



# STUDIES OF THERMAL AND RADIATION EFFECTS ON WATER-ROCK SYSTEMS RELATED TO ENVISAGED ISOLATION OF HIGH LEVEL RADIOACTIVE WASTES IN CRYSTALLINE FORMATIONS OF THE UKRAINIAN SHIELD (UKRAINE)

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## Abstract

In this work there are presented the general data on the study of thermal and radiation effects in minerals separated from rocks of the Ukrainian shield. These minerals (quartz, feldspar, amphiboles, apatite, biotite, kaolinite, etc.), exposed by doses  $10^4$ ,  $10^6$ ,  $10^8$  Gy by  $\text{Co}^{60}$  source, were studied by the complex of physical methods. The special attention was given to the study of radiation defects formation (electron-hole paramagnetic centres, OH- groups destruction, changes in a charge state of ions) in a mineral structure. The mentioned radiation defects were used in the extrapolation method.

The connection between structural peculiarities of minerals, containing uranium and thorium, and processes of their metamictization is considered. It is demonstrated that the minerals, which have large channels or interlayer spaces in their structure, as a rule, is not metamict. Using the spectroscopic methods of the extrapolation it is shown, that the crystalline massifs, which have not detectable amounts of hydroxylcontaining minerals (biotite, amphibole, etc.) and ions  $\text{Fe}^{2+}$ , are perspective for long-lived radioactive wastes (RAW) dumping. As it follows from obtained results, the rocks, containing minerals with OH- groups and gas-liquid inclusions, should be considered as the "mineral-water" system.

## INTRODUCTION

The problem of the long-lived radioactive wastes dumping in geological formations lays down a number of requests to rocks, where storage is planned to be built. One from these requests is the thermoradiative stability of minerals and rocks made up the bulk of the storage as the engineering construction. First of all it concerns the stability of physical and chemical properties of minerals and rocks during a time of their contact with radioactive wastes.

It should be noted that in the literature there is a great quantity of data on the study of influence of various sources of irradiation to physical and chemical properties of minerals and rocks. The nature of the formation of various types of radiation defects in minerals has been investigated in detail. The methods used in dating and dosimetry [1] have been developed around obtained results. As to the methods of the prognosis (the extrapolation) by which one can predict the behaviour of physical and chemical properties of minerals and rocks during long times of their contact to RAW, they are practically not present.

In the work the study of thermal and radiation effects in minerals separated from rocks of the Ukrainian shield has been performed. The minerals (quartz, feldspar, amphiboles, apatite, biotite, kaolinite, etc.), exposed by doses  $10^4$ ,  $10^6$ ,  $10^8$  Gy by  $\text{Co}^{60}$  source, were studied by the complex of physical methods. The special attention was given to the study of the radiation defects formation (electron-hole centres, structural OH-groups destruction, and changes in a charge state of ions) in mineral structure.

The connection between structural features of minerals, containing uranium and thorium, and processes of their metamictization is considered.

The main aid of this work was the use of results of the investigation of radiation defects in minerals for the extrapolation methodology. Such methodology can be used for the solution of the following problems:

- (1) The choice of crystalline massifs which are suitable for RAW dumping.
- (2) The predict of the thermoradiative stability of materials which can find use in sealing of spent nuclear fuel and also that for backfill.

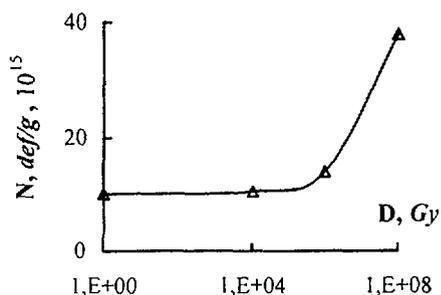
## EXPERIMENTAL

The investigated samples are represented by minerals separated from rocks of the Ukrainian shield (quartz, feldspar, amphiboles, apatite, biotite, kaolinite etc.). The minerals were subjected to the chemical and X-ray structure analyses.

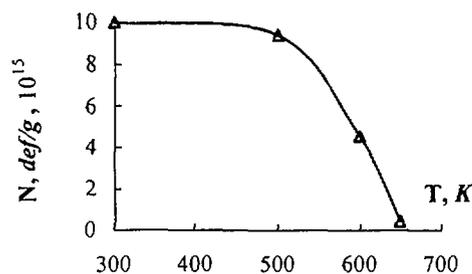
The specimens were exposed by  $\gamma$ -irradiation doses  $10^4$ ,  $10^6$ ,  $10^8$  Gy from  $\text{Co}^{60}$  source with 13.8 Gy/sec intensity. After that they were investigated by the methods of electronic paramagnetic resonance (ESR), nuclear magnetic resonance (NMR), IR-spectroscopy, nuclear gamma-resonance. The main attention was given only to those radiation defects, which concentration could exceed critical under treatment. Such concentrations, above which the fundamental changes of physic-chemical properties of a mineral could be observed, were selected as critical.

From this viewpoint the following radiation defects in minerals are of principal importance: electron-hole centres, structural OH-groups destruction, changes in a charge state of ions.

**Quartz –  $\text{SiO}_2$ .** Under g-irradiation in the quartz structure there appears a number of radiation defects varying both concentrations and thermostabilities [3]. E-centres ( $\text{O}_2^{3-}$ ) are of particular interest. The availability of a vacancy in the quartz structure results in the capture of a hole by two ions of oxygen with formation of  $\text{O}_2^{3-}$ -centre. The concentration of these centres in a specimen upon g-irradiation was determined from the intensity of the characteristic band ( $g = 2000$ ) in ESR spectrum of this sample. Figure 1 shows the E-centres concentration as a function of exposing dose. The dependence of the E-centres band's intensity in ESR spectrum on an annealing temperature of a sample is presented in Fig. 2. The specimen was heated during 20 min at each temperature.

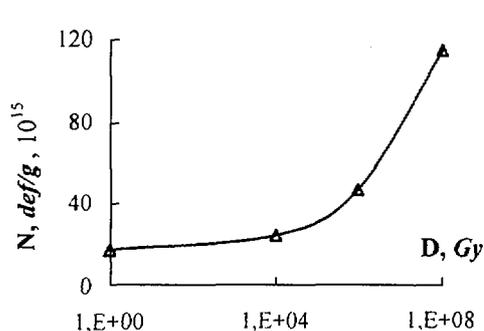


**Fig.1.** The influence of g-irradiation upon the E-defects formation in quartz.

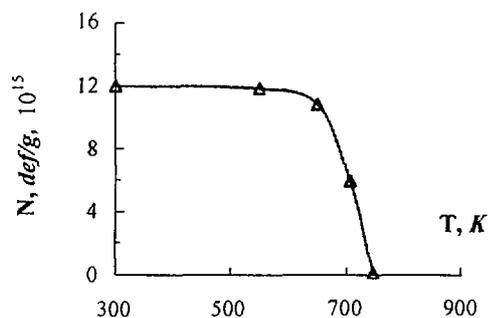


**Fig.2.** The dependence of E-defect quantity in quartz on the annealing temperature.

**Feldspar –  $\text{KAlSi}_3\text{O}_8$ .** In feldspar there was studied the  $E_1$ -centre that was the radical  $\text{SiO}_3^{3-}$ , in which the electron is captured by an oxygen's vacancy [4]. Figure 3 illustrated the concentration of  $E_1$ -centres versus an exposing dose by ESR data. The dependence of an amount of  $E_1$ -centres on an annealing temperature of a sample is displayed in Fig. 4. The specimen was heated during 20 min at each temperature.

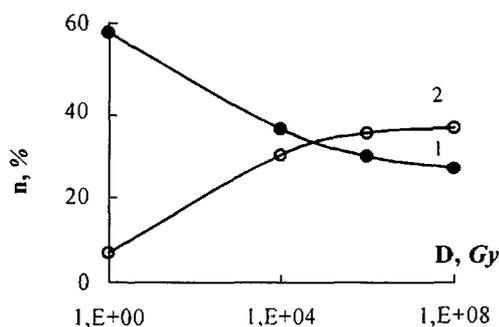


**Fig.3.** The influence of  $\gamma$ -irradiation on the  $E_1$ -defect formation in feldspar.



**Fig.4.** The dependence of  $E_1$ -defect quantity in feldspar on annealing temperature.

**Amphibole –  $\text{Ca}_2(\text{Mg, Fe})_5[\text{Si}_8\text{O}_{22}](\text{OH})_2$ .** The influence of g-irradiation to the oxidation processes of ions Fe ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) in hornblende was investigated. In such structure the iron ions are located in M1, M2, M3 positions. Located in these positions Fe ions respond variously to g-irradiation [5]. In the present work the Fe ions state in the M1 position was controlled. Under g-irradiation the  $\text{Fe}^{2+}$  amount reduction with the  $\text{Fe}^{3+}$  one increase is observed (Fig. 5). The ion concentration was determined by the method of nuclear gamma-resonance.



**Fig.5.** The relative amount of Fe ions ( $n$ ) in amphibole vs. dose  $D$  (1 -  $\text{Fe}^{2+}$ , 2 -  $\text{Fe}^{3+}$ ).

**Biotite –  $\text{K}_2(\text{Mg, Fe})_6[\text{Al}_2\text{Si}_6\text{O}_{20}](\text{OH})_4$ .** Under g-irradiation in the biotite structure the  $\text{Fe}^{2+}$  ion oxidation with OH-groups destruction is noted [5]. Since  $10^6\text{Gy}$  dose the detectable iron oxidation is found. By nuclear gamma-resonance data the velocity of iron oxidation in 1 g biotite is equal to  $3 \cdot 10^{13}$  ion/sec.

**Kaolinite –  $Al_4[Si_4O_{10}](OH)_8$ .** In kaolinite under  $g$ -irradiation influence the structural OH-groups destruction proceeds [2]. The velocity of OH-groups disruption was determined by the dependence of an amount of destroyed OH-groups on the value of an exposing dose. The control over the destroyed OH-groups amount was carried out both the weight losses upon igniting and the methods of NMR and IR-spectroscopy.

**Apatite –  $Ca_{10}(PO_4)_6(F, OH)_2$ .** Under  $g$ -irradiation there arises a number of radiation defects ( $PO_3^{2-}$ ,  $F^-O^-F^-$ ,  $O^-OH^-$ , etc.) in apatite. In present work the most intensive paramagnetic centre  $F^-O^-F^-$  in ESR spectrum of apatite was chosen to the extrapolation.

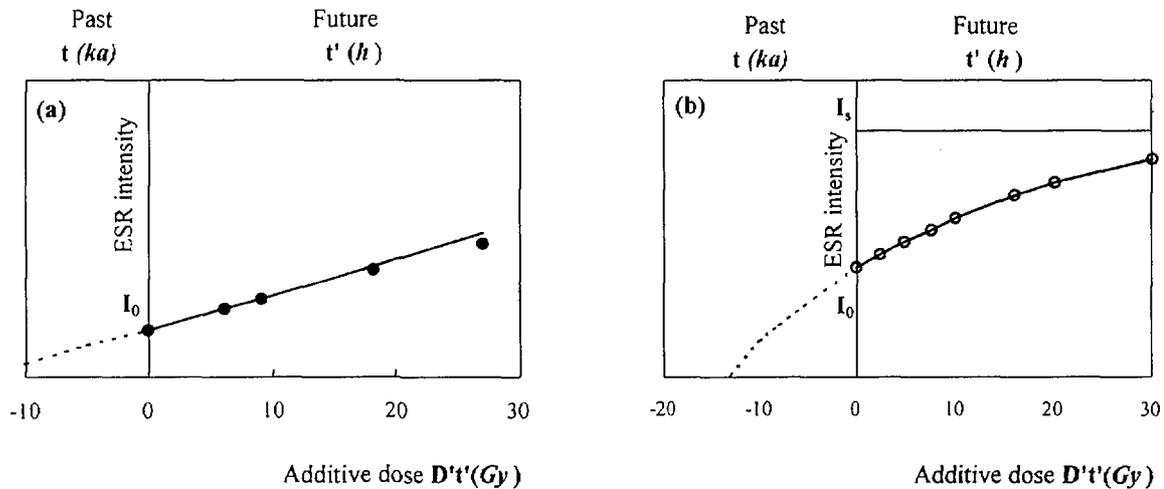
### THE EXTRAPOLATION METHOD

In the present work there is used the extrapolation method based on the analysis of radiation defects, which appear in mineral structures under  $g$ -irradiation. The following radiation defects were analysed:

- (1) Electron-hole paramagnetic centres;
- (2) Structural OH-groups destruction;
- (3) Changes in a charge state of ions in mineral structures (for example, transition  $Fe^{2+}$ ,  $Fe^{3+}$ ).

It is need to mention briefly the description of the extrapolation method for each from these cases.

**1. The use of results of the study of electron-hole centres in the extrapolation.** It is known that, depending on the radiation source type and the dose magnitudes, in substance there arise radiation defects of a various kind, which models and nature are described in the literature in detail enough. The defects in a paramagnetic state are convenient to investigate by the method



**Fig.6.** An additive dose method. The enhancement of ESR signal intensities by an additive artificial irradiation with the dose  $Q$  [ $Gy$ ] ( $Q=D't'$ ). The ED is obtained by the extrapolation to the zero ordinate. The additive irradiation is a kind of "time machine" to proceed an event to the future. (a) A linear growth of the signal intensity and least-square fitting to a line. (b) Saturation growth fitting to a saturation curve of Eq.(2).

of electronic paramagnetic resonance (ESR). This method is rather sensitive: so, for example, in a number of cases, by ESR the defects concentrations from the magnitudes  $\geq 10^{10} \text{ g}^{-1}$  can be determined (usually in minerals their amount can achieve  $10^{20}$  and more defects in 1 g of substance).

The methodology, which is used, for example, in archaeology for the determination of a subject age or in retrodosimetry [1], has been laid the foundation for the extrapolation. Its essence lays in the construction of the dependencies of radiation defects formation in a substance on g-irradiation dose. As an example such curves borrowed from [1] are indicated in Fig. 6. The dependence (Fig. 6, a) is described by the equation

$$I = I_0 (1 + D't' / ED) \quad (1)$$

and the another (Fig. 6, b) – by the equation

$$I = I_s [1 - \exp(-Dt + ED) / SD] \quad (2)$$

where

- $I$  – the relative intensity of the characteristic band in ESR spectrum of a sample;
- $I_0$  – the relative intensity of the same band in ESR spectrum of an initial sample;
- $D$  – the intensity of g-ray source;
- $t'$  – the time, during which the source influences on a sample;
- $D't'$  – the dose absorbed by a sample;
- $ED$  – the dose absorbed by a sample before an artificial exposure;
- $SD$  – the absorbed dose, upon which the saturation of defect formation proceeds.

It is easy to see that the presented equations described the experimental curves have the parameters, using which not only the age and the dose collected by a sample in nature but also the time, during which to a sample will not change essentially its physico-chemical properties at the certain dose, can be determined.

**2. The use of data of the structural OH-groups destruction in a mineral under  $\gamma$ -irradiation.** It is known that minerals containing OH-group under temperature can lose them owing to the dehydroxylation effect [2]. The OH-groups destruction follows by the formation of water or hydrogen molecules, which will diffuse outside the sample. The same effect is observed under g-irradiation effect. These data were used in the extrapolation methodology. Its essence lays in the determination of the OH-groups destruction velocity in 1 g of mineral subjected to a given exposing dose. For this purpose the experimental dependence of the destroyed OH-groups amount on an exposing dose must be obtained. The OH-groups amount was determined by the methods of weight losses, proton magnetic resonance (PMR) and IR-spectroscopy.

**3. The use of data of the changes in a charge state of ions made up the bulk of a mineral structure, for example,  $\text{Fe}^{2+}$ .** On exposure to temperature or  $\gamma$ -irradiation the fundamental changes of the iron ions valency result from its oxidation in a mineral. By the experimental dependence the iron oxidation velocity in 1 g of mineral under the g-irradiation source can be determined. With a knowledge of this velocity, one can determined the time, during which upon g-irradiation in a considered mineral there will not happen the fundamental changes influencing to its physico-chemical properties. The control over the charge state of iron ions was carried out the nuclear gamma-resonance method.

## RESULTS AND DISCUSSION

In Table 1 there are listed the results of the extrapolation short-term experimental observations to time (**T**), after which the mineral physico-chemical properties can vary over 10% on exposure to  $\gamma$ -irradiation. In order to **T** calculation it was supposed, that the parameters of  $\gamma$ -irradiation source with 1000 R/hour intensity would not change. The velocity (**V**) of the defect formation in a mineral structure was determined from experimental data.

It is evident from Table 1 that iron and hydroxyl-containing minerals are less stable upon  $\gamma$ -irradiation. The smaller sets of electron-hole centres have been found to form in layered minerals. Uranium and thorium containing minerals were analysed in order to elucidate of the structural peculiarities influence the radiation defects formation. The availability of  $\gamma$ -emitters in a structure of these minerals stimulates the metamictization processes. However not all uranium and thorium containing minerals are subject to such processes. The performed analysis has demonstrated that, as a rule, the minerals, which structure has large channels and interlayer space, are not metamictical. Most likely, the various type molecules located in indicated hollows are responsible for this. These molecules accelerate the radiation defects recombination. This fact is verified of the montmorillonite structure, in which, by ESR data, the  $\gamma$ -irradiation does not generate the detectable concentrations of paramagnetic centres [7].

However, it should be noted that the used extrapolation methodology is not yet perfect. First of all, the variations of radiation defects concentration must be checking immediately on exposure to  $\gamma$ -irradiation and heat. It should also be taken into account all radiation defects, including that which are detected by the luminescence methods. Besides the processes of the exchange in the OH-chain were not taken into consideration when a parameter **T** was determined. Earlier [8] it was demonstrated that in a system „clay mineral - heavy water“ there was the exchange between heavy isotopes of hydrogen and protons of structural OH-groups in normal conditions and under  $\gamma$ -irradiation.

Table 1. Extrapolation data

Mineral	Quartz	Fieldspar	Apatite	Amphibole	Biotite	Kaolinite
Defect type	$O_2^{3-}$	$SiO_3^{3-}$	$F^- - O^- - F^-$	$Fe^{2+} - Fe^{3+}$	$Fe^{2+} - Fe^{3+}$	$OH^-$
$N^{max}$ , def/g	$1 \cdot 10^{22}$	$1.2 \cdot 10^{22}$	$0.6 \cdot 10^{21}$	$0.3 \cdot 10^{21}$	$1.9 \cdot 10^{21}$	$9 \cdot 10^{21}$
<b>V</b> , def/g.sec	$0.3 \cdot 10^{10}$	$1.4 \cdot 10^{10}$	$0.2 \cdot 10^{10}$	$0.2 \cdot 10^{14}$	$0.3 \cdot 10^{14}$	$0.6 \cdot 10^{13}$
<b>T</b> , years	$5 \cdot 10^7$	$1.35 \cdot 10^7$	$7 \cdot 10^7$	$1.5 \cdot 10^3$	$1 \cdot 10^3$	$5 \cdot 10^3$

## CONCLUSIONS

- (1) It has been shown that the complex of spectroscopic methods can be successfully used in study of the processes of the radiation defects formation in minerals (rocks) for the development of the methodology of the extrapolation short-term observations to a period of long-lived RAW dumping.
- (2) That rocks which minerals do not contain appreciable quantities of ions  $Fe^{2+}$  and OH-groups have been demonstrated to be perspective for long-lived RAW dumping.

It was found that extrapolation to long periods is a complex problem, and contributions from geological, chemical, physical and biological sciences are required.

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