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**Development of Hydrogeological Modelling Approaches
for Assessment of Consequences of Hazardous
Accidents at Nuclear Power Plants**

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Abstract

This paper introduces some modelling approaches for predicting the influence of hazardous accidents at nuclear reactors on groundwater quality. Possible pathways for radioactive releases from nuclear power plants were considered to conceptualize boundary conditions for solving the subsurface radionuclides transport problems. Some approaches to incorporate physical-and-chemical interactions into transport simulators have been developed. The hydrogeological forecasts were based on numerical and semi-analytical scale-dependent models. They have been applied to assess the possible impact of the nuclear power plants designed in Russia on groundwater reservoirs.

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1. Introduction

The Chernobyl disaster and a few other accidents occurred at nuclear reactors during the last decade sharply changed people's attitude towards the safety of the atomic energy policy. People realized that it is impossible to exclude completely the possibility of such accidents at nuclear power plants (NPP) which should be treated as a potential sources of extremely hazardous radioactive impact on the environment. This understanding served as starting point for developing the risk assessment analysis that deals with impacts which can cause low-probability but high-consequence hazards.

Under this condition soil and groundwater becomes one of the most vulnerable objects for radionuclides released from the failed reactors (*Shestopalov and Gudzenko, 1993*). This circumstance was underlined in special requirements (*Hydrogeological Aspects...,1986*) elaborated by the International Atomic Energy Agency (IAEA). Unfortunately these requirements and methodical recommendations for the impact assessments were written in a very uncertain and formal manner. Thus they do not take into account the real character of the radioactive release process and say almost nothing about intensity of the formed contaminant sources. Besides, the mathematical models recommended in the referred publications are rather formal and do not meet the modern viewpoints on subsurface migration processes.

The study of the problem was stimulated by the necessity of carrying out ecological assessments for several NPP's projects in Russia. They are proposed to be located in the Cola Peninsula, the Far East and the St.-Petersburg Province. It means that different hydrogeological environment (such as porous, fractured and fractured-porous groundwater reservoirs) have been under consideration. Therefore different migration mechanisms and models need to be analysed and developed.

The above determines the priority in the field of risk assessment analysis (hydrogeological aspects) and we mobilized our research activities in the following directions:

(a) evaluation of the possible pathways for radioactivity releases from nuclear reactors in order to show how scenarios of concern could be combined with the set of hydrogeological models;

(b) reexamination of the applicability of classical mathematical schemes for describing nuclear transport problems;

(c) assessment of possible industrial impacts on groundwater reservoirs within the influence area of new NPP designed in Russia.

2. Radionuclide release scenarios and how they affect the choice of RNT models

To analyse the relevant impact hazards, we must first characterize the paths of introducing the radionuclides into the underground hydrosphere. For this purpose we have to consider the possible scenarios of hazardous accidents at nuclear reactors resulting from the risk assessment theory.

The emergency situations described below refer to the events which are hardly probable, however their aftereffects can be of catastrophic character. Such events conform to the 5 or 6 levels of the IAEA scale, and they include also the postulated over-hazardous accidents potentially exceeding their ultimate level taken into account within the projects. The probability of such accidents at the nuclear reactor plants can be estimated to be less than $\cdot 10^{-7}$ per one reactor a year.

The basic data on the possible radioactive impact are quoted from the results of mathematical modelling of the overhazardous accidents at nuclear reactors of the last generation in Russia (WWR-1000 and W-407/block NP-500 types). The analyses of the failures after-effects enabled us to distinguish two quite different pathways for radiation release from the reactor protective shell (Table 1).

The first pathway of radiation release facilitates the formation of a local (point) source for groundwater contamination by radionuclides. Its occurrence is associated with a number of postulated accidents when heavy damage of active reactor zone takes place due to

failure of the cooling system followed by a simultaneous malfunction of the equipment for failure localization. The long-term leakage of radioactive water (condensate or water from the emergency reservoir) could be a source of contamination for ground water. The potential radio-nuclide composition of wastes is rather variable (*Rumynin V.G. et al., 1992*), however, the analysis allows to detect four major isotopes extremely hazardous for ground water (Table 1).

The second pathway of radiation release facilitates the formation of an areal (nonpoint) source for ground water radioactive contamination, i.e. atmospheric precipitation followed by seepage through contaminated soils. The corresponding postulated scenarios assume also a damage or melting of the reactor active zone caused by failure of its cooling system, but without breaking of its protective shell. Radionuclides precipitation from the gas-aerosol mixture on the land surface occurs with the highest density, P_f (Table 1). This level of radioactive contamination may be reached: a) within the range of 2.5 km around a NPP - in the case of a low emergency plume; b) within the range of 25-30 km in the case of a high emergency plume.

The hazardous accidents at the NPP described above lead to a very specific impact on the underground hydrosphere. This poses a question whether existing analytical or numerical methods and approaches are efficient enough to study the outlined class of tasks.

The first pathway of radioactive release forms a contaminant source with extremely high radionuclide concentrations C_{max} which exceed the safety standard by eight to ten orders of magnitude C_{st} (Table 1). This requires that the model assessments should be reliable enough to simulate concentration plumes where the ratio C_{st}/C_{max} is some times less than $\cdot 10^{-10}$. The given limit is not easily reached by applying the "classical" numerical methods. This, in particular, has been shown by *Dougherty and Bagtroglou (1993)*. There are two major ways to improve the situation: (a) to use non-traditional and rather sophisticated digital algorithms and (b) to combine the existing algorithms with analytical techniques. In this paper we are following the latter (Section 3).

For the second pathway of radioactive release the overall model is to couple vertical transport through the unsaturated zone and subhorizontal (in the areal plane) transport

Table 1. Parameters of radioactive contamination caused by hazardous accidents at AS

Radio-nuclide	The first pathway			The second pathway	Safety Standard
	$C_0,$ $Ci \cdot l^{-1}$	$Q_0,$ $l \cdot h^{-1}$	$t,$ month	$P_f,$ $Ci \cdot km^{-2}$	$Ci \cdot l^{-1}$
J-131	14/14	30/10	24/1	20000/-	$2.0E(-9)$
Cs-137	1.5/2.0	30/10	24/1	1000/100	$1.5E(-8)$
Sr-90	0.3/0.2	30/10	24/1	10/10	$4.1E(-10)$
Ce-144	0.3/-	30/10	24/1	-	$1.2E(-8)$

Note: Enumerator - parameters for an accident at nuclear reactor "WWR-1000" (model of the Kola Research Centre); denominator - the parameters for an accident at the reactor (block) "W-407" (model of the institute "Atomenergoprojekt"); C_0 - radionuclide concentration in a condensate; Q_0 is the rate of leakage; t is the duration of leakage; P_f is the density of the surface contamination derived from atmospheric radionuclide precipitation.

in aquifers. The general solution of the problem is rather complex but can again be efficiently solved by combining numerical and analytical techniques (Section 6).

The key role in the RNT problem places the incorporation of hydrogeo-chemical interactions into the transport models. Two approaches are well-known and some times can be considered as fairly competitive. The first one is based on the so-called "Kd concept" (Appendix 1) and combines all kinds of heterogeneous chemical reactions in a single phenomenological coefficient of sorption distribution K_d . According to the second approach the interactions are reflected explicitly in the calculation schemes that imply using multicomponent models. Being more rigorous the multicomponent models however often are not available because of the lack of thermodynamic data for heterogeneous interactions. Therefore from a practical point of view the choice between the two mentioned approaches turns out to be far from trivial - see Section 5.

Multidimensionality of the transport process and manifestation of heterogeneous properties of groundwater reservoirs affect the choice considerably.

3. On numerical-and-analytical solutions of mass-transport problems

It seems expedient to include analytical elements into the calculation procedures in order to take into consideration processes which place the most significant role in reducing the mass flux in porous or fractured media such as: (a) radioactive decay and (b) mass-exchange between mobile and immobile water in heterogeneous reservoirs with double porosity e.g. in fractured-porous rocks.

The first approach is valid for analyzing linear processes. It is based on the representation of the final solution in an integral form (Appendix 2), where the concentration function $C'(\theta)$ can be distinguished - as a numerical solution associated with nonreactive transport in equivalent homogeneous strata, and some analytical function $H_0(t, \theta)$ (or its derivative $\partial H_0(t, \theta) / \partial \theta$) which describes of radioactive decay and/or mass-exchange processes in heterogeneous aquifer (Rumynin, 1983):

$$C = \int_0^t \frac{\partial C'(\theta)}{\partial \theta} H_0(t, \theta) d\theta. \quad (1)$$

Having integrated by parts the last expression (*Lindstrom, 1976*) we obtain:

$$C = C'(\theta) H_0(t, \theta) \Big|_0^t - \int_0^t C'(\theta) \frac{\partial H_0(t, \theta)}{\partial \theta} d\theta, \quad (2)$$

which is more suitable for the further recalculation of the model data.

In Appendix 2 one can find the basic representations for the $H_0(t, \theta)$ function and its derivat for the case of the RNT in fractured-porous reservoirs where the radioactive decay takes place.

The approach under consideration have been applied to simulation of the RNT taking place after the hypothetical hazardous accidents at NPP designed in Russia. The major results of the model assessment and practical conclusions are presented in Appendix 3.

According to the second approach an analytical sink-function w_s , responsible for mass-exchange and decay, is directly included into the finite-difference equations. Thus for the heterogeneous fractured-porous media equation (1) is valid, which describes diffusion of decayed species from water in the fractures into the porous matrix. In this case there is a possibility to study nonlinear processes as will be discussed in the next Section.

4. Simplified models for the RNT by colloids in fractured-porous groundwater reservoirs

The problem of RNT in groundwater in colloid form is widely debated nowadays. The colloids could be of natural origin associated with processes of rock weathering, or their formation may be due to the influence of radioactive contamination on the host rocks (*Castaing, 1991; Torok et al., 1990*). A significant importance of microbiological processes in colloid formation (*King and Killoy, 1990*) hampers their study under laboratory conditions. In natural water of deep horizons concentration of colloids (cores of which are very often represented by molecules of silicon acid or by clay particles) do not exceed several $mg \cdot L^{-1}$ (*Vilks et al., 1992*). In groundwater they can reach a few tens of $mg \cdot L^{-1}$ which is rather essential in comparison with the radionuclides concentrations.

For understanding the role of colloid formation during radionuclide migration three aspects are of prime importance: 1) poor sorption of migrating elements in colloidal form by the mineral surfaces; 2) redistribution of substances between the sorptive fracture surfaces and migrating colloids in favour of the latter and 3) rather low diffusive permeability of micro-porous materials for colloidal particles; the latter aspect is of principal significance for the analysis of migration in fractured-porous strata.

In the simplest case colloid formation can be included into the model of mass-transport by the reaction of radionuclide adsorption (M_1) on colloidal particles (M_2):



causing the formation of the compound M_1M_2 . The equation (3) is conjugated with the standard equation of radionuclide adsorption by rocks.

Hence, the equilibrium relationships between concentrations of the substance in a solution C_1, C_2, C_{12} and on rock \bar{C}_1 are governed by formulae of the following kind:

$$C_{12} = K_{12}C_1C_2, \quad (4)$$

$$\bar{C}_1 = K_1C_1; \quad (5)$$

the coefficients of proportionality (of equilibrium) can be defined by the following obvious relationships:

$$K_{12} = FK_d, K_1 = \rho K_d \quad (6)$$

where K_d is the adsorption distribution coefficient, F - some coefficient of "strengthening" ($F \gg 1$), showing more strong colloid-nuclide interaction in comparison with sorption on the mineral framework of the rock (*Vilks and Deguelare, 1991; Vilks et al., 1991*).

By formulating the balance equation for the elementary stream tube, it is easy to obtain an expression which enables to control the degree of sorption retardation due to the presence of colloids in a solution:

$$R = 1 + \frac{\rho K_d}{n(1 + FK_d C_1)} \quad (7)$$

It is obvious from the equation (7) that formation of the colloids becomes essential for the migration process when $FK_d C_1 > 0.2-0.5$. According to *Vilks et al., 1991*, the magnitude of

FK_d can reach the value of $N \cdot 10^4 \text{ cm}^3 \text{ g}^{-1}$, i.e. the colloids transport plays a remarkable role in radionuclide migration for sufficiently high content of colloidal particles in ground water ($C_2 > 10 \text{ mg} \cdot \text{L}^{-1}$).

During migration in heterogeneous fractured-porous media the absorption of dissolved radionuclides by the porous matrix leads to the disturbance of initial equilibrium in the system as well as to the partial rejection of colloids. This process involves the overall area of transport and for its stringent mathematical description one should refer to the system of differential balance equations:

$$\begin{aligned} n \frac{\partial C_1^T}{\partial t} + n \lambda C_1^T + \frac{\partial \bar{C}_1^T}{\partial z} + \lambda \bar{C}_1 + w_s &= L(C_1^T), \\ n \frac{\partial C_2^T}{\partial t} &= L(C_2^T), \end{aligned} \quad (8)$$

where C_1^T and C_2^T are total concentrations $C_1^T = C_1 + C_{12}$, $C_2^T = C_2 + C_{12}$, $C_{12} = K_{12} C_1 C_2$; $L(z)$ - linear differential operator for convective-dispersive mass-transport; the function w_s is defined in compliance with the expression (A.3) when $C = C_1$.

Nonlinear equations (8) can be easily transformed (Lewis et al., 1986) into a form convenient for numerical calculations by the method of finite differences. We have implemented a computer realisation of a corresponding algorithm for the one-dimensional version.

Particular results of the model assessments are depicted in Fig.1. Due to the presence of the colloid fraction in the moving solution the RNT potential is changed. It is important to underline that in combination with the longitudinal hydrodynamic dispersion the colloid-forming process leads to increasing concentration values at the advanced front of the concentration wave - in comparison with the case $K_{12} = 0$. The relevant differences can reach one to two orders of magnitude (Fig.1). The effect is the more significant the higher concentration of radionuclides and colloids are in solution. In this context it can alter the view on the consequence of the RNT by groundwater.

The problem under consideration has a rather trivial analytical solution in the case where colloid concentration considerably exceeds radionuclide concentration ($C_1 \gg C_2$).

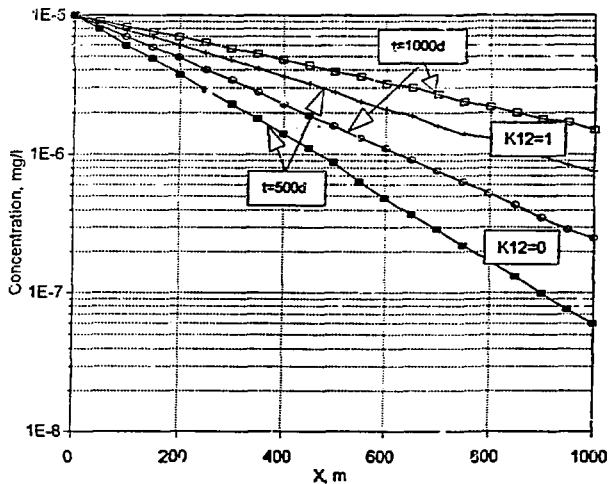
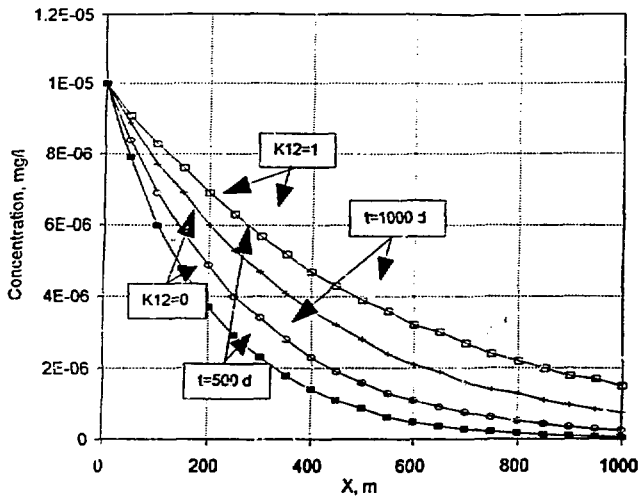


Fig.1. Influence of the colloidal fraction on radionuclide transport
 $v = 0.05 \text{ m d}^{-1}$, $n = 0.001$, $K_d S_b = 0.005$, $\lambda_m = 0.0001 \text{ d}^{-1}$,
 $C_{0m} = 0.00001 \text{ } \mu\text{g L}^{-1}$, $C_{0col} = 1.0 \text{ } \mu\text{g L}^{-1}$,
 $\Delta x = 5 \text{ m}$, $\Delta t = 1 \text{ d}$, $t = 1000 \text{ m}$

When it occurs the set of equations (8) is transformed into a linear equation which has been solved by *Tang et al., 1981*. In this solution, however, one should use some effective parameters instead of the relative volume of fractures (n) and complex mass-exchange parameter (λ_m). So, for the model based on the assumption of Elemental Representative Volume (Appendix 2) the correction procedure can be represented as follows:

$$\begin{aligned} n \rightarrow n_e &= n + \frac{K_a S_b}{1 + FK_d C_{20}}, \\ \lambda_m \rightarrow \lambda_{mc} &= \frac{\lambda_m}{(1 + FK_d C_{20})^2}. \end{aligned} \quad (9,10)$$

It can be seen that the presence of colloids in solution makes radionuclides move faster because both the values of effective sorption and complex mass-exchange parameters have been decreased.

Finally, some useful assessment showing the influence of colloid formation on mass-transport in fissured-porous rocks can be obtained by using the method of "integral balance". Hence, if one supposes that the motion of an advanced front of a displacing solution is determined by the characteristic

$t = t(x)$ which controls the intensity of ion saturation of porous blocks (*Castaing, 1991*)

$$w_s \approx \frac{\sqrt{\lambda_m}}{\sqrt{\pi(t-t_f)}} C_{20}; t > t_f \quad (11)$$

then the integration of the equation (A2) without decay, will yield:

$$t_f = \frac{n + K_a S_b / (1 + a)}{\nu} \cdot x + \left[\frac{\sqrt{\pi \lambda_m}}{2\nu(1 + a)} \right]^2 x^2, \quad (12)$$

where $a = FK_d C_{20}$. As in the previous evaluations, one can see that high values of the constant "a" ($a \gg 1$) will decrease not only the sorption potential of the fracture surfaces, but also reduce the damping role of the porous matrix. For the limiting case $t_f = nx/\nu$, which corresponds to the transport of nonreactive components in homogeneous media.

5. Analysis of the RNT in multicomponent systems

The models have been just analyzed and examples of their practical use are based on the Kd-concept. Meanwhile the concept has been acutely criticized for the last decade. The reason is that in real geochemical systems the distribution coefficient is changed over time and space because of the non-steady-state concentration field within the area influenced by industrial impact on groundwater.

This Section is concerned with the assessment of the level of expected errors that appear because of applying the simplified Kd-approach. Similar attempts have been made in numerous previous studies. Nevertheless we wanted to check some calculation situations which are close to the problem of the risk assessment strategy developed for the NPP' projects.

To imitate the migration process a special computer model of multicomponent transport has been worked out (MST1). It includes a hydrogeochemical module for equilibrium thermodynamic computations in "groundwater/minerals" systems based on the MINEQL code (the version SURFEQL by *Bales, 1987*). The code has an option for simulating sorption processes by treating them as surface complexation reactions (Appendix 4). Among the traditional geochemical interactions taken into account are: (a) complexation species in liquid phase, (b) dissolution/precipitation of the mineral phase; (c) acid/alkaline and oxide/redox reactions. Accepted technique for mathematical formalization of chemical interactions and easily updatable thermodynamic data-base allow to study a wide range of problems.

The transport module of MST1 provides numerical solution of the set of 1D differential equations of advective dispersion (*Yeh and Tripathi, 1991; Carnahan, 1992*):

$$\begin{aligned}
 n \frac{\partial C_i^T}{\partial t} + \lambda_i n C_i^T + w_i^T &= L(C_i^T), i = 1, \dots, N_c, \\
 w_i^T &= \frac{\partial}{\partial t} \left[S_i + \sum_{k=1}^{N_p} a_{ik} P_k \right] + \lambda_i \left[S_i + \sum_{k=1}^{N_p} a_{ik} P_k \right], \\
 C_i^T &= C_i + \sum_{j=1}^{N_i} a_{ij}^T X_j, \\
 L(\cdot) &= nD\nabla^2(\cdot) - v\nabla(\cdot),
 \end{aligned} \tag{13}$$

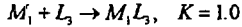
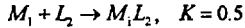
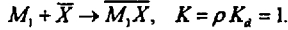
where C_j ($j = 1, \dots, N_c$) is the concentration of the basic species C_j containing component j ;
 X_i ($i = 1, \dots, N_x$) is the fluid-phase concentration of complex X_i ; S_j is the sorbed-phase concentration; P_k is the concentration of a precipitate P_k ; a_{ij} is the number of moles C_j per mole X_i ; a_{ik} is the number of moles of basic species per mole of solid P_k ; w_i is the sink-term, λ is the decay constant.

Solution of the equations (13) is carried out with the finite-difference method including an implicit scheme and a *Gauss-Seidel* iteration procedure with upper relaxation.

Coupling hydrogeochemical and transport modules is based on a so-called "two-step" technique. According to it two modules work consequently: during the first step the equations of advective dispersion are solved with the assumption that all species are conservative; the obtained concentration distributions are used for the thermodynamic calculations including sorption equilibria that result in computing the mobile forms of the basic components and the sink-function w_i . In addition to the simulation procedure for the surface complexation reactions, it is allowed to use a special code option for physical adsorption governed by the linear *Henry's law*. For the latter it is supposed that only components migrating in the simplest ionic forms are allowed to be adsorbed thus the number of the coefficients $K_{d,i}$ is equal to the number of the basic components.

The MST1 code has been supplemented with an option for simulating the mass-exchange processes in fractured-porous reservoirs. Effective approaches described above (Section 3) are used for this purpose.

At the present time the first stage of testing program procedure has been implemented. Thus, by switching off the geochemical module we managed to get numerical results which were in good agreement with the well-known analytical solutions for the "single-component" transport case. In order to quantify the reliability of the procedure coupling geochemical and transport modules three-component transport process have been simulated. It was supposed that a reactive component M_1 participates in reactions of complexation involving ligands L_2 and L_3 :



The model results were compared with the output data obtained with the **SATRA-CHEM** code by Lewis *et al.*, 1986 based on a "one-step" technique of coupling the geochemical and transport parts of the numerical problem (Fig.2). As one can see both models lead to results which agree fairly closely: maximum differences are monitored within peak values of ligand concentrations and do not exceed 5%-7%. The nonmonotonic character of L_2 and L_3 curves is explained by the decay of M_1L_2 and M_1L_3 complexes near the moving boundary interface of two solutes that results from disturbing equilibrium because of metall-ion M_1 adsorption.

Further the **MST1** code was used to study some aspects of the RNT under conditions of releasing radionuclides during failure of nuclear reactors (the first pathway of the radioactive release process). These conditions are outlet characterized by the presence of radionuclides in groundwater at extremely high concentrations. The major aim of this analysis is to assess the feasibility of applying the simplified K_d models for the migration process.

Two variants of the model assessments serve as a basis for the analysis (Table 2). In the first variant (I) the differences in the concentrations of the main components in the background water and in the contaminant source were assigned to be very significant; it was done to enhance the intensity of interactions between components in the liquid and solid phase. In the second variant (II) the differences were smoothed out to diminish the interactions.

Transport parameters of the model were assigned to be:

- Darcy velocity, $v = 0.1 \text{ md}^{-1}$
- Porosity, $n = 0.1$
- Dispersivity, $\delta = 1.0 \text{ m}$

Length of the model, $L = 320 \text{ m}$. Grid parameters of the model: $\Delta x = 4 \text{ m}$, $\Delta t = 5 \text{ d}$.

The governing geochemical reactions are as follows:

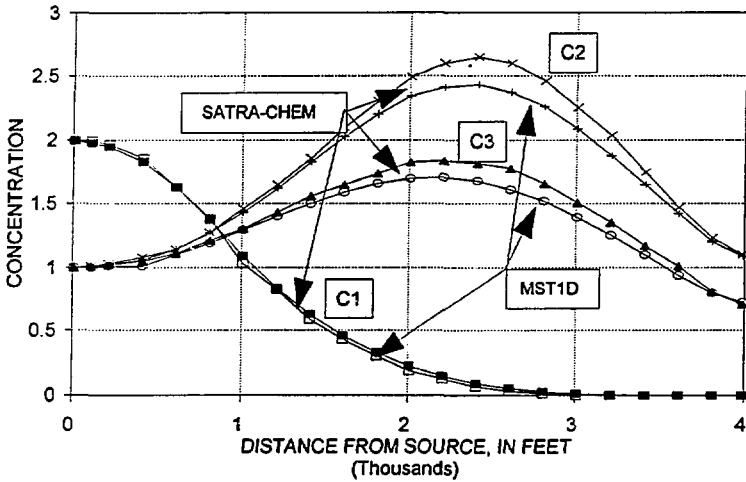
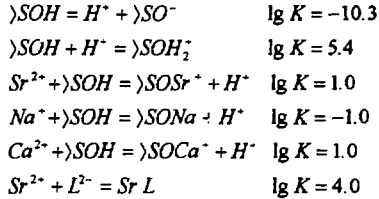


Fig.2. Test example: Transport with equilibrium sorption
(simulation with SATRA-CHEM and MST1)

Table 2 Hydrogeochemical characteristic of initial and boundary conditions for the basis (I and II) modeling variants

Number of variant	Initial and boundary conditions	Total concentration of the basic components, mol·l ⁻¹						
		Sr	Na	Ca	Cl	L	pH	>SOH
I, II	t = 0 x > 0	4.9E(-10)	0.8E(-4)	9.7E(-4)	3.0E(-3)	1.0E(-4)	5.0	5.0E(-3)
I	x = 0	1.0E(-3)	1.0E(-1)	1.0E(-2)	1.0E(-1)	1.0E(-4)	5.0	5.0E(-3)
II	x = 0	1.0E(-6)	2.0E(-3)	2.0E(-3)	6.0E(-3)	1.0E(-4)	5.0	5.0E(-3)



The parameters used to model the surface complexation (Appendix 4) are as follows:

- Layer capacitance, $C = 1.0 \text{ F m}^{-2}$;
- Solid surface area, $S_A = 1.0 \text{ m}^2 \text{ g}^{-1}$;
- Solid-to-water mass ratio, $C_s = 1000 \text{ g L}^{-1}$;
- Specific surface area, $S_{AS} = S_A \cdot C_s / n = 1.0 \cdot 10^7 \text{ m}^{-1}$.

Besides several chlorid - and hydro-complexes were taken into consideration however they did not play any principal role in the process.

The obtained concentration curves $C(x,t)$ are shown in the plots (Fig.3 and 4). On the other plot (Fig.5) one can see the changes of the effective values of the distribution coefficient K_d^{Sr} calculated through current ratio S_{Sr}/C_{Sr} , where C_{Sr} and S_{Sr} are the total concentrations of strontium in the liquid and solid phases (in composition of the surface complexes) phases.

It is of interest that intensive exchange processes taking place at the model variant I resulted in extreme behavior of the $K_d^{\text{Sr}}(x)$ function. This can be explained by calcium accumulation

in the solution by being replaced from surface complexes by sodium. This decreases the strontium sorption because of the competition phenomenon. Therefore the sorption ability of strontium diminishes within the dispersion zone where the peak of calcium concentration occurs is locally reduced.

At the same time the variant II illustrates the relative stable behaviour of the K_d^{Sr} parameter that results from low values of concentration gradients.

For the next step of model investigations averaged values of K_d^{Sr} parameter were used in

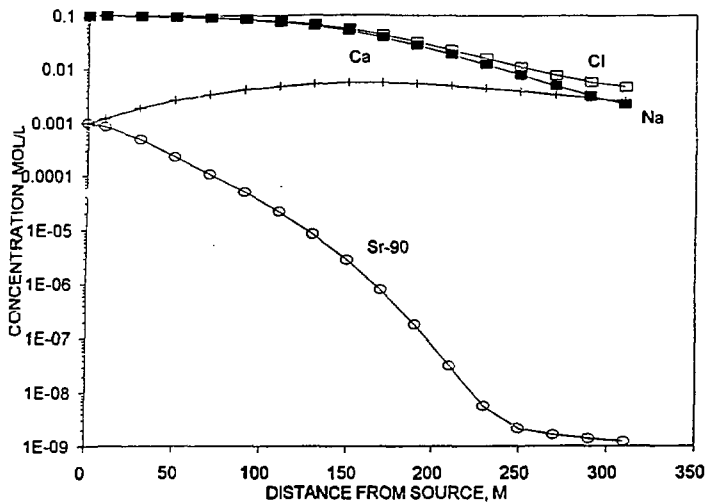


Fig.3. Concentration curves $C_i(x)$ for the model variant I

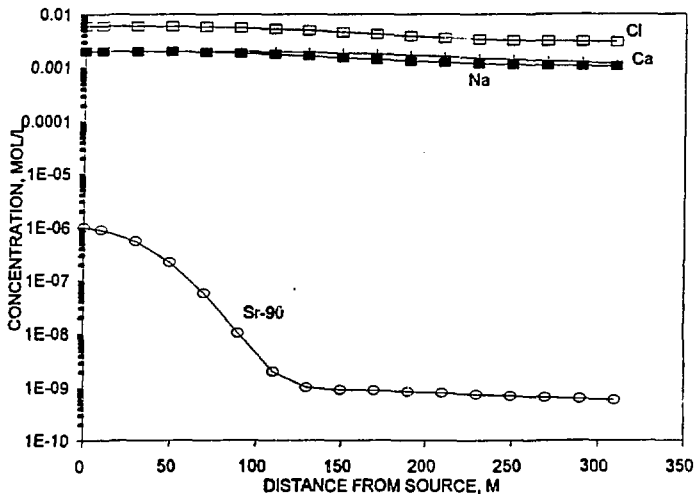


Fig.4. Concentration curves $C_i(x)$ for the model variant II

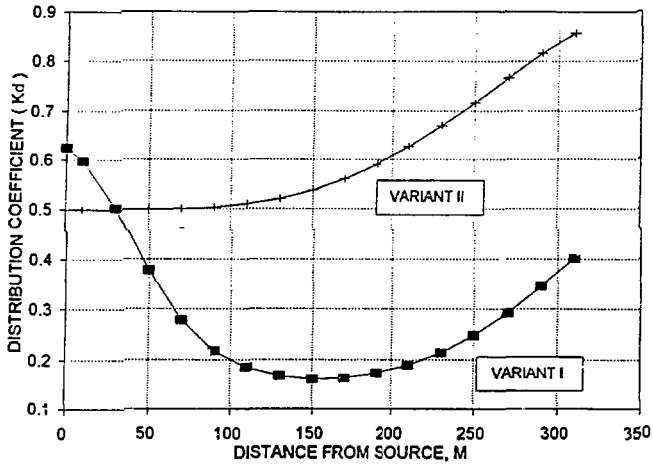


Fig. 5. Plot of the distribution coefficient versus distance ($t=150$ days): I and II are model variant (see Table2)

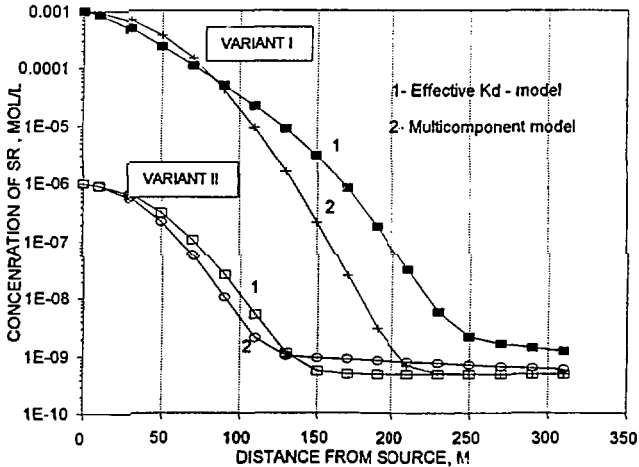


Fig. 6. Comparing numerical solutions obtained in the context of: (1) the Effective Kd-model, (2) The Multisolute model

the finite-difference model of "one-component" transport. C_{sr} - distributions obtained were compared with the results of the multicomponent transport simulation (Fig.6). Thus it enables us to evaluate the efficiency of two approaches. The main conclusions of this analysis are as follows:

1. If the relation between component concentrations and thermodynamic parameters of the hydrogeochemical system is such that radionuclides migrate under unsteady-state conditions caused by changes of other concentration functions one can expect unstable behaviour of the sorption distribution coefficient. As a result it is impossible to choose an appropriate (averaged) value of the K_d constant which would be good enough to describe the RNT process: errors in the area of low radionuclide concentrations can reach several orders of magnitude.

2. If the radionuclide concentration in the contaminant source is much less than the concentrations of the main components and major changes of the latter take place in front of the waste/groundwater interface one can try to pick out the K_d -constant satisfactorily describing radionuclide migration.

3. For a given type of industrial impact on the underground hydrosphere the Kd approach is supposed to be reliable for forecastings of the subvertical RNT that is conditioned by the areal recharge of water polluted by precipitated radionuclides (the second pathway of radioactive release). In this case the transport process is not associated with strong changes of chemical composition of groundwater.

For the first scenario the forecasts would require using the multisolute transport models.

6. A simplified model for analysis of the infiltration type of groundwater pollution

Participating recharge in forming a groundwater flux requires the intimate linkage between the flow and mass-transport parts of the problem. Model construction needs to take into account the nonuniform character of the radionuclide input to the water table, which

is conditioned by variations of the physical properties of the unsaturated zone (Shestopalov and Gudzenko, 1993). This has to be reflected in the calculation scheme as well.

The model is based on a fundamental solution for a fixed flow path (Fig. 7). If a short length $x_1 < x < x_2$ of the flow path is polluted with intensity P_ε (Fig 8) the solution for the output concentration function is expressed as

$$C = P_\varepsilon^* \exp\left[(-\lambda + \varepsilon^*)t\right] \quad \text{when } t_2^0 < t < t_1^0 \text{ or}$$

$$C = 0 \quad \text{when } t < t_2^0 \text{ and } t > t_1^0, \quad (14)$$

$$\text{where } t_i^0 = mn \int_{x_i}^L (B_x / Q_x) dx$$

is the residence-time for particles coming into the aquifer at points x_1 and x_2 ($L > x_1$ and x_2); B_x is the current width of the flow path determining the flow rate Q_x ; $\varepsilon^* = \varepsilon / (mn)$ (ε is recharge rate, m is the thickness of the aquifer, n is the porosity); $P_\varepsilon^* = P_\varepsilon / (mn)$, P_ε is the density of groundwater surface pollution,

$$P_\varepsilon = P_f \exp(-\lambda t_A), \quad (15)$$

P_f is the density of the land surface pollution, t_A is the residence time for the radionuclide transport through the unsaturated zone.

For determining the time-characteristic t_A^0 one can use numerical as well as analytical techniques. It is important that solution (14) can be generalized for a case of variable recharge rate $\varepsilon = \varepsilon(x)$ (in X-direction), which can be associated with the non-uniformity of hydraulic conductivity in the unsaturated zone. For step-functions of $\varepsilon(x)$ and $Q_x(x)$ superposition of solution (14) leads to the equation:

$$C = P_\varepsilon^* \exp(-\lambda t) \exp\left(-\sum_{j=1}^{N_j} \varepsilon_j^* \Delta t_j^0\right), \quad (16)$$

which is valid in the interval $t_1^0 < t < t_2^0$, where $t_j^0 = \sum_{j=1}^{N_j} t_j^0$ (ranges from $j=1$ to N_j , j is the current number of the block, N_j is the finite block belonging to the cross-section $x=L$).

Finally, using the superposition principle for the case of variable intensity of land surface pollution yields

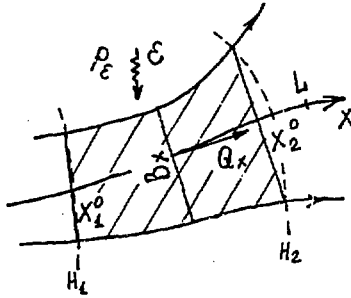


Fig.7. Schematic representation of the flow-path with elements of flow discretisation.

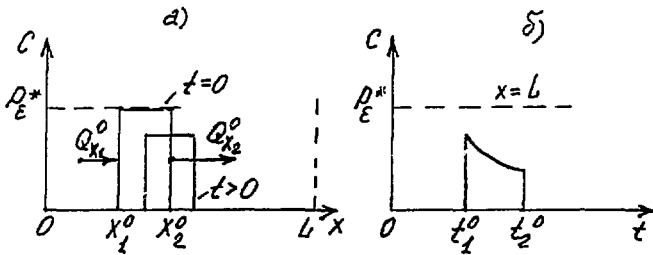


Fig.8. Scheme of zonal distribution of component on groundwater table (a) and schematic plot for output function (b)

$$C = \sum_{k=1}^K P_{kk}^* \exp(-\lambda t) \exp\left(-\sum_{j=j_k}^n e_j^* \Delta t_j^0\right), \quad (17)$$

where K is the number of the j_k^* zone providing radionuclides input at crosssection $x = L$ at time $t = t_{j_k}^0$.

The analytical-and-numerical approach considered above have been applied to analyze relevant environmental problems for the NPP design. Output concentration functions resulted from the analysis of concrete situations (*Rumynin et al., 1993*) turned out to be rather complicated that is associated with nonuniform character of land surface pollution as well as a variety of hydraulic conductivity of surface deposits.

7. Conclusions

The major conclusions of our analysis are as follows:

(1) The substantial discrepancies between the formal IAEA requirements for the hydro-geo-environmental assessments of NPP projects and the present design practice derive from uncertainties concerning including the parameters of radioactive release (for different scenarios of hazardous accidents at NPP) into the set of hydrogeological models. Having analyzed the output characteristics of the risk-assessment models (for some type of industrial nuclear reactors) we managed to conceptualize the hydro-geo-environmental problem under consideration.

(2) The forecasts of the PNT in groundwater are based, principally, on proper mathematical models of the advective- dispersive type. Such statement of the problem with due regard to dispersive components of mass-transport is of particular importance for the first pathway of an emergency radioactivity release which facilitates the formation of local (point) sources of contamination. In this case a transversal spreading of a substance appears to be a significant factor retarding the overall scale of contamination.

At the same time, forecastings of regional groundwater contamination by radionuclides precipitated on the land surface (the second pathway) may be reduced to the consideration of

the most simple convective balance schemes for water-bearing strata coupled with one-dimensional solutions for transport within the unsaturated zone.

(3) Description of the advanced fronts of contamination plumes characterised by rather low values of relative concentrations ($C < 1 \cdot 10^{-10} - 1 \cdot 10^{-12}$) is of prime interest for the hydro-geological forecasts under consideration because the radio-nuclide content at the contamination sources are ($10^8 - 1 \cdot 10^{10}$) times more than the maximum admissible levels. To improve the accuracy of the RNT forecastings special mathematical techniques have to be applied. They can be based on coupling numerical and analytical approaches.

(4) For example, being supplemented by analytical modules the traditional numerical codes allow to take into account the internal heterogeneity in fractured-porous reservoirs attributed to the diffusive exchange between fracture water and pore water: very often the kinetics of this exchange result in a more substantial influence on the dispersion process than the spatial nonuniformity of the permeable medium or variations of fracture properties and morphology. In fractured-porous strata radionuclide decay proceeds not only in the fractures but also in the porous matrix. This could substantially shift the permissible range of application for different calculation schemes used for describing mass-exchange between mobile and immobile water. Preliminary estimations show that the scheme of "unlimited matrix capacity" could be preferable to the scheme of "quasi-steadystate regime" for long-term forecasting, especially in the case of intensive sorption inside the porous matrix.

(5) To modify the governing equations (for nonreactive solute transport) one has to include a source function transformed by taking into account the radioactive decay. So far we have obtained some analytical solutions for the mentioned basic schemes which can be extended to cases of linear sorption of radionuclides in mobile and immobile zones.

In order to couple ionic and colloidal migration forms within the combined RNT model the regularities of their interactions in liquid phase have to be analyzed. Following previous investigations we assumed the analogous to the simplest equilibrium complexation reactions. Such an approach leads to a nonlinear set of equations which can easily be transformed into a form convenient for numerical simulation by the finite differences method. We have implemented a computer realization of appropriate algorithms in a one-dimensional version.

In case of excessive colloidal concentration in the solution the results are rather trivial: the set of equations is transformed into a linear equation for which some useful analytical solutions and criterions can be found.

(6) Under certain conditions many of the existing one-component K_d models are not always suitable for long-term forecasts because of the high sensitivity of the empirical parameter K_d (or K_o) to possible variations of hydrogeochemical conditions along the flow path. On the other hand the multicomponent transport models require an enormous number of thermodynamic constants which can not be provided in real practice. It makes one look for a compromise between these two approaches which is supposed to be found by further development of conceptualization principles for the migration process under consideration.

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Appendix I
A short comment on "Kd-approach"

Traditionally equilibrium sorption is incorporated into a retardation factor (R) through an empirical coefficient of sorption distribution (so called "Kd concept"). There are two major forms of introduction of the retardation factor: the first one is for granular (porous) sediments (Bear, 1972 and others), the second one is for fractured media (Vandergraaf and Abry, 1982).

Sufficiently detailed examination has been given to radionuclide adsorption in porous sediments. The main parameters controlling such interactions are the total cation exchange capacity (E_c) and the ionic strength of groundwater (I). For example, having generalized experimental data over several sites of the NPP location we obtained a plot (Fig. A.1) which reflects a linear raise of the distribution coefficient K_d with increasing E_c . On the contrary, an increase of I leads to an abrupt drop in radionuclide adsorption. So, by our data, in sufficiently mineralized ($I > 0.5$) water of sand aquifers strontium-90 can behave as a nonreactive component. An abrupt decrease of adsorption for strontium-90 and cesium-137 with the increase of bulk dissolved solids content has been verified by batch experiments performed with montmorillonite clays (Janhke and Radke, 1987).

In the references one can also find data on radionuclide sorption in a matrix of consolidated porous blocks sampled from a fractured rock mass. A noticeable sorption (K_d up to $N \cdot 10 \text{ cm}^3 \text{ g}^{-1}$ and more) of such radionuclides as strontium-90 and cesium-137, is inherent both to the rocks of sedimentation origin and to highly metamorphosed and even intrusive rocks with matrix porosities of less than 1% (Rasmuson and Neretnieks, 1986; Intraval - Project Report, 1989).

Adsorption onto the fracture surfaces which is characterised by a parameter K_a (dimensional representation $-L$) has been studied rather poorly. Nevertheless, a number of the conducted experiments is quite sufficient to prove a noticeable influence of this process, which could be characterised by the dimensionless parameter of adsorption retardation:

$$R = 1 + 2K_a/b, \quad R = 1 + K_a S_0/n, \quad (1)$$

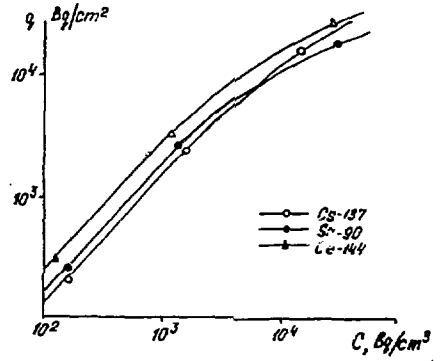
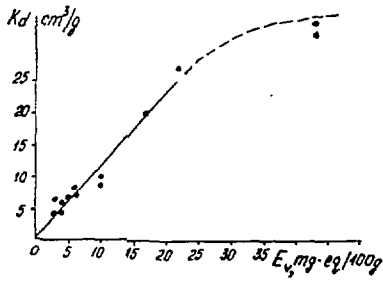


Fig. A.1. K_d parameter as a function of the E_v .

Fig. A.2. Isotherms sorption of radionuclides onto the surface of fissures

- respectively, for a model of a single fracture with aperture " b " and for the statistically averaged model of uniformly fractured rocks (when the assumption of the Representative Elemental Volume is valid) characterised by a specific surface of blocks, S_b , and a relative fracture volume, n .

For example, in the investigations (*Vandergraaf and Abry, 1982*) the following ranges of parameter K_a (cm) variations have been established for different radionuclides absorbed at the surface of granite blocks: Sr-90 - 0.09-2.1; Cs-137 - 1.5-53; Cs-134 - 2.2-24; Pu-237 - 1.4-70. We (*Rumynin et al., 1992*) have obtained the same range of values $K_a = 0.8-1.2$ cm for these isotopes absorbed on granodiorites (Fig.A.2).

The specification of radionuclide adsorption on fracture surface by autoradiographic analysis seems to rather efficient and compatible with the mineralogical study of specimens (*Kamineni et al., 1983; Vandergraaf et al., 1984; Ticknor and Vandergraaf, 1986; Ticknor et al., 1989; Ticknor et al., 1991*).

On the whole, the obtained data confirm that adsorption onto fracture walls strongly reduced the total potential for mass-transport of radionuclides under consideration (usually $R \gg 1$).

In the natural geochemical systems the retardation factor (or the distribution coefficient) is not a constant but depends on numerous hydrochemical interactions in the liquid as well as in the solid phase within the contamination plumes. That explains the errors of predictions of the pollutant's fate in aquifers using distribution coefficients determine under idealized laboratory conditions which differ from the field one. Similar errors occur when hydrogeochemical conditions are variable (as it occurs during remediation measures carried out to restore groundwater quality in polluted sites).

The mentioned alteration in the RNT potential in the multi-component systems can be caused by complexation reactions and sorption of the radionuclides on mobile colloidal particles (Section 4) in the liquid phase.

Formally speaking, the role of all of these interactions should be taken into consideration by numerical algorithms for the multicomponent transport problem, but in many cases such numerical approach would not be supported by the available thermodynamic data. Although many authors are very sceptical about the K_d -concept it is difficult to deny the

important advantages of this approach for the description of solute transport in heterogeneous groundwater reservoirs. In this situation the analytical approach or one-component simulation implicitly including homogeneous (in liquid phase) interactions into linear parameters of traditional equations might be preferable in comparison with multicomponent models.

Appendix 2

Some generalized solutions for mass-transport in fractured-porous reservoirs

Let's consider the general problem of subsurface transport of a decaying substance in fractured-porous reservoir. If the assumption of the "Representative Elemental Volume" (REV) is valid the advective-dispersion equation, the differential form can be written as follows:

$$n \frac{\partial C}{\partial t} + \lambda n C + w_s = L(C), \quad (\text{A.2})$$

where n is the active fractured porosity (relative volume of fractures); λ is the decay constant; $L(C) = n D \nabla^2(C) - v \nabla(C)$; D is the dispersion coefficient, v is the Darcy velocity.

The function w_s reflects the solute diffusion from fracture water into the porous matrix as well as decay within the latter. The analytical representation of the w_s - function depends on the mathematical and physical conceptualization of the transport process within the porous matrix and should be connected with the time and space frames of it (*Mironenko and Rumynin, 1986*). Two practically important approximations have been suggested

$$w_s = \sqrt{\lambda_m} \left[\sqrt{\lambda} (\operatorname{erfc} \sqrt{\lambda t}) - \exp(-\lambda t) / \sqrt{\pi t} \right] \cdot C \quad (\text{A.3})$$

- it is often referred to as the "unlimited capacity" approximation,

$$w_s = n_0 \frac{\partial C_b}{\partial t}, \quad \frac{\partial C_b}{\partial t} = \alpha_m (C - C_b) - \lambda C_b \quad (\text{A.4})$$

- can be referred to as the "quasi-steady state" approximation;

here C and C_b are solute concentrations in fractured and porous water, n is the matrix porosity, λ_m and α_m are the complex mass-exchange parameters ($\lambda_m = S_b D_M n_0^2$, $\alpha_m = \lambda_m / n_0^2$. S_b is the specific surface of the matrix blocks, D_M is the coefficient of molecular diffusion).

The general solution of the equation (A.2) can be represented as (Rumymin, 1983):

$$C = \int_0^t \frac{\partial C'(t-\theta)}{\partial \theta} H_0(t, \theta) d\theta, \quad (\text{A.5})$$

where $C'(t-\theta)$ is a solution describing stable component transport in equivalent homogeneous media,

$$H_0(t, \theta) = L^{-1} \left\{ \frac{1}{p} \exp \left(-\frac{G_p \theta}{n} + \lambda \theta \right) \right\}_{p \rightarrow t-\theta} \quad (\text{A.6})$$

L^{-1} symbolizes the inverse Laplace transformation; G_p is some function of the complex argument p :

$$G_p = \sqrt{\lambda_m (p + \lambda)} \quad (\text{A.7})$$

- for the *unlimited capacity* approximation, and

$$G_p = \frac{\lambda_m n_0}{p + \lambda_m + \lambda} \cdot p$$

- for the *quasi-steady state* approximation.

Thus for the basic approximations we found:

$$1) \quad H_0(t, \theta) = \frac{1}{2} \exp(-\lambda \theta) \left[\exp(-\eta) \operatorname{erfc} \left(\frac{\eta}{2\sqrt{\tau}} \right) + \right. \\ \left. + \frac{1}{2} \exp(-\lambda \theta) \left[\exp(\eta) \operatorname{erfc} \left(\frac{\eta}{2\sqrt{\tau}} + \sqrt{\tau} \right) \right] \right] \quad (\text{A.9})$$

$$(\tau = \lambda(t - \theta), \quad \eta = \theta \sqrt{\lambda \lambda_m / n});$$

$$2) \quad H_0(t, \theta) = \exp(-\eta) \left[\exp(-\tau) J_0(2\sqrt{\eta\tau}) + \int_0^1 e^{-\tau z} J_0(2\sqrt{\eta z}) dz \right] \quad (\text{A.10})$$

$$(\tau = \gamma(t - \theta), \quad \eta = \beta \theta, \quad \gamma = \alpha_m + \lambda, \quad \beta = \alpha_m n_0 / n, \quad J_0(\cdot) - \text{ordinary Bessel function}).$$

It is easy to notice that substitution of into $t_f(t_f)$ is the residence - time for particles traveling along arbitrary stream-lines) in formulae (A.9) and (A.10) leads to the well-known solutions (for the dimensionless function C) obtained under the assumption of solutes transport in fractures with a sharp interfaces (*Tang et al., 1981*).

Further formula (A.10) can be transformed such that

$$C = H_0(t, t_f) = \exp(-\lambda t_f) J(\tau, \eta), \quad (\text{A.11})$$

where $J(\tau, \eta) = 1 - \exp(-\tau) \int_0^\tau e^{-z} I_0(2\sqrt{\tau z}) dz$ is a well-known function describing transport of stable components in fractured-porous media [$\tau = \alpha_m(t - t_f)$, $\eta = \alpha_m t_f n_0 / n$] (*Mironenko and Rumynin, 1986*). Therefore:

$$C_{\lambda > 0} = \exp(-\lambda t_f) C_{\lambda=0} \quad [\tau \rightarrow \tau' = (\alpha_m + \lambda)(t - t_f)] \quad (\text{A.12})$$

The other expression for solution (A.5) can be obtained in the form:

$$C = C'(\theta) H_0(t, \theta)'_0 - \int_0^t C'(\theta) \frac{\partial H_0(t, \theta)}{\partial \theta} d\theta. \quad (\text{A.13})$$

For example for a *quasi-steady state* approximation we get

$$\frac{\partial H_0(t, \theta)}{\partial \theta} = -\exp(-(\eta + \tau)) [\beta I_0(2\sqrt{\eta\tau}) + \gamma\sqrt{\eta/\tau} I_1(2\sqrt{\eta\tau})] \quad (\text{A.14})$$

$$C'(\theta) H_0(t, \theta)'_0 = C'(t) \exp(-\beta)$$

In the particular case for solute transport in homogeneous groundwater reservoir we have:

$$C = C'(t) \exp(-\lambda t) + \lambda \int_0^t C'(\theta) \exp(-\lambda \theta) d\theta. \quad (\text{A.15})$$

If the component decays simultaneously in the contaminant source (A.13) is transformed into

$$C = C'(t) \exp(-\lambda t). \quad (\text{A.16})$$

Appendix 3

A brief overview of the performed hydrogeological assessment for hypothetical accidents at industrial and experimental nuclear reactors in Russia

Several new nuclear power plants are planned to be built in Russia. Among them the Kola (in the third stage), the Far-East and the St.-Petersburg (a new extension project) plants are under construction. Simultaneously geological exploration takes place within these areas. This Section presents some preliminary results associated with problems of hydro-geo-environmental substantiation of the designed stations.

1. Kola nuclear power station. The construction site of the station is located within the lake lowland, being framed by a chain of low hills (foothills of the Khibini Mountains) and by the Imandra lake (*Rumynin et al., 1993*). Fractured granite-gneiss rocks of homogeneous type (porosity of matrix is less than 1%) serve as the major reservoir for groundwater. This produces preconditions for rapid propagation of pollutants within the aquifer. The high vulnerability of the lake water is explained by the small distance (no more than 1 km) from the reactor compartment - a potential source of contamination - to a shore line - the boundary of underground flow discharge.

The presence of active flow through fractures was confirmed by a specific series of hydrogeological investigations within the key sites (Table A.1) including: a) tracer (NaCl) injection during multi-well pumping tests; b) isotope ($J-131$) injection into the natural gradient water flow; c) well dilution technique. The results of the different methods are in good agreement; in particular, they showed that the flow velocity (U) ranges from 0.8 to 3.6 m/day and the relative fracture volume $n = 0.001-0.004$

The data obtained were used for the verification of a numerical two-dimensional model of mass-transport (on the basis of the **MOC** code by *Konikov and Bredehoeft, 1985*). This code was supplemented by analytical subroutine to take into account radioactive decay (see Section 3 and Appendix 2).

The first stage of this model construction - its flow substantiation - was associated with an identification of the permeability field; for this purpose an inverse flow problem was solved. The reliability of these results seems to be rather high taking into account the

Table A.1. Characteristics of convective transport

Site	Groundwater velocity (U), m*day ⁻¹ *	Darcy velocity (V), m*day ⁻¹ **	Active porosity (relative volume of fractures) (n) ***
N1-Special housing	0.8 - 1.2	0.001-0.002	2.4E(-3)
N2-Reactor compartment	2.0 - 3.6	0.001-0.02	1.5E(-3)

Note:

- * - Isotope (¹³¹J) injection under natural gradient flow condition;
- ** - Well-dilution technique;
- *** - Injection of salt tracer (NaCl) into piezometers during multi-well tests.

increased density of flow monitoring network. This conclusion is confirmed by a good agreement of the velocity distribution obtained on the model and by direct field measurements.

Therefore, the relative fracture volume may be directly used for predicting ground water contamination by the chemically non-reactive radionuclide J-131. The corresponding results for the first pathway of radioactivity release have shown that in spite of the high rates of mass-transport, the rapid decay of the radionuclide facilitates the decrease of concentrations essentially below the Safety Standard Concentration (Fig.A.3).

The transport velocity of the other radionuclides (e.g.Cs-137, Sr-90, Ce-144) depends on their sorption onto the fracture walls. The laboratory tests indicated the average value of the constant $K_s = 1 \text{ cm}$ to be typical for these three isotopes (Fig.A.2). Hence the average value of $R=100$ which was determined using the specific surface of blocks (S_b) ranging from 0.1 to 0.2 cm^{-1} .

Despite the great sorption retardation for long-living radionuclides a complete autoepuration of groundwater from radioactive contamination will not occur because of the very high concentration at the contaminant source in case of the first pathway of radionuclides release: residual concentrations within the area of flow discharge into the lake exceed permissible values by several orders of magnitude (Fig.A.4). However, the long duration of contaminant migration allows to rely on a timely realization of the necessary measures for protective drainage.

One can note an uncertainty in the performed evaluation of the retardation factor because of the potential errors in the determination of S_b . This requires performing further investigations based a the probabilistic analysis.

2. The Far-East nuclear power station. Major reservoirs of groundwater within this region are represented by fractured-porous strata (sandstones and siltstones). The site is located within the catchment at a distance of about 3 km from the river, where the flow discharge takes place (Fig.A.5). Such a combination of conditions - heterogeneity of the medium and long paths of migration - produce the favourable conditions for efficient self-cleaning of groundwater under influence of sorption and radioactive decay.

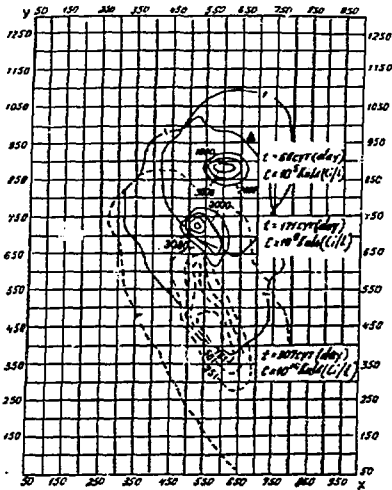


Fig. A.3. Contaminant plume (I-131) formed in the aquifer after a hypothetical accident at the Kola NNP
(low boundary of the model corresponds to the lake-shore line)

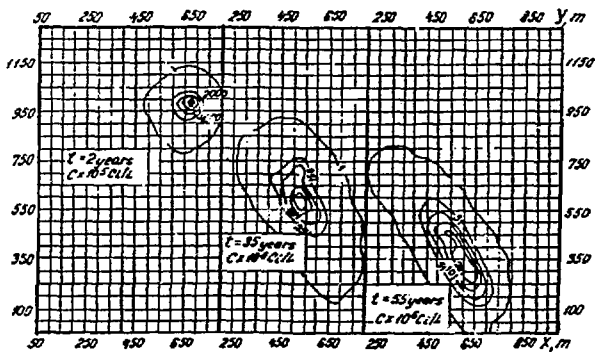


Fig. A.4. Contaminant plume (Sr-90) formed in the aquifer after a hypothetical accident at the Kola NNP

The possibility for an active role of these processes in a porous matrix was proved by laboratory experiments establishing rather high values of a molecular diffusion coefficient ($n_0 D_M = 2.2 \cdot 10^{-7} - 2.1 \cdot 10^{-6} \text{ m}^2 \text{ d}^{-1}$ while porosity n_0 is up to 8%). The intrablock sorption could be described by the minimum values of the adsorption distribution coefficient as follows: $K_d = 0.8 \text{ cm}^3 \text{ g}^{-1}$ for Sr-90 and $K_d = 1.3 \text{ cm}^3 \text{ g}^{-1}$ for Cs-137. The conclusions on the extent of groundwater protection from radionuclides contamination was based on the regional transport model. A particular case is shown in Fig. A.5.

For solving the inverse flow problem data from the groundwater monitoring were used. Suitable distribution on the model of "megaheterogeneity" zones within the area under study satisfactorily agree on the whole with the results of multi-well and slug pumping tests. At the same time it is evident that such a regional approach provides a rather high degree of averaging for aquifer flow properties over the area and in the cross section, which is not always permissible when considering mass-transport problems (*Mironenko and Rumynin, 1986*). Indeed, within the probable plume of contamination there could be local zones (due to tectonic jointing) with sharply increased permeability. However, they do not necessarily manifest themselves on the regional potentiometric surface map, information which has been obtained by a rather sparse network of piezometers. Meanwhile precisely these zones could be the principal carries of contaminants.

This kind of uncertainty was partially eliminated by detailed electric sounding. In combination with the study of drilled core material, it allowed detection within the construction site of the plant of at least two zones with different fracturing intensity. In principle, the relation between the permeability of these zones may vary over a wide range of values, however, it is limited by the value of the average permeability, obtained from the solution of the inverse problem on a regional scale. Thus such additional information has provided a background for further multivariant sensitivity analyses.

3. The St.-Petersburg Nuclear Power Plant (a new stage of construction). A geological cross section is represented by stratified granular (porous) deposits. According to the project nuclear reactors will be located at distance of about 1 km from the Finland Gulf where a regional groundwater flow discharges. Modelling techniques were similar to the previous example. Interpretation of field data obtained in a neighbouring wastes disposal

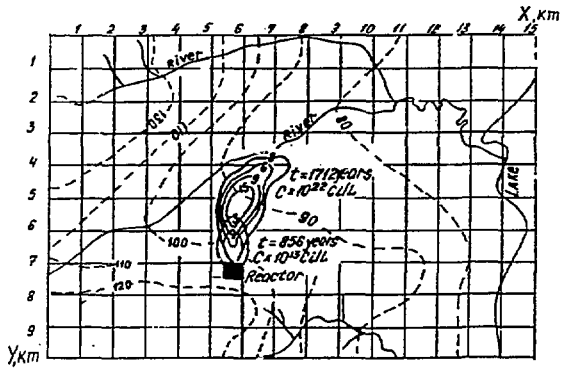


Fig. A.5. Contaminant plume (Cs-137) formed in the aquifer after a hypothetical accident at the Far East NPP

site under operation (about 0.5 km apart) enabled to increase the reliability of the forecasting. On that site one of the largest surface repositories of radioactive wastes in the North-West part of Russia is situated. A plume formed in the phreatic aquifer moves down the natural flow gradient. It is characterized by a rather complex nuclide composition. Detected concentration distribution of individual species within the plume show different retardation parameters. Having numerically solved the inverse migration problem we managed to determine some hydrogeological parameters which were used for the assessment of the consequences of hypothetical accidents at the designed nuclear plant.

Appendix 4

Surface complexation

The surface complexation models are described in detail in a number of earlier publications. The models postulate that the water molecules and chemical dissolved species form bonds with the exposed lattice-bound ions at mineral surfaces (*Van Cappelen et al., 1993*). The primary hydration surface sites are treated as hydroxylated surfaces ation centers: >SOH , where > symbolizes the mineral lattice and S is the mineralization.

The surface hydroxyl group of the >SOH site can be deprotonated (>SO^-) or protonated (>SOH_2^+). The relevant reactions are controlled by the pH of the solution. Dissolved cations and anions may specifically adsorb at the interface by exchange with H^+ or OH^- at >SOH surface sites.

Two surface-complexation models are included in SURFEQL's modular: constant-capacitance (CCM) and triple-layer (TLM) models.

In CCM adsorption all components is characterized by a surface potential Ψ_0 , hence:

$$[i]_s = [i] \exp\left(-\frac{zF\Psi_0}{kT}\right), \quad (\text{A.17})$$

the subscript "s" refers to surface concentration, Z is the charge of the surface complex, F is Faraday's constant (96486 C/mol). The potential can be defined from the relation

$$\Psi_0 = \frac{\delta}{c},$$

where c is the capacitance (in $\mathfrak{I}m^{-2}$) of the electric double layer, and is the surface charge (in Cm^{-2}). The parameter δ could be calculated by means of a special iteration procedure via total surface component concentration and the specific surface area $S_s (m^2 \cdot dm^{-3})$. Thus, three interactive parameters must be entered: the capacitance (c , in $\mathfrak{I}m^{-2}$), the solid surface area (S_s , in $m^2 g^{-1}$), and the solid concentration, or solid-to-water mass ratio (C_s , $g L^{-1}$). Hence $S_s = S_s C_s / n$ (n is the porosity).

For the TLM, the inner layer contains the adsorbed H^+ and OH^- , and is characterized by the potential Ψ_1 . The outer layer contains all other adsorbed ions and is characterized by the potential:

$$[i]_s = [i] \exp\left(-\frac{zF\Psi_1}{kT}\right), \quad (A.18)$$

For mathematical convenience, the second term in both models equations (A.17) and (A.18) is formally treated as a electrostatic component with a concentration $\exp\left(-\frac{zF\Psi_1}{kT}\right)$.