Review of computer codes for modeling corrosion product transport and activity build-up in light water reactors

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Abstract. The corrosion products are among the leading sources of radiation in primary coolant circuits of pressurized water reactors leading to prolongation of reactor down-time for routine maintenance entailing substantial loss of revenues. These deposits affect adversely coolant flow rates resulting in elevation of fuel and cladding temperature and become activated by high neutron flux in reactor core consequently creating high radiation field by accumulating in the out-of-core reactor components. In the case of light water reactors (LWRs), prevailing corrosion products include ^{59}Fe, ^{99}Mo, ^{56}Mn, ^{58}Co, and ^{60}Co. The ^{56}Mn is the leading corrosion product activity source during operation while cobalt isotopes dominate the activity after reactor shutdown. This paper presents a detailed discussion on some computer codes developed for prediction and transport of corrosion product activity in LWRs.

Key words: corrosion product • light water reactors • fuel cladding • radiation field

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Introduction

Currently, more than 16% of world energy demand is fulfilled by nuclear power plants (NPPs). This amounts to 2800 TWh energy annually generated by more than 441 NPPs operating in 31 countries worldwide [17]. Amongst these NPPs, the LWRs contribute to more than 85% of total energy produced by all nuclear reactors [20]. With the advantage of being proven technology along with extensive operational experience, the light water NPPs are expected to continue playing a leading role in nuclear power production in both short and medium term scenarios.

In LWRs, water is used as neutron moderator and reactor coolant in primary circuits, secondary circuits of pressurized water reactors (PWRs) and pressurized heavy water reactors (PHWRs) and in the number of auxiliary systems [9]. Water is chemically aggressive medium at high temperature, especially when it comes in contact with the structural materials of reactor components. Over 50 years of experience with LWRs clearly shows that even under normal operating conditions some undesirable effects do occur including corrosion, erosion and deposition of corrosion products on heat transfer surfaces [9]. These corrosion products become mixed with primary coolant due to continuous interaction of turbulent flow of water with the corroded surfaces of primary coolant circuits. Some of the corrosion products remain in dissolved state, while the others become insoluble, forming a black granular material called crud. The corrosion rate of power plants depends on various factors including temperature, the type of material involved, strength of prevailing radiation field and the

age of the material etc. The initial rate of corrosion during the initial phase of power plants can be 10 to 20 times higher than the eventually reached equilibrium corrosion rate [10, 19].

Including adverse effect of corrosion on mechanical properties of various nuclear power plant materials, the corrosion products themselves become activated as they pass through intense neutron field inside the core region. Their deposition on out-of-core surfaces of the primary coolant circuits is the main source of radiation exposure for personals carrying out repair and maintenance work on primary circuit components of PWRs. Due to improvement in water chemistry and proper choice of structural materials in LWRs, the exposure levels during maintenance shows a steady decline in recent years. However, this problem is not fully resolved yet, as indicated by the measured difference of an order-of-magnitude higher exposure rate of LWRs in comparison with their contestants. Due to long term competition with future nuclear power plants (gas- or sodium-cooled reactors) which have one or two orders of magnitude lower steam generator surface dose rates compared with LWRs, there is still room for improvement [9, 21].

A coolant transient which occurs under abnormal operating conditions changes the concentration of these corrosion products. Due to solubility considerations, transients are typically accompanied by increase in particulate species in coolant. Initiating factors for these transients may be power changes, reactor start up, reactor trip situation and perturbations in coolant flow [8]. The operational problems caused by corrosion product deposits are of three basic types [22]:

– increased hydraulic resistance ultimately reducing coolant flow rates,
– increased thermal resistance, eventually resulting in elevated values of fuel and cladding temperatures,
– accumulation of radioactive corrosion products on out-of-core surfaces entailing corresponding raise in radiation exposure to maintenance crew.

These problems have been addressed via many alternate ways. One way of achieving reliability and safety is by using high integrity cladding and structural materials while taking special measures to limit excessive corrosion, erosion processes. For LWRs (including, boiling water reactors (BWRs), PWRs and PHWRs) reliable water chemistry regimes have been developed. In addition to problems of reduction in coolant flow rate and higher fuel and cladding temperature, accumulation of radioactive corrosion products on out-of-core deposits produce radiation field at various parts of primary coolant loop. These radiation fields prohibitively limit the access to reactor cooling system for routine repair and maintenance purposes. Generally, three major sources of radiation tend to limit the access of personnel to primary coolant circuits of PWRs. These sources are [10]:

– fission products and actinides leaking out of fuel pins,
– coolant activation due to irradiation, and
– activated corrosion products.

First, two sources have relatively lower importance mainly because of short half-lives of the corresponding radionuclide's. However, the activated corrosion
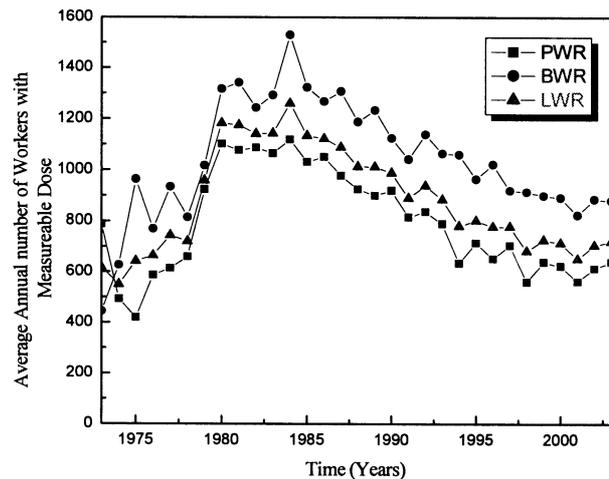
Fig. 1. A comparison of average annual number of workers with measurable dose for BWRs, PWRs and LWRs.

product contributes approximately to 70–90% of all occupational radiation exposure. The corrosion products are formed due to liquid-metal interaction. Various components of reactor, including cladding and piping, are sources of these corrosion products. After being dissolved into the primary coolant, these corrosion products carry radioactivity to various out-of-core parts of a reactor. Coolant activity is a function of corrosion rates, coolant flow rates, deposition and release of corrosion products. Comparisons of the annual average value and the collective dose per reactor of workers with measurable dose for BWRs, PWRs and LWRs have been shown in Fig. 1 [21].

Many models were developed for the estimation of radioactivity build-up and corrosion product transport in LWRs. These include empirical and semi-empirical models containing empirical coefficients that must be derived from experimental data or plant design data. In this paper, two mathematical models along with several important computer codes developed for prediction of corrosion product activity transport have been discussed.

Main models for corrosion products

First model: Burrill's mechanistic model

This model was developed for the CANDU PHWR to describe the behavior of corrosion products. The CANDU system is a pressure tube reactor and is operated on constant coolant chemistry without boron addition or lithium hydroxide dosing. The Burrill's mechanistic model is based on the following assumptions [8]:

– Corrosion products appearing in soluble and insoluble particulate form come from the out-of-core structural materials of the system.
– Corrosion products are deposited on all coolant circuit surfaces including the fuel sheath and pressure tube surfaces in-core.
– Neutron activation of corrosion products takes place within the core.
– From core structural surfaces these activated corrosion products are released into the coolant by the process of dissolution.

– Coolant transports these dissolved radionuclide's to out-of-core surfaces where they make scaling.

Second model: Babcock & Wilcox model

This mathematical model is based on the following assumptions [8]:
1. Both radioactive and non-radioactive crud transport depends on the mechanism of particulate removal from the structural materials and both types of crud transport and redeposit on the flow path material of coolant.
2. Corrosion products come from the corrosion of stainless steel and Inconel surfaces.
3. These corrosion products deposit on all primary coolant circuit surfaces. These deposits on the in-core surfaces are tightly attached to various core surfaces by adherent form by a sintering process.
4. Some of loosely adherent deposits on all surfaces are released by the mechanism of erosion.

Detailed complex physical phenomena are involved in complete descriptions of the formation, transport and deposition of radioactive corrosion products in both PWR and BWR reactors. It is quite difficult to model all of these phenomena presently, as some of the mechanisms cannot be identified with certainty and are suspected to be essential to an adequate description of system. Currently, we are also not sure which one of the phenomenon should be included and which one can be omitted. That is why models are developed from a simplified network of routes, each of which may be described either mechanistically or phenomenologically, according to the current state of understanding. So, the above discussed both models have their own limitations in the sense of covering generally more relevant physical phenomena assumed to be occurring in the system.

ACE-II code

In order to predict the residual radiation fields in the components of Japanese designed PWRs, an empirical code ACE-II was developed. Following sequence of physical phenomena involved in the process of activity transport and diffusion of activated isotopes have been used in the ACE-II model [3]:
1. Due to corrosion, the inner and outer oxide layers are formed on the wetted surfaces of the primary coolant loop components.
2. Due to the mechanism of dissolution and erosion of the outer oxide layer corrosion products are released into the primary coolant.
3. There are two types of corrosion products in the coolant: dissolved and particulate.
4. The dissolved and particulate corrosion products become activated as they pass through the intense radiation fields (high neutron flux) in the core.
5. Both the activated and normal particulate or dissolved corrosion products, are precipitated onto the wetted surface of the primary coolant loop components, resulting in a build-up of CRUD (chalk river unidentified deposits).
6. Activated isotopes in the CRUD diffuse into the outer layer oxides, and then into the inner layer oxides, and eventually into the construction materials themselves by isotopic exchange.
7. The parent elements considered in this model are nickel, iron and cobalt, and the radioactive nuclides are ^{58}Co and ^{60}Co.

However, in the ACE-II code all of the above-mentioned processes are quantified through empirical measurements and none of the processes are introduced by fundamental principles. Since this model is based on empirical data, so it cannot be applied to other reactors with different styles and geometries.

CRUDTRAN code

The CRUDTRAN code is an empirical code developed for both soluble and particulate corrosion products (iron, nickel and cobalt) [12]. Main feature of this code is that it considers ion dissolution in the steam generators and ion deposition on in-core areas. In the same way it considers particle nucleation in the core regions and particle breakdown in the steam generators. The CRUDTRAN code considers in-core precipitation and out-core release of dissolved materials. The ^{58}Co and ^{60}Co radionuclides are formed in the in-core structural materials and then released into the coolant by isotope exchange and deposited on out-core surfaces. Corrosion product deposition is modeled around the entire primary coolant loop. Rate constants are responsible for the empirical nature of the CRUDTRAN code. Their values were determined using data obtained from the Massachusetts Institute of Technology's (MIT) PWR coolant chemistry loop. Activity transport depends upon rate of dissolution of corrosion films on the wetted piping surfaces of primary coolant loop. An important feature of this code is that it compares the amounts of mass transport and activity transport and accounts for the sensitivity of corrosion to radiation levels in the core region. CRUDTRAN is modeled on a simple physical observation. The major shortcoming of the model is that it considers very few regions, e.g., isothermal surfaces are not modeled, and for this reason the model is probably not useful for predicting radiation fields on any surface outside the steam generator (SG).

MIGA-RT computer program

The activity transport code MIGA-RT was developed by Dinov [6]. It predicts the radiation field in PWR and Russian VVER type reactors. This code is built on elaborate understanding of the chemical thermodynamics that determine the most stable oxide phase likely to exist under the chemistry and temperature conditions in each region of the primary circuit. The code emphasizes the importance of particle transport in determining radiation field growth, since the dissolved species do not seem to have the dominant role assumed in the first generation of activity transport codes [5]. Primary coolant water is responsible for release of corrosion products from wetted piping and reactor structural materials through erosion of the corrosion films on the wetted surfaces. Release rate of corrosion products

depends upon the elemental solubility of iron and nickel and the ratio of these elements in the construction materials of the primary loop. Corrosion products considered in modeling are magnetite, nickel ferrite, sub-stoichiometric nickel ferrite, metallic nickel and nickel oxide. MIGA-RT considers only ^{58}Co and ^{60}Co radionuclides. MIGA-RT is developed in FORTRAN language. It does not consider time explicitly. The change in time is simulated by changing the water chemistry conditions as appropriate for the duration of a normal fuel cycle [5, 6]. This code also does not have capability to simulate the coolant transients effects on corrosion product activity build-up on out-of-core surfaces.

PACTOLE code series

PACTOLE computer code was initially developed by Beslu and co-workers in France [2]. It predicts the time dependent behavior of activated corrosion products. PACTOLE series of codes are considered most updated activity transport codes. PACTOLE-2 is a current version of code in practice, which solves many models while using analytic solution. PACTOLE-3 is an advanced version of PACTOLE-2, which is currently under development stage. PACTOLE-3 uses numerical methods and object oriented programing (OOP) languages to solve mathematical models.

Main features of PACTOLE-2 are that it takes into account plant history, e.g., power and chemistry changes and the effect of coolant purification on activity transport. Most of basic physical processes like corrosion product release, erosion, precipitation, dissolution of particulates and particulate transfer are included in it. Fe, Ni, Cr, Mn, and Co nuclides along with their activated nuclides ^{59}Fe, ^{51}Cr, ^{54}Mn, ^{58}Co and ^{60}Co are considered in the code. A series of differential equations involving the corrosion release rate from structural materials; thermophoresis; the activities associated with soluble and insoluble corrosion species; the activities of deposits and surface oxides in each zone and corresponding local dose rate are solved in the code. The primary coolant loop is divided into 70 sections, eight for the chemical and volumetric control system (CVCS) four for each steam generator; 42 are included in the core, while the rest of the sections are other supporting structures of the primary loop [2, 12].

CORA code

This computer code was developed at the Westinghouse by Kang and Sejvar [11]. The code can be represented by nodal transport diagram as shown in Fig. 2. The crud transport mechanism is modeled semi-empirically
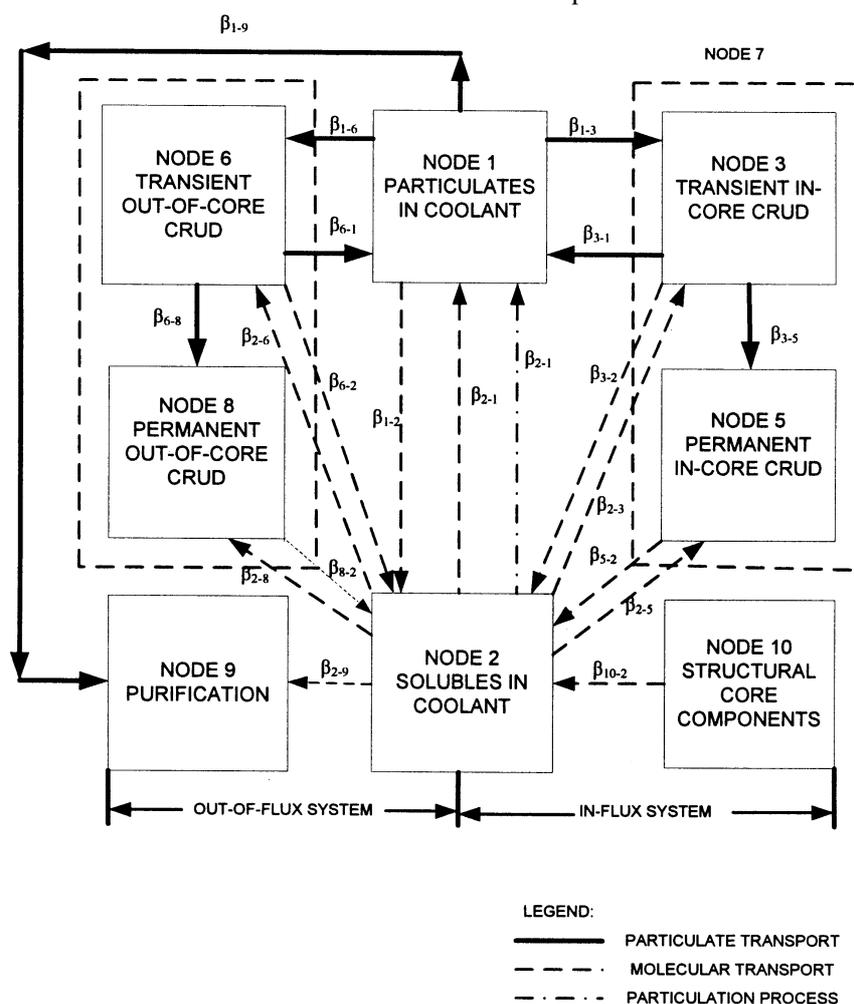
Fig. 2. CORA code: diagram of nodes used for PWR primary coolant circuit [11].

between the indicated nodes. Nodes represent homogeneous sources and sinks of the corrosion products in a PWRs primary coolant system. The semi-empirical model used in the code is based on a theoretical understanding of the physical processes involved in radiation field build-up it also uses experimental data from plants. Therefore, it is primarily useful for evaluating the effect on radiation level and crud characteristics for system or chemistry changes. Structural materials release corrosion products in soluble forms. Rate of corrosion product release is proportional to solubility. Crud is transported in various parts of primary coolant loop in both particulate and soluble forms. These crud particles are deposited on various structural materials.

DISER computer code

This computer code was developed by Zmitko for a coolant containing corrosion products in the three states: soluble, colloids, and particles [23]. This is a unique feature of this code which makes it prominent from the other codes. The DISER code models release of dissolved corrosion products into the coolant by assuming an inner single oxide layer, whose thickness is determined by parabolic kinetics and the saturation concentrations of magnetite and nickel ferrite in the coolant [16]. Mass transport is carried by the elements; iron, nickel, chromium, and cobalt; and their corresponding radioactive isotopes considered are ^{54}Mn, ^{59}Fe, ^{58}Co, ^{51}Cr, and ^{60}Co. These radioactive isotopes are generated when coolant passes through a high flux environment of core. So, thermal neutron activation is responsible for the generation of activated corrosion products [3].

When the coolant is unsaturated in dissolved iron or nickel and is based on magnetite or nickel ferrite solubility then the solute is formed by dissolution of the inner oxide layer. On the other hand, when the coolant is supersaturated in the boundary layer at the local surface temperature, then the precipitation of the dissolved corrosion products is predicted by DISER code which also predicts the conversion of solute into colloidal particles in the coolant when the bulk coolant is supersaturated, with respect to a specified iron oxide. In the same way colloids dissolve to form solutes, if the bulk coolant is unsaturated [16, 23].

Colloids are deposited on the internal surfaces of the primary loop components and their deposition can be determined by the water chemistry of the reactor coolant loop. If the colloid possesses enough energy from Brownian motion, to overcome the repulsive electrostatic force of the oxide layers on the pipes, it will deposit onto the pipe wall. DISER code considers colloid to be deposited onto the wall. Furthermore, if a colloid reaches a size above 0.767 pm in diameter, it is considered to behave as a particulate mass and is a subject to the sticking probabilities predicted by Beal's theory. For this code, the primary loop of a PWR is sectioned into 14 regions; five are for the steam generator, two are for the entrance and exit of the steam generator, two are for the hot and cold legs, and five are for the core [1, 7, 16].

CRUDSIM code

This program employs a conceptually simple model compared with the comprehensive models in CORA and PACTOLE. Only two nodes represent the PWRs primary coolant circuit. The radioactive elements considered are ^{58}Co and ^{60}Co. The crud and activity transport is predicted only on the basis of a solubility difference as a driving force. Therefore, the results of CRUDSIM calculations are used for comparisons of various coolant chemistry conditions. Good comparison with measured plant histories can be obtained using a parametrically selected transport characterization data [12]. CRUDSIM code overlooks the effect of coolant transients on corrosion product activity build-up.

COTRAN code

In order to improve cost economics of water cooled reactors, extended fuel burnup methods are in practice nowadays. In water cooled reactors the dominant fuel types are uranium dioxide and zirconium based alloys. Cladding corrosion and hydriding are important towards performance related characteristics of fuel. Cladding corrosion results in CRUD which is the major source of occupational radiation exposure. Song and Lee used a computer code COTRAN which simulates the behavior of the CRUD based on double layer concept model and solubility difference for long-term fuel cycle reactor operations. Their findings comprise of facts that with increasing pH value of the coolant, the activities due to CRUD decreases, and for the same period of different fuel cycle, the generation of the CRUD increases as the operating fuel cycle duration is increased [20].

CPAIR computer program

This program CPAIR (corrosion product activity in reactors) was developed by Mirza *et al.* in 1997 to account for the effect of flow rate and power transients on corrosion product activity in primary coolant of PWR [13]. Initially, the CPAIR code was developed to simulate corrosion product activity under flow rate transients, afterwards the code was modified to include power perturbations and the modified code was given a name CPAIR-P. This was later modified to include the flow rate transients and account for linearly accelerating corrosion rates during the reactor operation [4, 14, 15]. Most recent modification was carried out by Rafique *et al.* [17] to simulate corrosion product activity for non-linearly rising corrosion rates as well. This code was developed to simulate corrosion product activity build-up in reactor core, inner piping surface and primary coolant loop of PWRs. CPAIR-P has been also used to simulate corrosion product activity build-up in purification system of PWRs [18]. The original model included in CPAIR code is based on the following five physical processes:
1. The production of activated corrosion products due to their passage through the core in the environment of high neutron flux.
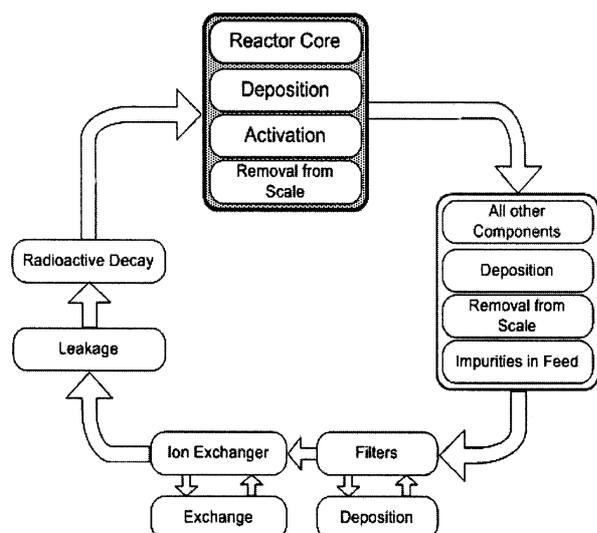
Fig. 3. Various processes modeled in CPAIR-P computer code [4, 14, 15].

2. The removal of these activated corrosion products due to purification of the water by ion-exchanger and filters.
3. The removal of activated isotopes from the primary coolant due to deposition on the interior surfaces of the primary coolant loop structures.
4. Leakage of coolant from the primary loop and radioactive decay of these corrosion products.
    CPAIR-P considers six radioisotopes: ^{24}Na, ^{56}Mn, ^{59}Fe, ^{58}Co, ^{60}Co and ^{99}Mo. It predicts that activity due to ^{56}Mn dominates during normal operation of reactor, while ^{58}Co activity dominates after reactor shutdown.

Figure 3 shows the diagram of the many possible paths of how the generation and removal of activated corrosion products may occur in the primary coolant of a typical PWR according to CPAIR-P computer code.

Conclusions

In the current article, various computer codes related with corrosion product transport and activity build-up in the primary circuits of typical PWRs have been reviewed. A diverse approach can be seen in various discussed codes. Most models consider mass transport of dissolved ions and particulates and their deposition on various components of primary coolant loop. Many of the above discussed codes are based on empirically determined parameters. In short, every model has its own importance, but at the same time cannot explicitly account for all complex physical phenomena in entirety. Various models developed so far are empirical or semi-empirical in nature. Their ability to predict moderate temperature changes on new alloys is quite limited. Clearly, development of more comprehensive and detailed computer codes based on possibly empirical and new mechanistic models, capable of modeling complex mechanisms involved in corrosion product deposition, transport and re-mixing, still remains a challenge for scientists and engineers.

References

1. Beal S (1972) Turbulent agglomeration of suspensions. J Aerosol Sci 3;2:113–125
2. Beslu P (1978) A computer code PACTOLE to predict activation corrosion products in PWRs. In: Proc of the Int Conf on Water Chemistry of Nuclear Reactor Systems, Bournemouth. British Nuclear Energy Society, London
3. Burrill K, Menut P (2001) Water chemistry of nuclear reactor systems 8. British Nuclear Energy Society, London
4. Deeba F, Mirza Anwar M, Mirza NM (1999) Modeling and simulation of corrosion product activity in pressurized water reactors under power perturbations. Ann Nucl Energy 26;7:561–578
5. Dinov K (1991) A model of crud particle/wall interaction and deposition in a pressurized water reactor primary system. Nucl Tech 94:281–285
6. Dinov K (1997) Modeling of activity transport in PWR by computer code MIGA. Presented at the 1st Meeting of the IAEA Coordinated Research Program on Activity Transport Modeling, 5–9 May 1997, Toronto, ON
7. Horvath LG (1991) Development of a corrosion product transport code in the primary circuits of nuclear power plants. VEIKI Report 93.92-077. Veiki Institute Budapest, Hungary
8. IAEA (1987) Reactor water chemistry relevant to coolant-cladding interaction. IAEA-TECDOC-429. International Atomic Energy Agency, Vienna
9. IAEA (1992) Coolant technology of water cooled reactors. Vol. 1. IAEA-TECDOC-667. International Atomic Energy Agency, Vienna
10. Jaeger RG (1970) Engineering compendium on radiation shielding. Vol. 3. Springer-Verlag, New York
11. Kang S, Sejvar J (1985) The CORA-II model of PWR corrosion product transport. EPRI-NP-4246, Westinghouse Electric Corp., Pittsburgh, PA, USA, Nuclear Technology Div
12. Lee CB (1990) Modeling of corrosion product transport in PWR primary coolant. PhD Thesis, Nuclear Engineering Department, MIT, Massachusetts
13. Mirza AM, Mirza NM, Mir I (1998) Simulation of corrosion product activity in pressurized water reactors under flow rate transients. Ann Nucl Energy 25;6:331–345
14. Mirza NM, Rafique M, Hyder MJ, Mirza SM (2003) Computer simulation of corrosion product activity in primary coolants of a typical PWR under flow rate transients and linearly accelerating corrosion. Ann Nucl Energy 30:831–851
15. Mirza NM, Rafique M, Mirza SM, Hyder MJ (2005) Simulation of corrosion product activity for nonlinearly rising corrosion on inner surfaces of primary coolant pipes of the typical PWR under flow rate transients. Appl Radiat Isot 62:681–692
16. Nuclear Energy Education Research (2006) Technical progress report. Electrochemistry of water-cooled nuclear reactors. Pennsylvania State University, USA
17. Rafique M, Mirza NM, Mirza SM (2005) Kinetic study of corrosion product activity in primary coolant pipes of a typical PWR under flow rate transients and linearly increasing corrosion rates. J Nucl Mater 346;2/3:282–292
18. Rafique M, Mirza NM, Mirza SM (2009) Simulation and modeling of radioactivity build-up due to corrosion products in ion-exchanger and filters of a typical PWR. Radiochemistry 51;1:40–46
19. Rockwell T III (1956) Reactor shielding design manual. National Technical Information Service, D. Van Nostrand Co., Inc., New York
20. Song MC, Lee KJ (2003) The evaluation of radioactive corrosion product at PWR as change of primary coolant

chemistry for long-term fuel cycle. Ann Nucl Energy 30;12:1231–1246

21. US NRC (2003) Occupational radiation exposure at commercial nuclear power reactors and other facilities. United States Nuclear Regulatory Commission, Washington, DC

22. Varovln JA, Eperin AP, Konstantinov YA, Sedov VM, Senin YV, Filippov YM (1983) Paper no. 23. In: Proc of the IAEA Specialists Meeting on Influence of Water Chemistry on Fuel Element Cladding Behaviour in Water Cooled Power Reactors', 6–10 June 1983, Leningrad, USSR

23. Zmitko M (1994) Investigation and modeling of activity transport in WER primary systems. In: Proc of the Int Symposium on Activity Transport in Water-Cooled Nuclear Power Reactors, 24–26 October 1994, Ottawa, Canada. AECL Report, RC-1334