phases with different lattice parameters throughout the range. The other two systems $\text{CeO}_2\text{-(Th}_{0.5}\text{YSZ}_{0.5})\text{O}_{1.94}$ and $\text{YSZ}\text{-(Ce}_{0.5}\text{Th}_{0.5}\text{O}_2)_{1.94}$ were characterized by a single phasic fluorite-type solid solution and a biphasic region consisting of two F-type solid solutions. The High Temperature XRD studies carried out on representative compositions in $\text{CeO}_2\text{-YSZ}$ series showed that the average lattice thermal expansion coefficient increases with increase in amount of CeO_2 due to higher thermal expansion coefficient of CeO_2 .

(d) Silicate systems

Core catcher sacrificial material will have SiO_2 also. In view of this, studies on metal silicates are also relevant. In view this, systems like $\text{ZrO}_2\text{-SiO}_2$, $\text{ThO}_2\text{-SiO}_2$ and $\text{ThO}_2\text{-CeO}_2\text{-SiO}_2$ were investigated. All the samples were prepared by a high temperature solid state synthesis method and characterized by XRD. In $\text{Zr}_{1-x}\text{Ce}_x\text{SiO}_4$ series, the XRD pattern observed at $x = 0.0$ matched well with that of zircon and rest other compositions were biphasic thus showing no solubility of CeO_2 in the zircon lattice which could be attributed to the large ionic size mismatch between Ce^{4+} [0.90 Å] and Zr^{4+} [0.75 Å]. In $\text{Th}_{1-x}\text{Ce}_x\text{SiO}_4$ series, ~ 10 mol % CeO_2 stabilizes tetragonal modification of ThSiO_4 whereas undoped ThSiO_4 was found to be monoclinic.

(e) Red-mud

Red-mud is a semi solid waste product obtained in Bayer's process for production of alumina from bauxite. The chemical characterization of the red-mud indicated a composite system, primarily containing oxides of Fe, Al and Na in addition to TiO_2 , SiO_2 and oxides and hydroxides of Ca^{2+} . In addition, trace amounts of rare-earth are also incorporated in the red-mud whose concentration varies depending on the origin of the bauxite ore. Based on the primary composition, the red-mud can be used as a sacrificial material in core-catcher to retain molten corium. Therefore, it can be an abundant alternate sacrificial material for the usage as sacrificial material as against silicate based formulation proposed earlier. Though a number of studies with silicates as sacrificial materials have been initiated in post-Chernobyl accident period, the studies with $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ based systems are limited. Preliminary studies on $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ based composites are in favor of the red-mud, however, the presence of excess

Na either in the form of Na_2O and NaOH may be a concern in its direct usage due to their high volatility and reactive nature. In view of this the processing of red mud to reduce the free Na attempt have been carried out to remove the free Na components or use them to form strongly bonded chemical entities. Though the washing of the red mud may remove them, it may not be practical approach as it requires cumbersome separation process involving extra energy, time and cost. In order to avoid wet processing of red-mud high temperature reaction was attempted. From the thermogravimetry studies of mud it is observed that appreciable weight loss occur within 600°C which is due to loss of volatile impurities, like water, hydroxide, carbonate and free Na compounds. Studies were carried out by heating the red-mud sequentially up to 1000° and similar thermogravimetric studies were also carried out. This study indicated almost no weight loss even up to 1350°C . This suggests the Na ions are bonded as chemical compound with SiO_2 , which is confirmed from the melting of $\text{Na}_2\text{Si}_2\text{O}_5$. Studies were also carried out up to 1750°C , in reducing environment in anticipation of its behavior in corium-core catcher interaction conditions, which indicated the reduction of Fe_2O_3 to metallic Fe while other

components remained as slag. The studies were also carried out with physical mixture of Fe_2O_3 , CeO_2 and Al metal which indicated formation of metallic Fe and perovskite type CeAlO_3 phase, suggesting for a possible formation of stable compounds with lanthanides and actinides. These studies support for low silicate composites with Al_2O_3 - Fe_2O_3 system as potential core catcher material.

4. Conclusions

The ternary phase relations were established in CeO_2 - ThO_2 - ZrO_2 , CeO_2 - Gd_2O_3 - ThO_2 and CeO_2 - ThO_2 -YSZ, under slow cooled conditions, which revealed several interesting features. Interestingly neither ThO_2 nor CeO_2 could stabilize the cubic phase of ZrO_2 . CeO_2 - ThO_2 -YSZ exhibited wider cubic phase field as compared to CeO_2 - Gd_2O_3 - ThO_2 which was relatively richer in cubic phase field as compared to CeO_2 - ThO_2 - ZrO_2 system. This could be attributed to the structures of end members employed for these three systems. ThSiO_4 lattice was found to accommodate about 10 mol % of CeO_2 and in turn was observed to get stabilized as tetragonal structure. Potential of red-mud for sacrificial materials in future nuclear reactors is also presented in this article.

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