

# Restriction of Iodine Release under Severe Accident Conditions at NPP MIR.1200

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**Abstract**—Iodine radionuclides in accident releases under severe accident conditions at NPP with VVER are the most radiation-important with a view to population dose generation at the beginning of the accident. To decrease radiation consequences of severe accidents the technical solutions for severe accidents management have been proposed in MIR.1200 project, with consideration of the measures for suppression of volatile iodine forms generation in the containment. Behavior dynamics of different iodine forms in the containment under severe accident conditions has been analyzed for the purpose of these technical solutions justification.

**Keywords**—Iodine radionuclides, VVER, severe accident.

## I. INTRODUCTION

UNDER severe accidents condition with the melt fuel at NPP with PWR one way of decrease the emergency release of radionuclides iodine is suppression of volatile forms of iodine in the containment. According to international recommendations [1] maintenance in the emergency pool pH above 7 is an effective measure for reducing the generation of volatile forms in an emergency conditions in the containment.

The project MIR.1200 justification of technical solutions to maintain the pH in the emergency pool in a severe accident is performed with use of Russian integral code.

## II. CALCULATION MODELS AND CODES

Russian computer code SOKRAT is developed for calculation accident at NPP with WWER [2]. This code contains Kupol-M code which is used for calculation heat-hydraulic parameters in containment at NPP with WWER. The SOKRAT/B3 code's new version contains module for calculation an accumulation of fusion products (FP) in active zone of reactor, transfer FP in first circuit and release to atmosphere of containment. The new modules have been developed for estimate behavior FP in containment and for estimate release radioactivity to environment.

### A. Aerosols Behavior

The special module for Kupol-M code has been developed for estimate aerosols behavior (including Cesium iodine) within rooms of containment. The steam condenses on dry particles coupled the interaction of dry aerosol particles with water vapors and other chemicals. Equation [3] is used for a description of this process:

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$$\frac{\partial q_i}{\partial t} + \frac{\partial}{\partial m} (V q_i) = V_i n \quad i = 1, \dots, N_c \quad (1)$$

where  $n(m,t)$  is total count of particles, the mass of this particles changes from  $m$  to  $m+dm$ ,  $q_i(m,t)$  is total mass of  $i$ -th component is contained in particles with masses from  $m$  to  $m+dm$ ,  $V_i = dm/dt$  is growth velocity of mass of  $i$ -th component,  $V$  – summary velocity of growth.

The coagulation of particles is occurred when particles interact together in the Brownian motion, turbulent fluctuations and gravitational settling.

$$\frac{\partial n(m,t)}{\partial t} = \frac{1}{2} \int_0^m K(m-k,k) n(k,t) n(m-k,t) dk - \quad (2)$$

$$n(m,t) \int_0^\infty K(m,k) n(k,t) dk$$

where  $K(m-k,k)$ ,  $K(m,k)$  are coagulation cores.

The trait condensation process under several accident conditions is multicomponent condensation (steams of different chemicals condense on composite particles).

The mathematical model and numerical algorithms are based on “internally mixed” or composite particle approximation. All particles of same size have similar composition according of this approximation.

### B. Iodine Behavior

Calculation of iodine chemistry contains the following phases: calculation of sorption on the surfaces, the calculation of chemical reactions in the aqueous and gas phase mass transfer (gas  $\leftrightarrow$  liquid).

The dynamics of iodine in the volume of containment is shown in Fig. 1.

In a several accident with core meltdown, iodine releases to the containment in the form of CsI, RbI and other aerosols and in negligible quantity in the form of gases. When aerosol particles enter water (emergency pool), dissociate occurs. The iodide ion interacts with the products of radiolysis, forming volatile forms which diffuse through the interface between the phases and enter the atmosphere of the containment.

The key reaction determining the behavior of iodine in the containment is radiolytic oxidation of iodide-ion in water to volatile molecule iodine [4, 5]:  $2I^- \rightarrow I_2$ . This process is complex and occurs primarily via oxidation of the iodide ion by the radical OH followed by the formation of the molecular iodine:  $I^- + OH \rightarrow HOI^-$ ,  $HOI^- \rightarrow I + OH^-$ .

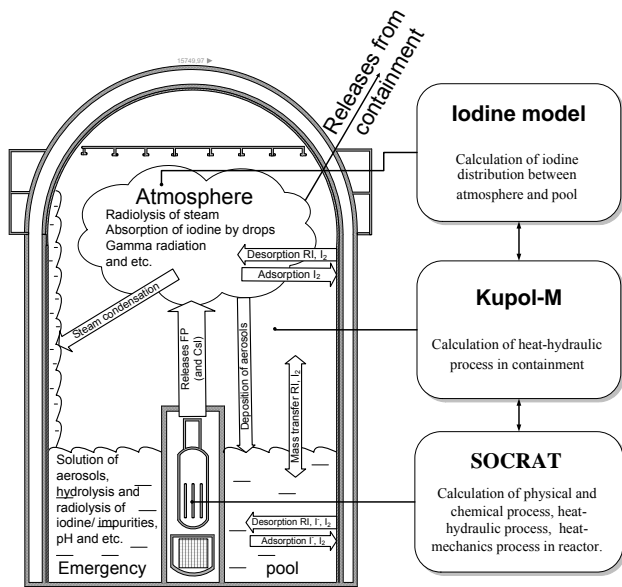


Fig. 1 Calculation diagram

A set of 54 reactions, describing the interaction of nine forms of radiolysis products [6], is proposed to model the process of water radiolysis.

In accidents a large number of impurities (fission products, construction materials) enters in pool, and they have an impact on the concentration of radiolysis products of water and the rate of formation of volatile forms of iodine. The model is provided 165 reactions to describe these interactions [5].

The general form of the system is described by the following type of equations:

$$\frac{d[Y_u]}{dt} = G_u D + \sum_{i,j=1}^M A_{i,j}^u \cdot K_{i,j} [Y_i][Y_j] + \sum_{i=1}^M B_i^u \cdot K_i [Y_i] \quad (3)$$

where  $[Y_u]$  are particles participating in the reactions;  $G_u$  is the track radiation yield of particles  $Y_u$ ;  $D$  is the dose rate;  $A_{i,j}^u$ ,  $B_i^u$  are the stoichiometric coefficients of the reactions leading to the formation (vanishing) of the particle  $Y_u$ ;  $K_i$ ,  $K_{i,j}$  are the rate constants of these reactions (mono- and bimolecular).

Significant influence on the formation of molecular iodine has a concentration of hydrogen ions. The main sources of impurities that affect the concentration of hydrogen ions, are the technology liquids (the first circuit, ECCS, tanks of boron reserve and etc.) and aerosols formed by the destruction of the core.

The mathematical model of the processes involved in the acid-base equilibrium includes the equations describing the electroneutrality of the solution and the mass balance, expressions for the thermodynamic constants for the dissociation of the weak electrolytes, as well as the dissociation constants for water [7]. The method of successive

approximations is proposed to solve the basic equation pH.

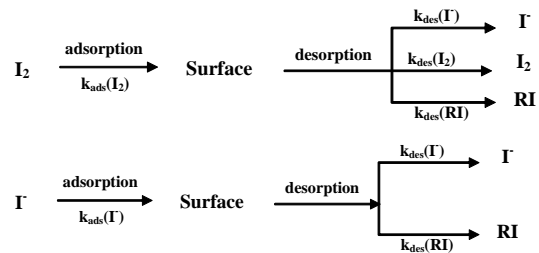
The ranges of possible concentrations of the components are estimated on the basis of analysis of accidents at NPP, but the program design possibilities are wider. The program calculates the pH of the solution in which the concentration of one or more components reaches 1.0 mole per kg, the pH calculate range is 0 ... 14. At an ionic strength of the solution, more than 0.05 mole per kg, the activity coefficients of ions in solution are taken into account. For such solutions, the ionic strength and the corresponding secondary ion activity coefficient are calculated.

**Sorption.** Form "A" adsorption from water by of steel, organic and polymeric coverings surfaces is described by the equations:

$$\frac{d[A]_{aq}}{dt} = \{-k_{ads}[A]_{aq} + k_{des}[A]_s\} \cdot \frac{S_{noxp}}{V_{aq}}, \quad (4)$$

where  $k_{ads}$ ,  $k_{des}$  are adsorption and desorption rate constants of A-form,  $s^{-1}$ ;  $S_{surf}$  is the area of a surface of coverings,  $m^2$ ;  $V_{aq}$  is volume of water phase,  $m^3$ .

Adsorption  $I_2$  or  $I^-$  (for the aqueous phase) and desorption from the surface occur follows:



Records of the sorption-desorption equations for concrete iodine forms in water and gas phases, and also rate constants base for these processes are given in [8-10].

The basic iodine water form - iodine-ion  $I^-$  possesses the expressed property to sorb on surfaces of iron hydroxide particles (sludge) in water solution. Therefore, the sorption of iodide ion can be described by the following equations:

$$\frac{dC_{aq}(t)}{dt} = \alpha [C_s(t) - \chi C_{aq}(t) + \lambda C_s(t) C_{aq}(t)] \quad (5)$$

$$\frac{dC_s(t)}{dt} = \alpha [C_s(t) + \chi C_{aq}(t) - \lambda C_s(t) C_{aq}(t)] \quad (6)$$

Constants  $\chi$  and  $\alpha$  can be picked up from comparison of simulated and experimental dependences ( $\alpha$  influences only time scale of process),  $\lambda$  – the constant equal to the ratio of the rate constant for adsorption to the desorption rate constant,  $K_d$  – constant the depends on the temperature, the nature of the

oxide, and the alkaline-acid index pH.

The dependence of  $K_d$  on the pH for the iodide ion and the iron hydroxide is presented in [11]. The experimental values of the constants are  $\alpha=2,5 \cdot 10^{-6} \text{ s}^{-1}$ ;  $\lambda=300$ .

**Reactions in the atmosphere.** Containment atmosphere is a complex physico-chemical system, in which the processes of chemical reaction, condensation, etc occur. The radiolysis process of the steam-air mixture occurs in the emergency conditions [12, 13]. All reactions are separated by two types of reaction with iodine and the reaction impurities that affect the exposure to iodine.

The first type of reactions are:

- $\text{I}_2$  thermal reducing ( $\text{I}_2 + \text{H}_2 \leftrightarrow 2 \text{HI}$ );
- $\text{I}_2$  radiation reducing ( $\text{I}_2 + \text{H}_2 \rightarrow 2 \text{HI}$ );
- HI radiation decomposition (chain reaction  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ );
- HI oxidation ( $4\text{HI} + \text{O}_2 \rightarrow 2\text{I}_2 + 2\text{H}_2\text{O}$ );
- $\text{CH}_3\text{I}$  formation ( $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$  and  $\text{CH}_4 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{HI}$ );
- $\text{CH}_3\text{I}$  radiolytic disintegration ( $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$ );
- $\text{CH}_3\text{I}$  thermal decomposition ( $\text{CH}_3\text{I} \rightarrow \text{CH}_3 + \text{I}$ );
- $\text{CH}_3\text{I}$  oxidation ( $\text{CH}_3\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}$ );
- Reaction  $\text{I}_2$  with ozone ( $\text{I}_2 + \text{O}_3 \rightarrow \text{IO}_3 + \text{I}$ );
- Recombination of atomic I ( $\text{I} + \text{I} \leftrightarrow \text{I}_2$ ).

The second type of reactions are:

- Oxidation of nitrogen to form oxides of nitrogen and nitrates ( $\text{O}_3 + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{O}_2$ ,  $\text{NO} + \text{O} \rightarrow \text{NO}_2 + \text{hv}$  (gamma photon) and etc.);
- Reaction of ozone radiolytic formation and decomposition ( $\text{O}_2 \leftrightarrow \text{O} + \text{O} \Rightarrow \text{O}_2 + \text{O} \leftrightarrow \text{O}_3$ );
- Interaction with the products of radiolysis of steam ( $\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \text{H}_2\text{O} + 2\text{O}_2$ ,  $\text{H}_2 + \text{OH}^\bullet \rightarrow \text{H}_2\text{O} + \text{H}^\bullet$  and etc.)

**Mass exchange.** Mass transfer through the interface between phases occurs by means of diffusion in accordance with the two-film model.

Mass transfer can be described by the expressions [14]:

$$\frac{dC_{\text{aq}}}{dt} = k_t \frac{S}{V_{\text{aq}}} (H \cdot C_{\text{g}} - C_{\text{aq}}); \quad (7)$$

$$\frac{dC_{\text{g}}}{dt} = k_t \frac{S}{V_{\text{g}}} (C_{\text{aq}} - H \cdot C_{\text{g}}), \quad (8)$$

where  $C_{\text{g}}$ ,  $C_{\text{aq}}$  are concentrations of the volatile form of iodine ( $\text{I}_2$ , I, HOI,  $\text{CH}_3\text{I}$ ) in gas and water phases,  $\text{mol}/\text{dm}^3$  ( $C_{\text{aq}}(t)$  is taken from the solution of system of the iodine radiolysis equations);  $V_{\text{g}}$ ,  $V_{\text{aq}}$  are volumes of gas and water phases,  $\text{dm}^3$ ;  $k_t$  is the interphase constant of transfer,  $\text{s}^{-1}$ ;  $H$  is factor of distribution between phases of the given form of iodine (Henry's constant - dimensionless quantity);  $S_{\text{aq}}$  is the area of a surface of a water phase,  $\text{dm}^2$ .

### C. Radioactive Decay

During the passing of exvessel stage by radioactive decay next parameters are changing:

- the isotopic composition of the products and actinides;
- activity of fission products and actinides;
- energy from FP and actinides.

The developed code has been verified by experiments data such as VICTORIA [15], ISP [16], etc. Also a cross-verification has been made by MELCOR.

### D. Calculation Accident at NPP

The calculation of severe accident has been made respiratory pressurizer pipeline rupture overlay complete blackout unit for 24 hours. The input data for the calculation are the outputs of mass and energy and aerosols obtained from the calculation results of the accident using the code SOCRAT.

Analysis of the dynamics of the medium under containment has been made taking into account the work of three-channel passive management accident system of PHRS.

In addition the effect of the model of the condensation aerosol particles in the containment have been estimated.

## III. THE RESULT OF ANALYSIS

In the project MIR.1200 for reliable binding of iodine, pH of emergency pool is maintained at above 8 during the first twenty-four hours through spill alkaline solution to emergency pool. The operator spills alkaline solution by indication starting of fuel melting. In subsequent phases of the accident after restoring electricity at NPP the pH level is not significantly reduction as shown by estimation. The pH level is still controlled at least 8, which is provided through the supply of alkaline solution tanks chemical of spray system.

## IV. CONCLUSION

The technical solutions adopted in the project MIR.1200 provide to:

- reduction of the formation of volatile forms of iodine and emergency release during severe accidents;
- execution of the acceptance criteria of radiation safety to make of modern project NPP with PWR [1].

## REFERENCES

- [1] European Utility Requirements for LWR nuclear power plants (rev.C).
- [2] L. Bolshov, V. Strizhov "SOCRAT – The System of Codes for Realistic Analysis of Severe Accidents", Proceedings of ICAPP'06 Reno, NV USA, June 4-8, 2006, Paper 6439.
- [3] C. Pilinis, *Derivation and numerical solution of the species mass distribution equations for multicomponent particulate systems*, Atmos. Environ. 1990. V. 24. P. 1923-1928.
- [4] Beahm E.C., Weber C.F., Kress T.S. at all. *Iodine Chemical Form's in LWR Severe Accidents*. NUREG/CR-5732, 1992.
- [5] Dickinson S., Sims H.E. *Modification to the INSPECT model*. In The Chemistry of Iodine in Reactor Safety. Proceed. of the Fourth CSNI Workshop, Würenlingen, Switzerland. 1996. NEA/CSNI/R(96)6. – p.487-500.

- [6] V. I. Bugaenko and V. M. Byakov, "Quantitative model of the radiolysis of liquid water and dilute water solutions of hydrogen, oxygen, and hydrogen peroxide. I. Formulation of the model," Preprint ITEF, No. 74 (1991).
- [7] J. Butler, *Ionic Equilibria (mathematical description)*, Khimiya, Leningrad (1973).
- [8] Ewig F., Schwarz S., Weber G., Allelein H. Multi-Compartment Iodine Calculations with FIPLOC/ IMPAIR// Wiirehlingen, Switzerland.- NEA/CSNI/R (96)6.- 1996- P.487-614.
- [9] Marchand C., Petit M. Small scale experiments on organic iodide production from iodine – painted surface interaction. In Iodine Aspects of Severe Accident Management. Workshop Proceed. Vantaa, May 1999. NEA/CSNI/R(99)7. – p.135-150.
- [10] Wren J.C., Ball J.M., Glowa G.A. Studies on the Effects of Organic-Painted Surfaces on pH and Organic Iodide Formation. In: Iodine Aspects of Severe Accident Management Workshop Proceed. Vantaa, 1999. NEA/CSNI/R(99)7. – p.181-196.
- [11] F. Kepak, "Contribution to the study of the sorption of radionuclides on hydrated oxides," Radioanalyt. Chem., 51, No. 2, 307–314 (1979).
- [12] Beahm E.C., Shockley W.E., Culberson O.L. Organic iodide formation following Nuclear Reactor Accidents. Rep. NUREG/CR-4327 Oak Ridge Nat.Lab., 1985.
- [13] Ono S., Fujita N., Fujiwara K. at all Radiochemical effect on the formation of inorganic and organic iodine species. In Water Chemistry for Nuclear reactor Systems. 4. BNES, L., 1986. – p.177-182.
- [14] Beahm E.C., Shockley W.E., Weber C.F. Chemistry and transport of iodine in the containment. Nucl.Technol. V.78, 1987. – 34p.
- [15] T.J.Heames et al. "VICTORIA : A Mechanistic Model of Radionuclide Behavior in the Reactor Coolant System Under Severe Accident Conditions", NUREG/CR-5545 SAND90-0756 Rev 1 R3, R4, 1992.
- [16] 7. International Standard Problem (ISP) No.41. Containment iodine computer code exercise based on RTF experiment. NEA/CSNI/R (2000)6/vol.1. OECD/OCDE, Paris, 2000, p. 51-63.