Amendment to AERB/NPP-PHWR/SM-D2

Clause 4.4.2

Existing:

In view of this, hydrogen mitigation, if required, is recommended to be achieved by catalytic recombination principle. The suitable recombiner device based on platinum/palladium catalyst shall be considered for installation in the plant only after satisfactory demonstration of its efficacy in safe manner in a separate experimental set-up under suitably simulated containment environment conditions arising out of an accident. These recombiner devices shall be qualified as per the following criteria.

Revised:

In view of this, hydrogen mitigation, if required, is recommended to be achieved by catalytic recombination principle. The suitable recombiner device based on platinum/palladium catalyst shall be considered for installation in the plant only after satisfactory demonstration of its efficacy in safe manner in a separate experimental set-up under suitably simulated containment environment conditions arising out of an accident. For the inert atmospheric conditions (both dry and wet atmospheres), the steam concentration should be as per the Shapiro-Moffette diagram. Under wet conditions, from among the total test matrix recommended for recombiner performance under clause 4.4.3 below, the qualification tests above 10% (v/v) and up to 30% (v/v) hydrogen concentration are required to characterise the recombiner behaviour in oxygen lean atmospheres.

While designing the hydrogen mitigation system for a specific plant following sub-clauses should also be addressed suitably:

(i) The mean hydrogen concentration in the compartments of the containment where recombiners are installed shall not exceed 9% (v/v) during the progression of the accident and in post-accident conditions.

(ii) The safe performance behaviour of multiple recombiners installed within single/multiple compartments may also be assessed and substantiated, if necessary.

Accordingly, the recombiner devices shall be qualified as per the following criteria.

Clause 4.4.3

Existing:

Qualification Parameters for Catalytic Recombiners

Based on the functional requirements of the recombiners and the technology available for conducting the experiments, following qualification guidelines are worked out:

(a) demonstration of efficacy of hydrogen removal process shall encompass the following parameters and their ranges:

(i) Hydrogen concentration range : 0.05% to 8% V/V (in dry air medium) and up to 30% V/V (in steam environment)[1]

(ii) Steam concentration : 0% to 60% V/V

(iii) Pressure : LOCA based peak pressure

(vi) Poisons : Iodine, CO, oil vapour and lubricant, dust/ aerosols, as expected under accident condition

(v) Minimum temperature for the onset of recombination process : 25°C

(b) during the demonstration tests specified above, the temperature of the catalyst/substrate shall not exceed 400°C so that adequate margin exists between maximum operational temperature and the auto-ignition temperature of 550°C and spalling of catalyst from the substrate is prevented;

(c) structural integrity of the recombiners be demonstrated to withstand various likely loads due to blowdown jets, seismic events, etc.; and

(d) accelerated ageing studies of the catalyst be carried out to arrive at its deterioration characteristics with time. Based on this, the frequency of in-situ maintenance checks of catalyst shall be specified.

Revised:

Qualification Parameters for Catalytic Recombiners

Based on the functional requirements of the recombiners and the technology available for conducting the experiments, following qualification parameters are worked out.

a. Qualification under inert atmosphere

i. Hydrogen concentration[2] : up to 4 % v/v (in dry air medium)
up to 30% v/v (in inert steam environment)[3]

ii. Steam concentration : As per Shapiro-Moffette diagram to ensure inert conditions.

b. Qualification under non-inert (deflagrable) atmosphere

The safe operational behaviour of recombiners shall be demonstrated for gas mixture compositions within the deflagrable region.

During these tests, it shall be suitably demonstrated that any local ignition within or in the vicinity of recombiners does not lead to any sustained ignition as depicted by rapid and sustained pressure, temperature and concentration transients. **These qualification tests should be performed in a graded risk manner (starting from least deflagrable compositions).** The following range of gas concentrations shall be considered for qualifying the recombiners.

i. Hydrogen concentration : Up to 10% v/v (in steam environment)

---

[1] Composition of steam and hydrogen concentration during test to be outside the deflagration region.

[2] The term "concentration" means concentration of the species (H_2, steam) at the recombiner inlet.

[3] As explained in clause 4.4.2, beyond 10% and up to 30% concentration of hydrogen and at a steam concentration of 60 % (inert atmosphere), it is intended to characterise the recombiner behaviour in oxygen lean atmosphere.

ii. Steam concentration : 10-50 % v/v

c. The catalyst shall be demonstrated to be free from spallation phenomena up to a catalyst temperature of 1000 °C in separate-effect tests (or otherwise) in air for different heat up and cooling down cycles. These test conditions should be decided based on the data collected during the performance evaluation of recombiners under inert atmospheres.

During the actual tests the mechanical deformation if any shall not adversely affect the performance of the recombiner function.

d. Pressure: LOCA based peak pressure

e. Poisons: Iodine, CO, oil vapour & lubricant, dust/aerosols as expected under accident conditions

f. Minimum temperature for the onset of recombination process: 30°C or lower

g. The structural integrity of the recombiners should be demonstrated to withstand thermal loads as well as various other likely loads such as blowdown jets, seismic etc.; and

h. Ageing studies be carried out to arrive at its deterioration characteristics with time. Based on the results of ageing studies, the frequency of in-situ maintenance checks of catalyst should be specified.

****

MANUAL NO. AERB/NPP-PHWR/SM/D-2

MANUAL NO. AERB/NPP-PHWR/SM/D-2

GOVERNMENT OF INDIA

AERB SAFETY MANUAL

HYDROGEN RELEASE AND MITIGATION MEASURES UNDER ACCIDENT CONDITIONS IN PRESSURISED HEAVY WATER REACTORS

ATOMIC ENERGY REGULATORY BOARD

AERB SAFETY MANUAL NO. AERB/NPP-PHWR/SM/D-2

HYDROGEN RELEASE AND MITIGATION MEASURES UNDER ACCIDENT CONDITIONS IN PRESSURISED HEAVY WATER REACTORS

Atomic Energy Regulatory Board
Mumbai 400 094
India

March 2004
(Amended in November 2017)

Price:

Orders for this manual should be addressed to:

The Administrative Officer
Atomic Energy Regulatory Board
Niyamak Bhavan
Anushaktinagar
Mumbai - 400 094
India

FOREWORD

Activities concerning establishment and utilisation of nuclear facilities and use of radioactive sources are to be carried out in India in accordance with the provisions of the Atomic Energy Act, 1962. In pursuance of the objective to ensure safety of members of the public and occupational workers as well as protection of environment, the Atomic Energy Regulatory Board (AERB) has been entrusted with the responsibility of laying down safety standards and framing rules and regulations for such activities. The Board has, therefore, undertaken a programme of developing safety standards, codes of practice and related guides and manuals for the purpose. These documents cover aspects such as siting, design, construction, operation, quality assurance, decommissioning and regulation of nuclear and radiation facilities.

Codes of practice and safety standards are formulated on the basis of internationally accepted safety criteria for design, construction and operation of specific equipment, systems, structures and components of nuclear and radiation facilities. Safety codes establish the objectives and set minimum requirements that shall be fulfilled to provide adequate assurance for safety. Safety guides elaborate various requirements and furnish approaches for their implementation. Safety manuals deal with specific topics and contain detailed scientific and technical information on the subject. These documents are prepared by experts in the relevant fields and are extensively reviewed by advisory committees of the Board before they are published. The documents are revised, when necessary, in the light of experience and feedback from users as well as new developments in the field.

The Code of Practice on 'Design for Safety in Pressurised Heavy Water Based Nuclear Power Plants (AERB Code No. SC/D, 1989)' lays down the minimum requirements for ensuring adequate safety in plant design. This safety manual is one of a series of manuals, which have been issued or are under preparation, to describe and elaborate the specific methodology for estimation of hydrogen release and mitigation measures under accident conditions.

The manual is based on the current designs of 220 MWe and 540 MWe pressurised heavy water reactors (PHWRs). The code requires that during postulated loss of coolant accident, the emergency core cooling system (ECCS) should ensure that core cooling is adequate such that possible chemical reactions are limited to an acceptable value with regard to hydrogen generation in the containment and systems shall be provided to control the hydrogen concentration in the containment atmosphere during accident condition to prevent detonation or deflagration which could jeopardise containment integrity. The manual provides a method for estimating hydrogen generation due to metal-water reaction and radiolysis during accident conditions in pressurised heavy water reactors and the hydrogen mitigation measures in containment.

Consistent with the accepted practice, 'shall', 'should' and 'may' are used in the manual to distinguish between a firm requirement, a recommendation and a desirable option, respectively. Appendices are an integral part of the document, whereas annexures, footnotes, references/bibliography and lists of participants are included to provide information that might be helpful to the user. Approaches for implementation different to those set out in the manual may be acceptable, if they provide comparable assurance against undue risk to the health and safety of the occupational workers and the general public and protection of the environment.

For aspects not covered in this manual, applicable and acceptable national and international standards, codes and guides should be followed. Non-radiological aspects of industrial safety and environmental protection are not explicitly considered. Industrial safety is to be ensured through compliance with the applicable provisions of the Factories Act, 1948 and the Atomic Energy (Factories) Rules, 1996.

This manual has been prepared by specialists in the field drawn from Atomic Energy Regulatory Board, Bhabha Atomic Research Centre, Indira Gandhi Centre for Atomic Research, Nuclear Power Corporation of India Ltd, and other consultants. It has been reviewed by the relevant AERB Advisory Committee on Codes and Guides and the Advisory Committee on Nuclear Safety.

AERB wishes to thank all individuals and organisations who have prepared and reviewed the draft and helped in its finalisation. The list of persons who have participated in this task, along with their affiliations, is included for information.

Suhas P. Sukhatme

(Suhas P. Sukhatme)
Chairman, AERB

DEFINITIONS

Acceptable Limits

Limits acceptable to the regulatory body for accident condition or potential exposure.

Accident

An unplanned event resulting in (or having the potential to result in) personal injury or damage to the equipment, which may or may not cause release of unacceptable quantities of radioactive material or toxic hazardous chemicals.

Accident Conditions

Substantial deviations from operational states[1], which could lead to release of unacceptable quantities of radioactive materials. They are more severe than anticipated operational occurrences and include design basis accidents as well as beyond design basis accidents.

Deflagration

Vigorous burning with emission of large heat and intense light accompanied by subsonic flame propagation.

Design Basis Accidents (DBAs)

A set of postulated accidents which are analysed to arrive at conservative limits on pressure, temperature and other parameters which are then used to set specifications to be met by plant structures, systems and components and fission product barriers.

Detonation

An exothermic chemical reaction due to combustion of a substance which propagates through reactive material at supersonic speed.

Event

Occurrence of an unplanned activity or deviations from normalcy. It may be an occurrence or a sequence of related occurrences. Depending on the severity in deviations and consequences, the event may be classified as an anomaly, incident or accident in ascending order.

Loss of Coolant Accident (LOCA)

An accident resulting from the loss of coolant to the fuel in a reactor due to a break in pressure retaining boundary of primary coolant system.

---

[1] Substantial deviation may be a major fuel failure, a loss of coolant accident (LOCA), etc. Examples of engineered safety features are an emergency core cooling system (ECCS) and containment.

Metal-Water Reaction

Reaction of water/steam with fuel cladding as a function of time and temperature during accident conditions.

Mitigation

Process of minimising the severity of a consequence following an incident/accident.

Physical Separation

A means of ensuring independence of equipment through separation by geometry (distance, orientation etc.), appropriate barriers or combination of both.

Postulated Initiating Events (PIE)[2]

Identified events that lead to anticipated operational occurrence or accident conditions, and their consequential failure effects.

Potential

A possibility worthy of further consideration for safety.

Prescribed Limits

Limits established or accepted by the regulatory body.

Purging

Displacement of an existing medium in a system by continuous injection of the same or another media, e.g., process of injection of air/CO_2 (carbon dioxide) to eject hydrogen generated in the reactor building containment to reduce hydrogen concentration.

---

[2] The primary causes of PIE may be credible equipment failures and operator errors, both within and external to the NPP, design basis natural events and design basis external man-induced events. Specification of the PIE should be acceptable to AERB.

CONTENTS

1. INTRODUCTION

1.1 General

1.1.1 In the event of occurrence of certain postulated accidents of very low probability in Pressurised Heavy Water Reactors (PHWRs), the excessive heat-up of the fuel cladding (zircaloy) to elevated temperatures (around or higher than 1000^0C) may lead to significant metal-water reaction[3] between zircaloy and steam in the reactor core. As an example, this might occur during an accident scenario such as loss of coolant accident (LOCA) with impaired functioning/non-availability of emergency core cooling system (ECCS) and cause rapid generation of hydrogen[4] due to metal-water reaction. Subsequent to this rapid short-term release of hydrogen, there may be further release of hydrogen into containment (on a slower long-term basis) on account of radiolysis of water due to radiation from fission product decay.

1.1.2 The metal-water reaction during accident conditions, mentioned above, would have the following effects which require considerations:

(i) Oxidation of fuel cladding due to metal-water reaction, beyond certain limits of clad thickness, can lead to fuel failure; the energy from the exothermic reaction can further add to the heat-up of the fuel which needs to be considered in evaluation of the accident; and

(ii) Hydrogen generation from the reaction, together (subsequently) with that from radiolysis, can lead to unacceptable concentration of hydrogen in the containment atmosphere; also the energy released to containment from the exothermic reaction may need consideration.

1.1.3 The safety code [14] requires that the effects of possible chemical and radiolytic reactions should be limited and considered in design. In this context, the present safety manual gives methods for calculation of the metal-water reaction and associated hydrogen generation rates and also for hydrogen generation rates from radiolysis under accident conditions. Approaches for management of predicted hydrogen release into the containment are also covered.

1.2 Objectives

The objectives of the safety manual are to specify the following under accident conditions:

(a) method for calculating the metal-water reaction (zircaloy-steam reaction) and associated exothermic energy release rates;

(b) methods of assessment of

  (i) hydrogen release rates into the containment, from metal-water reaction and by radiolysis; and

  (ii) spatial and temporal hydrogen concentrations in the containment;

(c) the performance requirement of ECCS with regard to limiting the metal-water reaction and associated

---

[3] In PHWR metal-water reaction is between zircaloy and D_2O/H_2O. However, in this safety manual the terms ‘water’ and ‘hydrogen’ have been used, interchangeably with ‘D_2O’ and ‘Deuterium’ respectively.

[4] A typical time period of rapid generation of hydrogen from metal-water reaction would be of the order of ~1h. The zircaloy of fuel clad is the predominant participant in the metal-water reaction, although pressure tubes also may contribute to a much lesser extent.

hydrogen release is covered in section 4.3.2. However, comprehensive ECCS acceptance criteria are given in safety guide on ‘Primary Heat Transport System for Pressurised Heavy Water Reactors’ AERB/SG/D-8; and

(d) acceptance criteria for hydrogen distribution in the containment and mitigation methodologies.

1.3 Scope

This safety manual provides the important considerations relevant to metal-water reaction during accident condition and related issues, viz. hydrogen generation and mitigation in containment. Within this framework, sources of hydrogen generation of relevance are:

(a) metal-water reaction; and

(b) radiolysis of water.

This safety manual is applicable to reactors using zircaloy-2, zircaloy-4 and/ or Zr-Nb and such other Zr-bearing alloys as fuel cladding/pressure tube materials with particular reference to PHWRs.

2. CALCULATION OF HEAT AND HYDROGEN GENERATION RATES FROM METAL-WATER REACTION

2.1 General

2.1.1 Heat as well as hydrogen is generated during metal-water reaction. This section describes the kinetics of metal water reaction and methodology for calculation of heat and hydrogen generation rates.

2.2 Metal-water Reaction

2.2.1 Chemical reaction between zircaloy and steam

The chemical reaction between zircaloy and steam is exothermic and is represented by the following equation:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + 586.6 \text{ kJ/mole} \qquad \text{... (1)}$$

The quantitative assessment of heat release rate and the hydrogen release rate shall be based on the kinetics of the above reaction. The rate controlling mechanism for the above oxidation reaction in unlimited steam is considered to be diffusion of oxygen anions through the anion-deficient zirconium defect structure. In such diffusion-controlled solid state reactions, the kinetics is characterised by a parabolic rate law such that:

$$W^2 = K_p \cdot t \qquad \text{... (2)}$$

where t = Time of isothermal exposure of zircaloy to steam (s)
W = Mass of zirconium reacted per unit area (mg/cm^2)
K_p = Parabolic rate constant $[mg(Zr)/cm^2]^2 s^{-1}$.

The temperature dependence of the parabolic rate constant K_p is defined by the Arrhenius equation:

$$K_p = A \cdot \exp(-Q/RT) \qquad \text{... (3)}$$

where A = Pre-exponential factor
Q = Activation energy ($J.mol^{-1}$)
T = Reaction temperature (K)
R = Universal gas constant ($8.314\ J.mol^{-1}K^{-1}$)

Based on study of extensive data-base on kinetics of the reaction (equation-1) as reported in literature [Annexure-I] three-temperature zone model has been considered for the form of equation-3. The values of pre-exponential constant A and activation energy Q to be used in the respective temperature range are as tabulated below:

S.No.	Temperature (T) range	A $[\mathrm{mg(Zr)/cm^2}]^2\mathrm{s}^{-1}$	Q ($\mathrm{J.mole}^{-1}$)
1.	$T < 1000^{o}C$	2.496×10^{5}	147989
2.	$1000^{o}C \le T < 1500^{o}C$	9.170×10^{5}	149926
3.	$1500^{o}C \le T \le 1852^{o}C$	3.330×10^{7}	190465

It may be noted that equation-3 with above tabulated values of A and Q in respective temperature ranges includes uncertainty and scatter of experimental data so as to provide conservative values of reaction rate constant K_p. Details and basis of above recommendation are given in Annexure-I.

2.3 Methodology for Modelling the Equations

2.3.1 For the estimation of time dependent and total oxidation of zircaloy and associated hydrogen release during accident conditions, it is required to use the above mentioned kinetic rate equations in conjunction with the safety analysis code which performs the thermal analysis of the fuel clad in the core as a function of time during the accident progression. The recommended equations in this mannul should be integrated into the safety analysis code so as to perform coupled calculations. This is necessary since the exothermic metal-water reaction adds to the enthalpy of zircaloy, which in turn influences the reaction rate. This coupling is particularly important for zircaloy temperature above 1000°C.

To get a proper estimate of the hydrogen release, it is necessary to consider the spatial variation in zircaloy temperature in the core. For this purpose, proper nodalisation should be done in radial and axial direction to suitably represent the variations in the fuel-clad temperature within the core due to flux profile and varying cooling conditions.

If the analysis predicts any local melting of zircaloy, the resulting geometric changes and exposure of additional fresh metal should also be considered in the analysis. Since such assessment is subject to uncertainties, appropriate simplified assumptions may be made in this regard, which should be conservative.

2.4 Hydrogen Release Rate

2.4.1 Following an accident, hydrogen release rate, if any, into the containment shall be calculated using methodology described in the previous sub-sections. However, for predicting the subsequent behaviour of hydrogen in the containment, along with its release rates, specific enthalpy or temperature (when it is released into the containment) shall be appropriately calculated using the accident analysis computer codes, assuming temperature of hydrogen released at the reaction site the same as the prevailing reaction temperature and by accounting for heat dissipation to the piping and other structural components in its passage from the point of source to the point of release. To the extent codes are not fully validated, appropriate conservative assumption in modelling/inputs may be used.

3. HYDROGEN RELEASE RATES BY RADIOLYSIS

3.1 General

3.1.1 In a nuclear reactor, apart from the metal-water reaction described in the previous section, hydrogen would also be generated due to radiolysis of water.

3.1.2 Radiolysis of water occurs during both normal operation and accident conditions. It involves the decomposition of water molecules by radiation (alpha, beta, gamma and neutron), producing various radicals such as e^- aq, OH, H, HO_2 and molecular products such as H_2 and O_2. The net result is the production of both H_2 and O_2 molecules essentially in a stoichiometric ratio [15,16&26]. During accident conditions, with containment boxed-up, the hydrogen generation from radiolysis can build up its concentration in the containment over a period of days. In case the reactor is in shutdown state, radiolysis is mainly due to gamma radiation.

3.2 Sources and Mechanism of Radiolysis

3.2.1 Source

Radiolytic decomposition of water can take place in primary coolant, moderator, sump water and suppression pool water (along with ECCS water, in case of LOCA).

During normal operation, radiolysis is mainly limited to the primary coolant and moderator system. However, with proper chemistry control in the primary coolant system and a cover-gas system with recombiners for moderator system, hydrogen concentration is maintained well below safe limits. During LOCA scenarios involving fission product release, suppression pool water along with water in primary heat transport (PHT) system may experience significant radiolysis due to presence of fission products. The resulting hydrogen generated in water would migrate to gas space of the containment, the rate of migration depending on turbulence and convection, diffusion processes in water, and water surface area exposed to gas.

3.2.2 Mechanism

The rate of hydrogen generation is controlled by the following factors:

(a) energy of radiation;

(b) the fraction of this energy that is absorbed by water;

(c) the rate of hydrogen and oxygen production per unit of energy absorbed by water. This rate (expressed as ‘G’ value) is influenced by impurities as well as temperature of water; and

(d) effect of pre-existing hydrogen concentration in reducing the radiolysis rate (effect of backward reaction/ recombination)[5].

---

[5] In an operating reactor at power, with gamma doses for radiolysis being high, in closed system like primary heat transport (PHT) system, moderator, etc., the net ‘G’ value may be only 3% [15] to 5% [16] of the initial ‘G’ value, due to predominance of recombination reaction. However, in the present context of a shutdown reactor, the gamma doses are too low for radiolysis to build up to levels at which backward (recombination) reaction will have significant impact on the ‘G’ value [25].

The yield of H_2 due to the radiolysis of water is generally expressed as a 'G' value, which means number of molecules of H_2 formed per 100 eV of energy absorbed. The value of the net radiolytic yield or 'G' for beta/gamma radiations should be taken as 0.44 molecule of H_2 per 100 eV of energy absorbed as recommended in the reference [17]. The yield of deuterium (D_2) in radiolysis of heavy water is less (0.38) as compared to that of hydrogen (H_2) [18]. Sources of water that should be considered for estimation of hydrogen generation, due to radiolysis following LOCA, are brought out in section 3.3. For assessing the transfer (migration) of the radiolytically generated hydrogen, from the liquid in which it is generated to the air space, the parameters to be considered are [25]: mass transfer co-efficient of hydrogen, concentration of hydrogen dissolved in water, surface area of water-air interface, and average gamma power causing the hyphem radiolysis. The mass transfer co-efficient of hydrogen is, in turn, a function of turbulence, convection and diffusion in water. Thus, while the liquid to air transfer of hydrogen in a closed stagnant system (e.g., from moderator in calandria) may be very low, the transfer in open and circulating system (e.g., water spilling out from break) may be very high.

The composite effect of hydrogen generation in liquid, and its transfer to gas space, could be represented by an effective 'G' value.

$$\text{Effective } G = G.\, f_R \qquad \text{... (4)}$$

where, f_R is the 'hydrogen release factor', which could vary from near unity for open/turbulent situation (e.g., water spilling out from break) to low value for closed stagnant system (typical average value 0.05 [25] for moderator in calandria of 220 MWe PHWR).

3.3 Estimation of Hydrogen Generation [22]

3.3.1 Hydrogen generation due to radiolysis of water at various sources is described below. The total generation is the sum from all sources, which are relevant to the accident scenario considered.

3.3.2 Radiolysis Due to Core Gamma

3.3.2.1 *PHT coolant*: Decomposition of coolant water due to absorbed energy from core gamma should be considered for estimation of hydrogen generation, considering the time-dependent decay of gamma field. PHT is considered to be filled up even after LOCA, due to presence of ECCS water.

3.3.2.2 *Moderator*: Depending on accident scenario if calandria is in communication with reactor building atmosphere (i.e., due to rupture of over-pressure relief device (OPRD), the system cannot be considered as closed one), the radiolytic decomposition of moderator should be considered. The decay of core gamma following reactor trip should be considered for attenuation by moderator.

3.3.3 Radiolysis by Beta from Tritium Activity

Due to long half-life of tritium the consequent hydrogen generation rate remains nearly constant for a long period.

3.3.3.1 *PHT coolant*: Radiolysis of PHT coolant due to beta activity should be assessed considering total equilibrium tritium activity in the coolant and its average beta energy. However, it may be noted that the hydrogen generation from this source is negligibly small.

3.3.3.2 *Moderator*: Similar to PHT coolant, radiolysis of moderator should be estimated considering total equilibrium tritium activity and average beta energy emanating from it. It may, however, be noted that compared to radiolysis on energy deposition due to core gamma, radiolysis due to beta activity is very low.

3.3.4 Radiolytic Decomposition of Sump/Suppression Pool Water due to Beta-Gamma Radiation from Volatile Fission Product Released from Core

3.3.4.1 The hydrogen generation from volatile fission products, trapped in the water, is the major contributor of hydrogen from radiolysis.

3.3.4.2 Following a postulated accident, the volatile fission products are released into the coolant. Of the various fission products, noble gases can be assumed to escape the coolant and the remaining volatile isotopes, including iodine, are condensed and trapped in the coolant. These fission products along with coolant may be transported to containment sump, fuelling machine vault/service area or pump room floor, suppression pool, etc.

3.3.4.3 Since the distribution of these fission products could vary depending on many factors, therefore, conservatively 100 percent of the beta-gamma energy liberated from those trapped volatile products should be assumed to be absorbed in the water causing radiolysis unless a lower number can be justified. The time-dependent decay of these fission products needs to be considered for hydrogen generation by radiolysis.

3.3.5 Calculation Methodology for Estimation of H_2

3.3.5.1 *Radiolysis of coolant in PHT system:* Radiolysis of coolant in PHT system should be assessed considering that the channel is filled with water. The amount of H_2 generated in coolant due to fuel decay core gamma depends on amount that gets absorbed by coolant. Gamma energy dissipation in coolant from individual fuel pin should be estimated, considering escape factor for the fuel bundle geometry. A simple modelling of fuel bundle, as a centre pin surrounded by concentric rings of fuel elements representing the intermediate and outer portions of the fuel bundle, can be considered. Each of these can be considered as an isotropic source of gamma radiation. Effect of neighbouring channel should also be considered; where an average gamma flux in coolant is to be estimated based on average burn-up of fuel. Also, the time-dependent gamma flux based on decay power has to be considered for radiolysis of water.

The effect of beta particles from fuel can be neglected since it can be assumed to get absorbed in the fuel pellet or cladding material. However, radiolysis by beta particles from tritium in the coolant should be estimated, considering maximum allowable tritium concentration in PHT coolant and an average energy of beta particles. Beta flux remains nearly constant due to long half-life of tritium; thus energy absorption rate remains almost constant. All the energy emanating from beta particle should be considered absorbed by water.

3.3.5.2 *Radiolysis in moderator:* The radiolytic decomposition of moderator due to core gamma should be calculated based on decay gamma that gets absorbed in moderator. The energy absorption in moderator from decay gamma can be assumed to be proportional to reactor decay power.

The radiolysis of moderator by beta particles from tritium in moderator should be estimated considering equilibrium tritium activity in moderator. All energy of the beta particles should be considered absorbed in water for radiolysis.

Whether the radiolytically generated hydrogen in moderator will end up in containment atmosphere will depend on the specific accident scenario.

3.3.5.3 *Radiolysis in suppression pool water:* As mentioned earlier it is difficult to estimate distribution of fission product in different areas where it can interact with water for radiolysis. It can be conservatively assumed that the 100 percent of the released volatile fission products (except noble gases) can find its way ultimately to suppression pool water. However, absorption of beta-gamma energy from these fission products by pool water will depend on the distribution of fission product within the pool water. However, as a conservative upper-bound estimate, it can be assumed that all the beta-gamma energy of fission products gets absorbed by water for radiolysis. For the estimation of hydrogen generation by radiolysis time-dependent decay power of these fission products should be considered for estimating beta-gamma energy.

3.3.5.4 *Estimation of hydrogen generation from radiolysis:* At any instant of time, the hydrogen generation rate due to radiolysis is calculated by the following formula:

$$H = E \cdot G \cdot M/(100Av)\ \text{gm/s.} \qquad \ldots (5)$$

where E = Energy absorption rate by water (eV/s)
G = 0.44 (for H_2O)[6] gm-mole/100 eV and
0.38 (for D_2O)[6] gm-mole/100 eV
Av = Avogadro's No. (6.023×10^{23})
M = Molecular weight of H_2 or D_2

(a) in case of gamma energy absorption in coolant and moderator, E can be estimated as follows:

$$E = f \cdot m \cdot v \qquad \ldots (6)$$

where f = Average energy flux (eV/cm^2-s)
m = Energy absorption coefficient (cm^{-1})
v = Volume of water (cm^3)

Usually, this 'E' value is calculated by physics computer codes and results from this are available as time vs heat generation for system design calculation. So, the same can be directly used for estimation of hydrogen generation due to radiolysis of moderator; and

(b) in case of beta energy in moderator from tritium and beta-gamma energy from fission products in suppression pool, 100 percent of the energy emitted can be considered as absorbed by water. This is because of the low penetrating power of beta particles and large amount of suppression pool water to absorb the gamma energy.

---

[6] These values are for 'open' system. In the closed containment, as the hydrogen concentration in gas space builds up, the effective 'G' value may get reduced. However, as a conservative approach, above values may be used, unless lower values can be justified. By using above 'G' values, it is implied that hydrogen generated in water is being removed (as in dynamic situation); this is conservative.

So, in this case,

$$E = 3.7 \times 10^{10} \times Q \times e \qquad \ldots (7)$$

where Q = Activity in curies
e = Average energy of radiation (eV) per disintegration

Since fission products decay with time, the activity and thus the energy absorption rate by water will also vary with time in proportion to decay power variation. So, for assessment of cumulative hydrogen generation, time integration of varying hydrogen generation rate should be carried out.

3.3.5.5 *Estimation of fraction of radiolytically generated hydrogen released into gas space [25]:* The fraction of the hydrogen generated from radiolysis in the water, that would get transferred to gas space (defined in this manual as hydrogen release factor f_R) would depend on factors brought out in section 3.2.2.

Guidelines for f_R to be used for various sources are as follows:

(i) Hydrogen generated in suppression pool water and in PHT system, considering that this water would spill out of the break in PHT system during recirculation phase of ECCS, may get released into gas space. Hence f_R may be taken as unity.

(ii) Hydrogen generated in moderator water where the water-gas interface is relatively stagnant, and value of f_R[7] would be significantly less than unity.

$$f_R = \frac{K_H \times S}{P_{avg} \times 2016} \qquad \ldots (8)$$

where K_H = Hydrogen mass transfer co-efficient (dm/s)
= 1.68×10^{-4} dm/sec for moderator in calandria
S = Surface area of moderator in calandria (dm^2)
P_{avg} = Average core gamma power attenuation in moderator in time span considered (MW)

---

[7] Typical average value of f_R for 220 MWe PHWR (NAPS onwards) is 0.05.

4. HYDROGEN BEHAVIOUR IN CONTAINMENT

4.1 General

4.1.1 The hydrogen released from the core due to metal-water reaction and by radiolitic process progressively disperses and mixes with the gaseous contents of the containment volume (i.e., air and steam) and under certain circumstances may form potentially combustible gas-mixture. Depending upon the concentration of hydrogen, deflagration and detonation can occur which result in additional pressure (static and dynamic) and temperature loads on the surrounding structures. To ensure containment integrity, hydrogen concentration in the containment should meet the recommanded acceptance criteria in section 4.3. If necessary, suitable mitigation means should be incorporated to control the concentration.

4.2 Hydrogen Transport within Containment

4.2.1 For the calculational model of hydrogen distribution within containment, the following shall be ensured:

(a) the momentum equations must include among others the buoyancy head term to represent buoyancy effects due to thermal and density gradients;

(b) the mass transport by molecular diffusion is included along with other conservation equations of mass, momentum and energy (this is important in long-term hydrogen transport calculation);

(c) heat transfer from gas to solid structures by natural and/or forced convection, steam condensation on walls and radiation;

(d) models to account for influence of turbulence (applicable for computational fluid dynamics (CFD) codes); and

(e) the computer codes shall be validated against experimental data. To the extent codes are not fully validated, appropriate conservative assumption in modelling/inputs may be used. Alternatively, results from more than one code should be compared.

4.2.2 The hydrogen distribution calculations within the containment are generally carried out using two types of codes: (i) lumped parameter model-based computer codes in which containment building is modelled as a network of volumes (to represent different rooms/compartment) interconnected by junctions (to represent inter-compartmental connections); and (ii) finite volume-based computational fluid dynamics (CFD) codes in which the entire containment free volume is discretised in detailed mesh of finite volumes.

4.2.3 The identified computer codes (commercial or in-house developed) meeting the requirements specified in section 4.2.1 should be used keeping in mind the following :

(a) if lumped parameter-based computer code is in use, every volume in this compartment in which natural circulation is important shall be further sub-divided into at least three sub-volumes in a configuration which allows looping;

(b) if the postulated break is such that it can cause release of high velocity jet in the upward direction, this effect should be appropriately considered (applicable for CFD codes);

(c) the calculations of hydrogen transport are known to be sensitive to levels of discretisation, numerical scheme, and computational time steps. In view of this, designers shall ensure that the results obtained by use of such codes are free from individual as well as combined influence of above-mentioned parameters by way of performing numerical experiments.

4.3 Acceptance Criterion for Hydrogen Concentration in Containment

4.3.1 The recommended acceptance criteria for H2 concentration in containment are based on the following considerations:

(a) In case of LOCA with safety systems including ECCS available, the hydrogen concentration at a location in the containment should generally be maintained outside the deflagration (flammability) limit in the ternary diagram [ref. Fig. 1]. This shall be achieved without taking credit for mitigating measures such as recombiners/igniters. However, credit for mixing and/or purging provisions may be considered in the design.

If hydrogen concentrations cannot be ensured outside the deflagration (flammability) limit, the following should be ensured:

i). the area has no potential ignition sources such as sparks or hot surfaces (however, this may be difficult to ensure over a period of time); or

ii). any components located in the area required for safety function will survive the hydrogen fire, or their failure will not impair relevant safety functions required during the particular accident sequence. Any consequential effect of the fire due to hydrogen shall be considered to ensure that such safety functions are not impaired.

(b) For catering to accident sequences, involving multiple failures considered in design (e.g., LOCA with ECCS not available), the global hydrogen concentration shall remain outside the deflagration (flammability) region in the ternary diagram as shown in the Fig. 1 [24]. However, local hydrogen concentrations shall be such as to prevent local detonation which could affect containment integrity through missile generation or otherwise. This may be achieved with the use of mitigating measures given in section 4.4**,** if required.

4.3.2 Consideration in developing acceptance criteria:

Since the containment acts as the last barrier to hold the fission products, it is necessary to prevent hydrogen concentrations reaching a level that could threaten its integrity. In this connection, following measures have been suggested in order of importance [19]:

(a) Priority**-1:** Exclude a global detonation or a deflagration with the potential to reach failure pressure of containment.

(b) Priority**-2:** Prevention of local detonation, which could affect containment integrity through missile generation.

(c) Priority**-3:** Prevention of local hydrogen concentration greater than 10 percent by volume [This Clause shall be read in conjunction with 4.4.2 (i)].

(d) Priority**-4:** Mitigation of the consequences of local, multiple burning, leading to high temperatures (failure of local equipment).

It is seen that the most important requirement is to prevent global detonations. Prevention of ignition deflagration is the next priority to ensure continued availability of systems required for safety.

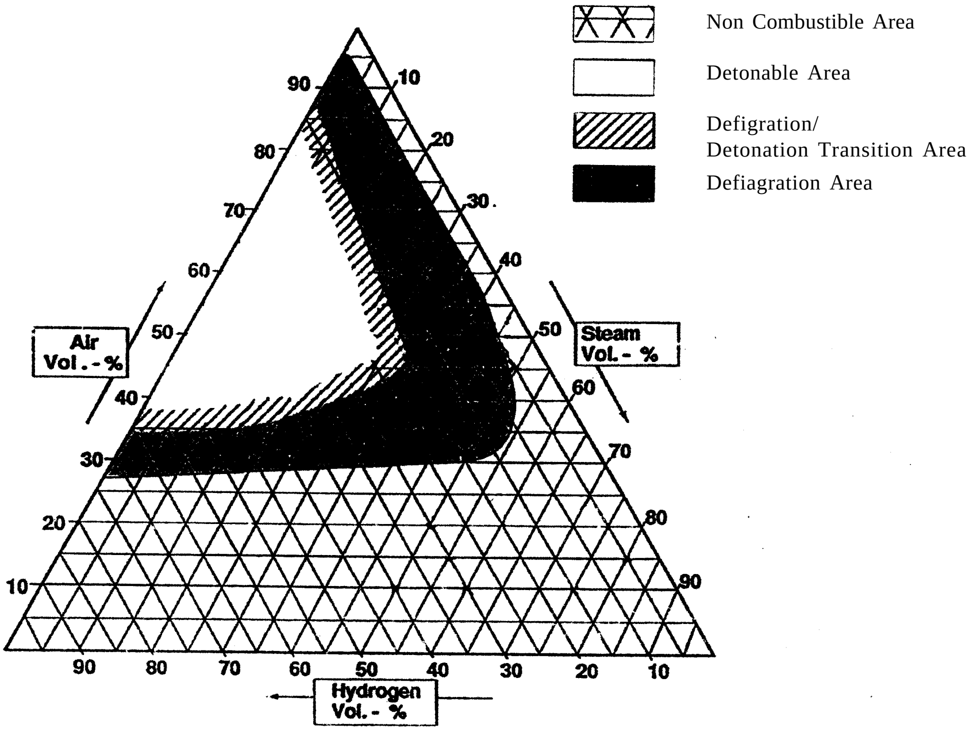


FIG. 1: TERNARY DIAGRAM FOR DEFLAGRATION(FLAMMABILITY) AND DETONATION LIMITS OF HYDROGEN-AIR-STEAM MIXTURE.

4.4 Hydrogen Mitigation[8]

4.4.1 Hydrogen mitigation provisions are required if the calculations for hydrogen transport in the containment carried out as per the guidelines of section 4.1 do not meet the acceptance criteria given in section 4.3.1.b. Some methods for mitigation are:

(a) deliberate ignition of hydrogen-air mixture;

(b) inerting of hydrogen-air mixture by N_2/CO_2 or by promoting mixing between the compartments by appropriate means;

(c) catalytic recombination of hydrogen with oxygen from air; and

(d) or a combination of these methods.

Among these, the one based on oxidation of hydrogen in the presence of catalyst such as platinum/ palladium or the alloys of platinum/palladium, has proved to be most attractive for the following advantages:

---

[8] Development of recombiners as hydrogen mitigation devices is currently an R&D activity.

(i). the catalytic recombiners can be designed as passive devices so that mitigation action is assured;

(ii). the method has been demonstrated to be efficient in removing hydrogen even in the presence of steam, at temperatures as low as ambient and at hydrogen concentration as low as 0.05 percent (V/V); and

(iii). during the process of recombination, which is exothermic, it also promotes homogenisation of gas mixture due to buoyancy-induced gaseous flow.

4.4.2 In view of this, hydrogen mitigation, if required, is recommended to be achieved by catalytic recombination principle. The suitable recombiner device based on platinum/palladium catalyst shall be considered for installation in the plant only after satisfactory demonstration of its efficacy in safe manner in a separate experimental set-up under suitably simulated containment environment conditions arising out of an accident. For the inert atmospheric conditions (both dry and wet atmospheres), the steam concentration should be as per the Shapiro-Moffette diagram. Under wet conditions, from among the total test matrix recommended for recombiner performance under clause 4.4.3 below, the qualification tests above 10% (v/v) and up to 30% (v/v) hydrogen concentration are required to characterise the recombiner behaviour in oxygen lean atmospheres. While designing the hydrogen mitigation system for a specific plant following sub-clauses should also be addressed suitably:

(i). The mean hydrogen concentration in the compartments of the containment where recombiners are installed shall not exceed 9% (v/v) during the progression of the accident and in post-accident conditions.

(ii). The safe performance behaviour of multiple recombiners installed within single/multiple compartments may also be assessed and substantiated, if necessary.

Accordingly, the recombiner devices shall be qualified as per the following criteria.

4.4.3 Qualification Parameters for Catalytic Recombiners

Based on the functional requirements of the recombiners and the technology available for conducting the experiments, following qualification parameters are worked out.

(a) Qualification under inert atmosphere

(i). Hydrogen concentration[9] : up to 4 % v/v (in dry air medium)
up to 30% v/v (in inert steam environment)[10]

(ii). Steam concentration : As per Shapiro-Moffette diagram to ensure inert conditions.

---

[9] The term “concentration” means concentration of the species (H_2, steam) at the recombiner inlet.

[10] As explained in clause 4.4.2, beyond 10% and up to 30% concentration of hydrogen and at a steam concentration of 60 % (inert atmosphere), it is intended to characterise the recombiner behaviour in oxygen lean atmosphere.

(b) Qualification under non-inert (deflagrable) atmosphere

The safe operational behaviour of recombiners shall be demonstrated for gas mixture compositions within the deflagrable region.

During these tests, it shall be suitably demonstrated that any local ignition within or in the vicinity of recombiners does not lead to any sustained ignition as depicted by rapid and sustained pressure, temperature and concentration transients. **These qualification tests should be performed in a graded risk manner (starting from least deflagrable compositions).** The following range of gas concentrations shall be considered for qualifying the recombiners.

(i). Hydrogen concentration : Up to 10% v/v (in steam environment)
(ii). Steam concentration : 10-50 % v/v

(c) The catalyst shall be demonstrated to be free from spallation phenomena up to a catalyst temperature of 1000 °C in separate-effect tests (or otherwise) in air for different heat up and cooling down cycles. These test conditions should be decided based on the data collected during the performance evaluation of recombiners under inert atmospheres. During the actual tests the mechanical deformation if any shall not adversely affect the performance of the recombiner function.

(d) Pressure: LOCA based peak pressure

(e) Poisons: Iodine, CO, oil vapour & lubricant, dust/aerosols as expected under accident conditions

(f) Minimum temperature for the onset of recombination process: 30°C or lower

(g) The structural integrity of the recombiners should be demonstrated to withstand thermal loads as well as various other likely loads such as blowdown jets, seismic etc.; and

(h) Ageing studies be carried out to arrive at its deterioration characteristics with time. Based on the results of ageing studies, the frequency of in-situ maintenance checks of catalyst should be specified.

4.5 Hydrogen Monitoring[11]

4.5.1. If the design intends to monitor hydrogen concentration in the containment during accidents, so as to facilitate operator action for effective hydrogen management, then the hydrogen concentration monitoring system to be installed shall qualify for its functionability under worst enviroment conditions expected during the course of accident including high radiation fields. This system should monitor concentrations at locations for which analysis indicates possibility of hydrogen concentrations exceeding: (i) ignition limit for design basis LOCA conditions [ref. 4.3.1.(a)]; or (ii) detonation limits for multiple failures [ref. 4.3.1.(b)].

---

[11] This area is still under development stage and needs to be pursued.

ANNEXURE-I

ZIRCALOY-STEAM REACTION KINETICS DATA FOR ACCIDENT CONDITIONS

I.1 Introduction

The temperature dependence of the parabolic rate constant is defined by an Arrhenius relationship:

$$K_p = A \bullet \exp(-Q/RT) \qquad \text{..... (A.1)}$$

where A = Pre-exponential factor
Q = Activation energy (J mol^{-1})
T = Temperature (K)
R = Gas constant (8.314 J mol^{-1} K^{-1})

A typical unit for K_p is $[mg\ (Zr)/cm^2]^2\ s^{-1}$ where amount of zirconium consumed is expressed in mg.

I.2 Rate Constants in Different Temperature Ranges

Zirconium oxide exists in three allotropic forms: monoclinic upto ~ 1000°C, tetragonal from 1000–1500°C and cubic above 1500°C. The kinetics data of zircaloy-steam reaction is therefore considered for three corresponding temperature ranges:

(i) below 1000°C;

(ii) 1000°C–1500°C; and

(iii) 1500°C–1852°C

The dependence of parabolic rate constant K_p in the above temperature ranges along with major experimental features, collected from the literature [1-10] are given in Table-A.1. The calculated values of K_p using these equations at select temperatures of 1000°C and above are summarised in Table-A.2.

It may be worthwhile to note that isothermal oxidation of zircaloy-2 cladding of fuel elements was studied in Radiometallurgy Division of BARC in the temperature range of 650°C–800°C and 1050°C–1150°C. Figures A-1 and A-2 depict these data with curves fitted for mean of the data points as well as to represent upper bound of the experimental data. Equations at No. 2 (below 1000°C) and at No. 9 (between 1000°C–1500°C) in Table-A.1 represent the curves corresponding to upper bound K_p of the data.

It can be noted from the data presented in Table-A.1 and Figures A-3 to A-7 that:

- the correlation by Baker-Just is one of the oldest and consistently conservative above 1000°C; the conservatism increases as the temperature increases;
- there are not many studies reported below 1000°C;

- most of the reported studies cover the temperature range of 1000°C–1500°C and confirm parabolic rate equation. However, as it can be seen from Fig. A-3, all the data sets [2-10] are consistently below that of Baker-Just [1];
- for the purpose of PHWRs, the Canadian data of Urbanic-Heidrik [9] and the Indian data of Sethumadhavan et al. [10] shown in Fig. A-4 are also in good agreement. Indian data in comparison to the mean of all the data [2-10] excluding Baker-Just shown in Fig. A-5 is only marginally lower in higher range of temperature. A constant multiplier of 1.4 to equation representing data of Sethumadhavan et al. (equation at No. 9 in Table-A.1) provide the upper bound for all the data [2-10] in the temperature range of 1000°C to 1500°C [Fig. A-6];
- in the temperature range of 1500°C – 1852°C (melting point of zircaloy) only two data sets are available due to obvious difficulties in conducting the experiments and data collection. The Baker-Just correlation, although highly conservative, still represents the upper bound of data sets and should be looked at as an equation covering uncertainties; and

The effects of some of the known influencing parameters are qualitatively discussed below.

I.2.1 Presence of Hydrogen in Steam

The oxidation of zircaloy by steam hydrogen mixture was studied from 1100°C-1600°C by Moalem and Olander [11]. Dilution of steam by H_2 in the region interest (i.e., upto 90 percent v/v H_2) had no effect on the parabolic oxidation rate of zircaloy-2.

I.2.2 Steam Purity

Cathcart et al. [12] oxidised zircaloy-4 in steam to which small amounts of potentially reactive gases had been added. Additions of 10 percent of nitrogen or oxygen or 5 percent of hydrogen were made to steam and oxidation carried out at 1374K and 1577K. Only a small number of tests were performed and there was some scatter in the results. Nevertheless the authors concluded that the additions made no significant difference to the oxidation rate constants.

Leistikow *et al.* oxidised zircaloy-4 in pure steam, oxygen and in air in the temperature range 1173-1423K. The weight gain was slightly greater in air and oxygen compared with steam.

I.2.3 Steam Pressure

Pawel *et al.* [13] studied the oxidation of zircaloy-4 in flowing steam at pressures upto 10.34 MPa at 900°C and 1100°C. Within experimental accuracy there was no effect of pressure on the oxidation. At temperatures below 900°C increase in pressure tends to increase the thickness of oxide layer.

I.2.4 Break-away Oxidation

The studies reported by Leistikov [8] on oxidation in lower temperature ranges (600°C – 1000°C) indicate that oxidation rate changes from cubic to parabolic and to linear in case of extended isothermal oxidation of zircaloy. The enhanced oxidation rate in the lower ranges of temperature was attributed to mechanical degradation of the oxide layer. However, such a phenomenon could not be observed in the studies reported by Sethumadhavan *et al.* [10] on the cladding tubes despite the reaction being continued upto four hours in the temperature range of 650°C – 800°C.

I.3 Recommendations

The recommended equations for parabolic rate constants for the three temperature ranges are given below:

I.3.1 $T < 1000°C$

The data available in this temperature range include one set of data from the work carried out on PHWR fuel cladding at Radiometallurgy Division, BARC. Oxidation kinetics of zircaloy may be influenced by surface condition and materials characteristics like composition and microstructure. As the fabrication method as well as some other physical and chemical parameters of the PHWR cladding are different from the cladding materials of other reactors, the data obtained on actual PHWR cladding is considered to be more representative than the data obtained on materials from other sources. The oxidation data on PHWR cladding has been obtained for exposure periods upto 4 h with close control of temperature during experiment and the data have high degree of reliability. In view of this, the oxidation kinetics data generated on PHWR cladding is recommended for use in this temperature range.

The expression for the parabolic rate constant derived from this study is:

$$K_p = 2.496 \times 10^5 \times \exp(-147989/RT) \qquad \text{.... (A.2)}$$

I.3.2 $1000°C \le T < 1500°C$

There are a number of data sets available in this temperature range. In view of the fact that data generated on our own cladding tube material is more appropriate for Indian PHWRs, the correlation of Sethumadhavan *et al*. is recommended for use in this temperature range. As discussed earlier, a multiplier of 1.4 to the correlation of Sethumadhavan *et al.* provides the upper bound to all the data set (except Baker and Just). On the basis of above considerations, the equation recommended for calculation of K_p values in this temperature range is given below:

$$K_p = 9.17 \times 10^5 \times \exp(-149926/RT) \qquad \text{.... (A.3)}$$

I.3.3 $1500°C \le T \le 1852°C$

There are only two data sets available in this temperature range. Baker & Just correlation [1] is more conservative than the correlation of Urbanic & Heidrick [9] (ref. Fig. A-7). In the absence of additional data the Baker & Just correlation [1] is recommended for use in this temperature range.

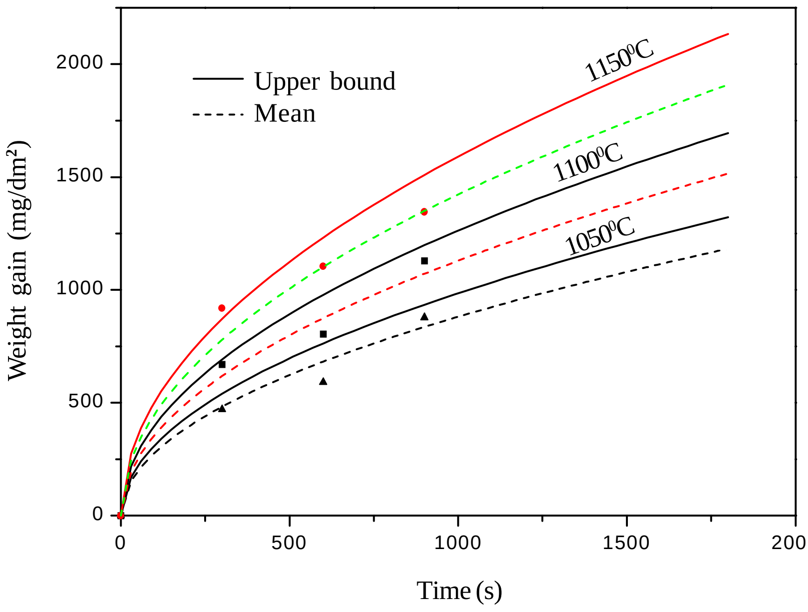
$$K_p = 333 \times 10^5 \times \exp(-190465/RT) \qquad \text{.... (A.4)}$$

TABLE-A.1: PARABOLIC RATE CONSTANTS REPORTED IN LITERATURE FOR DIFFERENT TEMPERATURE RANGES.

Investigators	**Equations for K_p [mg (Zr)/cm^2]^{2}s^{-1}**	**Experimental Details**				
		Temp. range	**Material**	**Shape**	**Heating mode**	**Environment**
$T < 1000^\circ C$						
1. Biederman et al. [2]	$K_p = 9.32 \times 10^3 \times \exp(-114445/RT)$	650-810°C	Zry-4	Tube	Internal	Steam
2. Sethumadhavan et al. [10]	$K_p = 2.496 \times 10^5 \times \exp(-147989/RT)$	650-800°C	Zry-2	Tube	Internal	Steam
3. Leistikow et al. [8]	$K_p = 42.58 \times 10^5 \times \exp(-174360/RT)$	700-1300°C	Zry-4	Tube	Internal & external	Steam
$1000^\circ C \leq T < 1500^\circ C$						
1. Baker & Just [1]	$K_p = 333 \times 10^5 \times \exp(-190465/RT)$	upto 1850°C	Zr	Wire	Condenser discharge	Water
2. Brown-Healey [3]	$K_p = 16.71 \times 10^5 \times \exp(-163116/RT)$	1000-1400°C	Zry-4	Tube	External	Steam
3. Pawel –Cathecart&Mckee[4]	$K_p = 29.32 \times 10^5 \times \exp(-167190/RT)$	900-1500°C	Zry-4	Tube	External	Steam
4. Kawasaki *et al.* [5]	$K_p = 38.03 \times 10^5 \times \exp(-170410/RT)$	1000-1330°C	Zry-4	Tube	External	Steam
5. Westerman & Hesson [6]	$K_p = 5.22 \times 10^5 \times \exp(-145255/RT)$	970-1250°C	Zry-4	-	Internal	Steam
6. Biederman *et al.* [7]	$K_p = 3.1 \times 10^5 \times \exp(-139690/RT)$	980-1480°C	Zry-4	Tube	Internal	Steam
7. Leistikow *et al.* [8]	$K_p = 42.58 \times 10^5 \times \exp(-174360/RT)$	700-1300°C	Zry-4	Tube	Internal & External	Steam
8. Urbanic & Heidrick [9]	$K_p = 2.96 \times 10^5 \times \exp(-139900/RT)$	1050-1500°C	Zry-2,4	Rod	Internal	Steam
9. Sethumadhavan *et al.* [10]	$K_p = 6.55 \times 10^5 \times \exp(-149926/RT)$	1050-1150°C	Zry-2	Tube	External	Steam
$1500^\circ C \leq T \leq 1852^\circ C$						
1. Baker & Just [1]	$K_p = 333 \times 10^5 \times \exp(-190465/RT)$	upto 1850°C	Zr	Wire	Condenser discharge	Water
2. Urbanic & Heidrick [9]	$K_p = 8.79 \times 10^5 \times \exp(-138155/RT)$	1500-1852°C	Zry-2,4	Rod	Internal	Steam

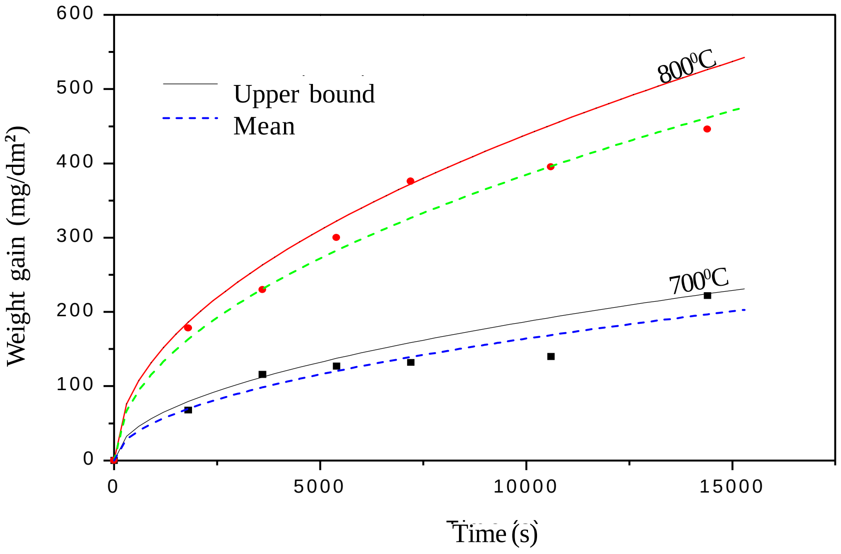
TABLE - A.2: COMPARISON OF K_p VALUES AT SELECTED TEMPERATURES

Source	**K_p [mg (Zr)/cm^2]^{2}s^{-1}**					
	1000°C	**1250°C**	**1000°C**	**1500°C**	**1700°C**	**1850°C**
Baker & Just	0.51	9.77	56.00	81.4	301.8	685.5
Leistikow *et al.*	0.30	4.45	22.03			
Biederman *et al.*	0.57	5.0	18.04			
Westerman & Hesson	0.57	5.44	20.60			
Kawasaki *et al.*	0.39	5.43	25.93			
Pawel-Cathecart & Mckee	0.40	5.4	25.03			
Brown–Healey [3]	0.34	4.25	18.95			
Urbanic & Heidrick	0.54	4.70	16.98	74.75	193.30	350.50
Sethumadhavan *et al.*	0.46	4.72	18.66			
Recommended in this guide	0.65	6.61	26.12	81.40	301.80	685.50



Points denote measured values
Dotted lines and solid lines represent values calculated using the equation of mean and upper bound K_p respectively.

FIG. A-1: **COMPARISON OF MEASURED AND CALCULATED WEIGHT GAIN VALUES ABOVE 1000^{O}C**
(DATA OF SETHUMADHAVAN ET AL.)



Points denote measured values.
Dotted and solid lines represent values calculated using the equation of mean and upper bound K_p respectively.

FIG. A-2: **COMPARISON OF MEASURED AND CALCULATED WEIGHT GAIN VALUES BELOW 1000^{O}C**
(DATA OF SETHUMADHAVAN ETAL.).

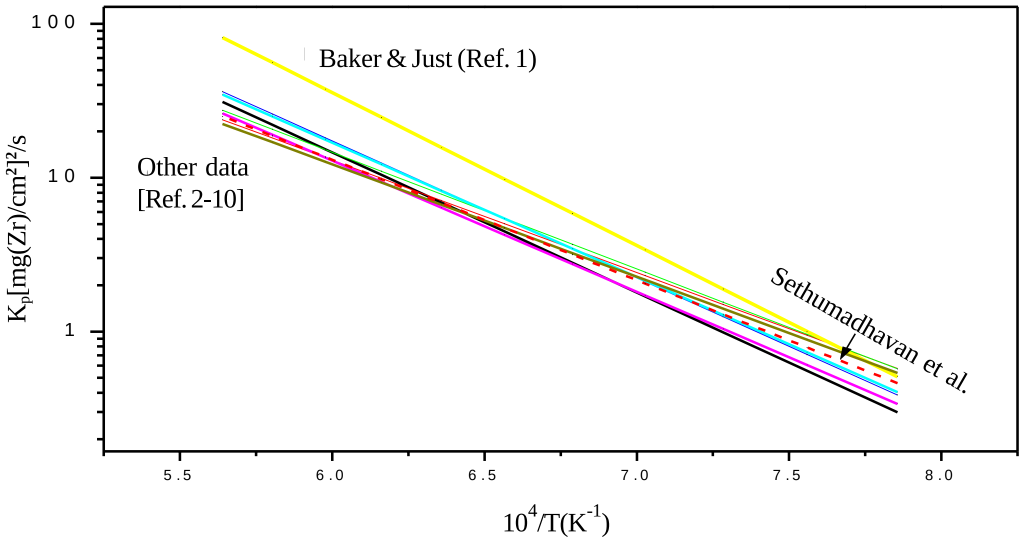


FIG. A-3: **COMPARISION OF BAKER AND JUST DATA WITH THE DATA OF OTHER INVESTIGATORS IN THE TEMPERATURE RANGE OF 1000^{O}C-1500^{O}C**

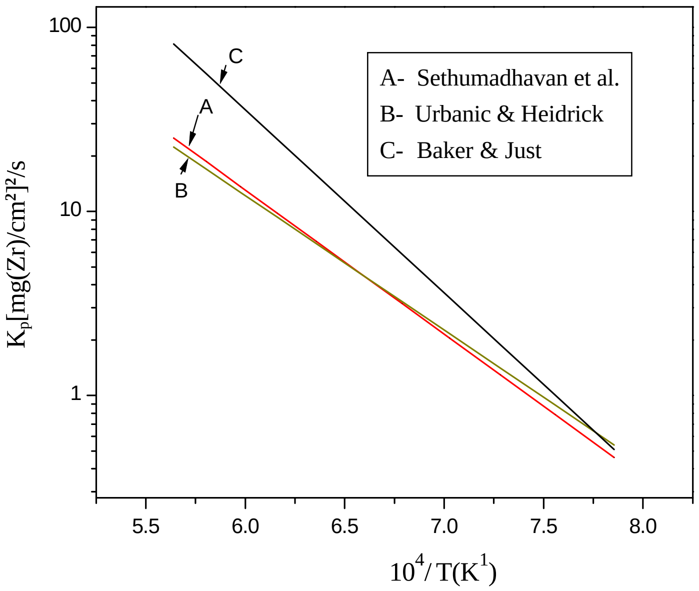


FIG. A-4: COMPARISON OF URBANIC AND HEIDRICK DATA WITH THAT OF SETHUMADHAVAN ET AL. (BAKER AND JUST LINE IS ALSO SHOWN)

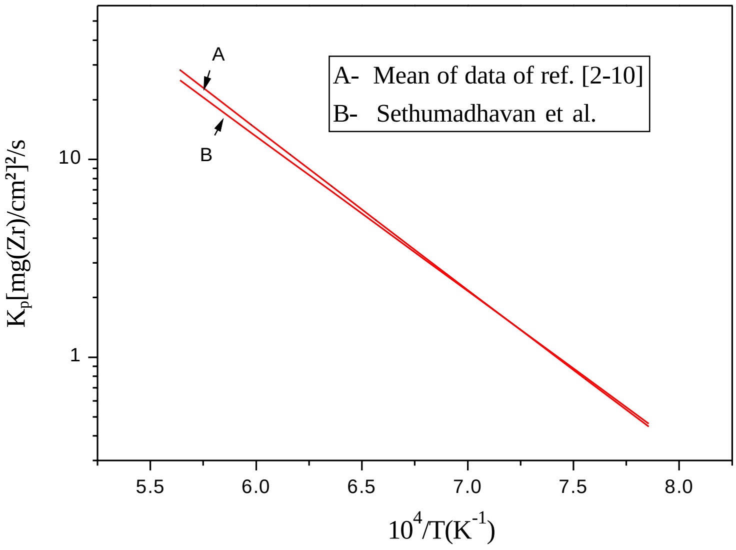


FIG.A-5: COMPARISON OF SETHUMADHAVAN ET AL'S LINE WITH THE MEAN OF DATA OF REF. [2-10]

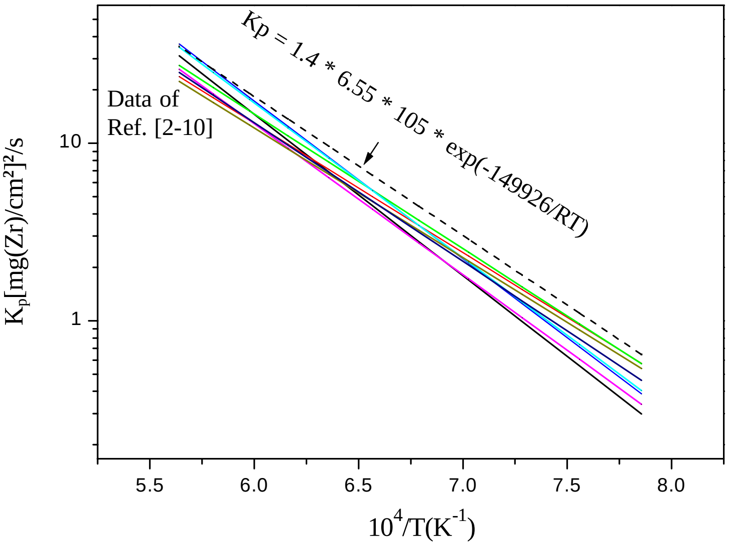


FIG. A-6: A CONSTANT MULTIPLIER OF 1.4 TO THE EQUATION OF SETHUMADHAVAN ET AL. (FOUND TO PROVIDE THE UPPER BOUND OF THE DATA OF REF. [2-10] IN THE TEMPERATURE RANGE 1000^{O}C - 1500^{O}C)

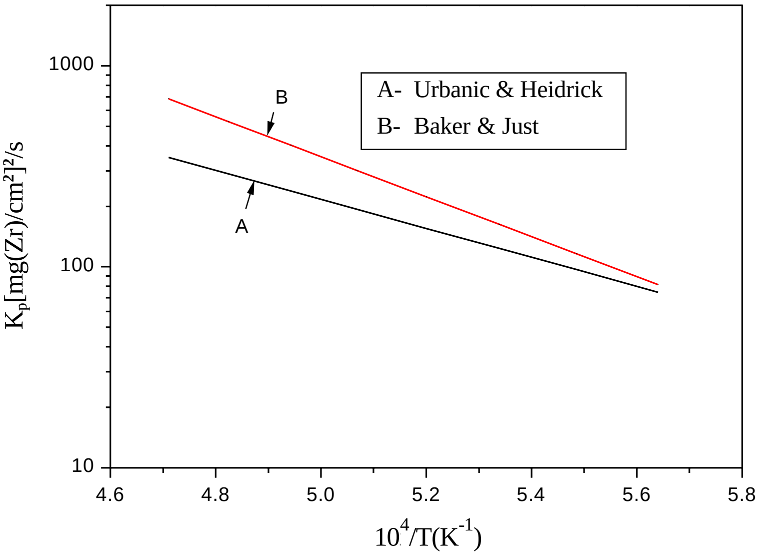


FIG. A-7 : COMPARISON OF PARABOLIC RATE CONSTANTS IN THE TEMPERATURE RANGE OF 1500^{O}C-1852^{O}C

REFERENCES

1. Baker L. and Just L.C., Argonne Report, ANL 6548 (1962).

2. Biederman R.R., Sisson R.D., Jones J. K. and Dobson W. C.,'A Study of Zircaloy-4 Steam Oxidation Reaction Kinetics', EPRI NP-734, Final Report (1978).

3. Brown F. and Healey T., 'The Kinetics of Total Oxygen Uptake in Steam Oxidized Zr-2 Between 1000-1400°C, Journal of Nuclear Materials, 88 (1980).

4. Pawel R.E., Cathecart J.V. & Mckee R.A., 'The Kinetics of Oxidation of Zircaloy-4 in Steam at Higher Temperatures', Journal of Electrochemical Society ,126, No. 7, p.1105 (1979).

5. Kawasaki S., Furuta T. & Suzuki M., 'Oxidation of Zircaloy-4 Under High Temperature Steam Atmosphere and its Effect on Ductility of Cladding' and Journal of Nuclear Science and Technology, 15, 589 (1978).

6. Westerman R.E. and Hesson G.M., 'Zircaloy Cladding i.d./o.d. Oxidation Studies', NP-525-1, Final Report (1977).

7. Biederman R.R., Ballinger R.G. and Dobson W.G. 'A Study of Zircaloy- 4 Steam Oxidation Reaction Kinetics'. EPRI NP-225, Final Report (1976).

8. Leistikow S., Schanz G. & Berg H.V., 'Kinetics & Morphology of Isothermal Steam Oxidation of Zr-4 at 700 - 1300°C', KFK 2587 (1978).

9. Urbanic V.F. and Heidrick T.R., 'High Temperature Oxidation of Zr-2 and Zr-4 in Steam', Journal of Nuclear Materials, 75, p. 251 (1978).

10. Sethumadhavan V., Sathe S. M., Kumar S., Khan K.B. and Sah D.N., 'High Temperature Steam Oxidation of Zircaloy-2 Cladding of PHWR Fuel Element', BARC Report, BARC/E/016/1997.

11. Moalem, M. and Olander D.R., 'Oxidation of Zircaloy by Steam' Journal of Nuclear Materials, 182, p. 170 (1991).

12. Cathcart J.V. et al., 'Zirconium Metal Water Oxidation Kinetics IV-Reaction Rates Studies', ORNL/NUREG-17, p. 85-93 (1977).

13. Pawel R.E. et al., 'The Oxidation of Zircaloy-4 at 900 ℃ and 1100 ℃ in High Steam', Journal of Nuclear Materials, 82, p. 129 (1979).

14. ATOMIC ENERGY REGULATORY BOARD; 'Code of Practice on Safety in Design of Pressurised Heavy Water Based Nuclear Power Plants; AERB code No. SC/D, Mumbai, India (1989).

15. Ramshesh V. and Venakteswarlu K.S., Water Chemistry Division, BARC, 'Radiolytic Generation of Gases in Reactors' (1988).

16. Moorthy P.N., Head Applied Chemistry Division, BARC, 'Assessment of Hydrogen Release in Containment due to Radiolysis under Accident Conditions', A communication to Shri S.S. Bajaj, CE(RSA), NPCIL vide no. APCD/NPC-500/873 dated 16.6.1992.

17. INTERNATIONAL ATOMIC ENERGY AGENCY, 'A Review of The Hydrogen Issues Related to the Safety of Nuclear Water Reactors', Report of 3rd Working Group Meeting of IAEA, held on 19-23 Nov. (1984) and Safety Report, Volume - II, Accident Analysis of NAPS (1989).

18. Vereschinskii I.V. and Pikeev A.K. ‘Introduction to Radiation Chemistry’, Israel Program of Scientific Translations, Jerusalem, p. 243 (1964).

19. Rohde J. *et al*., ‘Mitigation of Hydrogen Threats to Large Dry Containment (German Approach)’, Conference Proceedings (1991).

20. KAPS Safety Analysis Report Volume-II (1989).

21. Kaiga Safety Analysis Report Volume-II (1998).

22. NAPP Safety Analysis Report Volume-II (1989).

23. DAE Report of Task Force on Review of Indian NPP in the Light of the Accident at Chernobyl, reviewed and revised by DAE-SRC, December (1987).

24. Shapiro Z.M. and Moffette T.R., ‘Hydrogen Flammability Data and Application to PWR Loss-of-coolant Accident’, WAPD-SC-545, Bettis Plant (1957).

25. Report on ‘An Assessment of Post-LOCA Radiolytic Generation of Hydrogen in Reactor Containment of Indian PHWRs’ by S/Shri H. Bose and G.C.Shah, forwarded by Shri S.K.Sharma, Director, Reactor Group BARC to Shri S.S.Bajaj, vide note dated 12.12.2000.

26. Ramshesh V., Water Chemistry Division, BARC, ‘Safety Aspect Concerning Radiolytic Gas Generation in Reactors’, Science Progress , 84 (1), p 69-85 (2001)

LIST OF PARTICIPANTS

WORKING GROUP

Dates of meeting : September 27, 1996
September 19, 1997
October 15, 1997
August 20, 1999
March 30, 2001

Members of the working group:

Shri S.S. Bajaj (Chairman) : NPCIL

Shri S.G. Markandeya : BARC

Shri P.K. Malhotra : NPCIL

Shri R. N. Bhawal : NPCIL

Shri Nalini Mohan : NPCIL

Shri D.N. Sah : BARC

Shri S.A. Khan (Member-Secretary) : AERB

ADVISORY COMMITTEE ON CODES, GUIDES AND ASSOCIATED MANUALS FOR SAFETY IN DESIGN OF NUCLEAR POWER PLANTS (ACCGD)

Dates of meeting: February 6,1998
September 7,1999
May 26, 2001

Members of ACCGD :

Shri S.B. Bhoje (Chairman) : IGCAR

Shri S. Damodaran : NPCIL (Former)

Prof. N. Kannan Iyer : IIT, Bombay

Shri V.K. Mehra : BARC

Shri Umesh Chandra : NPCIL

Shri Deepak De : AERB

Shri S. Sankar : BARC

Late Shri C.N. Bapat : NPCIL (Former)

Shri S.A. Bhardwaj : NPCIL

Dr. S.K. Gupta : BARC

Shri K.K. Vaze : BARC

Shri S.A. Khan (Member-Secretary) : AERB

ADVISORY COMMITTEE ON NUCLEAR SAFETY (ACNS)

Dates of meeting:	September 2, 2000 May 26, 2001

Members of ACNS :

Shri S.K. Mehta (Chairman)	:	BARC (Former)
Shri Ch. Surendar	:	NPCIL (Former)
Shri S.M.C. Pillai	:	Nagarjuna Group, Hyderabad
Prof. U.N. Gaitonde	:	IIT, Bombay
Shri S.K. Goyal	:	BHEL, Hyderbad
Shri S.K. Sharma	:	BARC
Dr.V.Venkat Raj	:	BARC
Dr.U.C. Mishra	:	BARC (Former)
Shri S.P. Singh	:	AERB (Former)
Shri G.K. De	:	AERB (Former)
Shri K. Srivasista (Member-Secretary)	:	AERB

PROVISIONAL LIST OF SAFETY CODES, GUIDES AND MANUALS ON DESIGN OF PRESSURISED HEAVY WATER REACTORS

Safety Series No.	Provisional Title
AERB/SC/D	Code of Practice on Design for Safety in Pressurised Heavy Water Based Nuclear Power Plants
AERB/NPP-PHWR/ SG/D-1	Safety Classification and Seismic Categorisation for Structures, Systems and Components of Pressurised Heavy Water Reactors
AERB/SG/D-2	Structural Design of Irradiated Components
AERB/SG/D-3	Protection Against Internally Generated Missiles and Associated Environmental Conditions
AERB/SG/D-4	Fire Protection in Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/SG/D-5	Design Basis Events for Pressurised Heavy Water Reactors
AERB/NPP-PHWR/ SG/D-6	Fuel Design for Pressurised Heavy Water Reactors
AERB/SG/D-7	Core Reactivity Control in Pressurised Heavy Water Reactors
AERB/NPP-PHWR/ SG/D-8	Primary Heat Transport System for Pressurised Heavy Water Reactors
AERB/SG/D-9	Process Design
AERB/SG/D-10	Safety Critical Systems for Pressurised Heavy Water Reactors
AERB/SG/D-11	Emergency Electric Power Supply Systems for Pressurised Heavy Water Reactors
AERB/SG/D-12	Radiation Protection Aspects in Design of Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/SG/D-13	Liquid and Solid Radwaste Management in Pressurised Heavy Water Reactor Based Nuclear Power Plants.
AERB/SG/D-14	Control of Air-borne Radioactive Materials in Pressurised Heavy Water Reactors
AERB/SG/D-15	Ultimate Heat Sink and Associated Systems in Pressurised Heavy Water Reactors
AERB/SG/D-16	Materials Selection and Properties

PROVISIONAL LIST OF SAFETY CODES, GUIDES AND MANUALS ON DESIGN OF PRESSURISED HEAVY WATER REACTORS (CONTD.)

Safety Series No.	Provisional Title
AERB/SG/D-17	Design for In-service Inspection
AERB/SG/D-18	Loss of Coolant Accident Analysis for Pressurised Heavy Water Reactors
AERB/SG/D-19	Deterministic Safety Analysis of Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/NPP-PHWR/ SG/D-20	Safety Related Instrumentation and Control for Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/SG/D-21	Containment System Design
AERB/SG/D-22	Vapour Supression System for Pressurised Heavy Water Reactors
AERB/SG/D-23	Seismic Qualification of Structures, Systems and Components of Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/SG/D-24	Design of Fuel Handling and Storage Systems for Pressurised Heavy Water Reactors
AERB/SG/D-25	Computer Based Safety Systems of Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/SM/D-1	Decay Heat Load Calculations in Pressurised Heavy Water Reactor Based Nuclear Power Plants
AERB/NPP-PHWR/ SM/D-2	Hydrogen Release and Mitigation Measures under Accident Conditions in Pressurised Heavy Water Reactors

AERB SAFETY MANUAL NO. AERB/NPP-PHWR/SM/D-2

Published by : Atomic Energy Regulatory Board
Niyamak Bhavan, Anushaktinagar
Mumbai - 400 094
INDIA.

BCS