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RADIATION-THERMOCATALYTIC PROCESS OF HYDROGEN FROM RaO-SiO₂+H₂O MIXTURE

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Abstract: Radium silicates with different radium contents were synthesized. For comparison, the radiation catalytic activity of radium silicate with 6100 Bk/g radium and starting silicate during the radiolytic decomposition of water was studied. The heterogeneous radiolysis of water was investigated in the adsorbed and liquid states in contact with radium silicate and silicate samples. The effect of the radium cations, the state of water, and reaction temperature on the yield of molecular hydrogen was revealed. The mechanisms of heterogeneous radiolysis of water involving the radium silicate and silicate samples under study were suggested.

Keywords: radium silicate, heterogeneous radiolysis, the yield of molecular hydrogen, γ -radiation, activity

1. Introduction

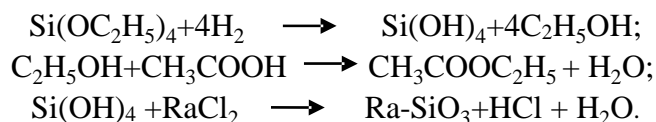
Due to their radiation and thermal stability and unique physicochemical properties, radium silicates are of great interest in various fields of nuclear and radiation technology. Interesting results on the effect of different types of radiation on the physicochemical properties of radium silicates were obtained [1–3]. Radium silicates are also of great interest as nuclear materials for high-temperature nuclear and radiation technologies. Therefore, recently there has been growth of interest in radium silicates, and large-scale research of their properties under the action of ionizing radiation is being pursued [4–6].

The purpose of this article is to identify the impact of the activity of radium in the water radiolysis and obtaining molecular hydrogen at the radiolytic decomposition of water in the system radiumsilicate + H₂O at different temperatures ($T=300\dots 673$ K).

Here, we studied heterogeneous radiation decomposition of water in the presence of radium silicate with 6100 Bk/g radium, a relatively pure silica gel.

2. Experimental

Radium silicates with different radium contents were synthesized by hydrolysis of tetraethyl orthosilicate in acetic acid at $T = 333$ K [7]:



The samples were treated at first at $T = 373$ K in air for $\tau = 24$ h and then at $T = 473$ K under vacuum $P \approx 10^{-3}$ Torr for $\tau = 36$ h, after which thermovacuum treatment was performed at $T = 873$ K for $\tau = 12$ h. The radium content in the synthesized samples was determined by γ - and α -spectrometry [7].

The radium content in the synthesized samples was varied from 260 to 6100 Bq/g. The radiation catalytic action of radium silicate was studied on the samples with relatively high radium contents; their activity was $A = 6100$ Bq/g. The heterogeneous radiolysis of water was performed under the static conditions in special ampules. The amount of radium silicate in the ampules was approximately $m=4 \cdot 10^{-2}$ g. Twice distilled water was used. Water was introduced in ampules by two techniques. The first method was adsorption from the vapor state (H_2O_s) on the surface of radium silicate at $T=77$ K. The amount of water introduced in ampules corresponded to the density of water vapors in the ampules $\rho = 5$ mg/cm³. In the temperature ranges under study, the amount of water in the vapor state is in equilibrium with that in the adsorbed state. In the second procedure, water from the calibration volume was introduced in ampules until the radium silicate sample was completely covered with liquid water with a mass of $m_{liq} = 0.2$ g. The ampules with the samples were then cooled to 77 K and sealed.

The radiation and thermal radiation processes were performed on a ⁶⁰Co isotope source. The absorbed gamma radiation intensity was determined with chemical (ferrosulfate, cyclohexane, and methane) dosimeters [8, 9]. The products of heterogeneous radiation processes were analyzed on a “Svet-102” gas chromatograph and “Gazokhrom-3101” gas analyzer.

3. Results and Discussion

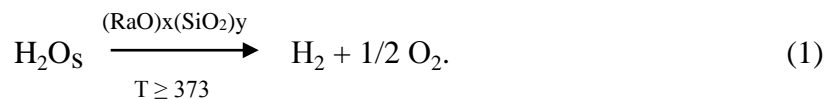
The kinetics of accumulation of molecular hydrogen during the heterogeneous radiolysis of water in the $RaO \cdot SiO_2 + H_2O_s$ and $RaO \cdot SiO_2 + H_2O_{liq}$ systems was studied. Fig.1. shows the kinetic curves of hydrogen accumulation during the heterogeneous radiolysis of water in the presence of radium silicate in two states. The rates and the radiochemical yield of hydrogen in the systems were determined from the initial linear segments of the kinetic curves. According to Fig.1, the kinetic curves of molecular hydrogen accumulation have the same shape for both systems. Two segments can be isolated on them:

I – on which the hydrogen accumulation rate on the initial linear segments is relatively high, II – with a relatively slow molecular hydrogen accumulation stage.

The molecular hydrogen accumulation rates and the radiochemical yields were determined from the initial linear segments of the kinetic curves.

According to Table 1, in heterogeneous radiolysis of water in the state of complete coverage of the radium silicate layer (radium silicate+ H_2O_l), the observed radiochemical yields of hydrogen are ~ 3,6 times higher than in the heterogeneous radiolysis of water in the adsorbed state on the surface of radium silicate. This indicates that in the case of radium silicate, an effective energy transfer from the solid phase to the water molecules occurs in water. The presence of the second slow stage of radiolysis on the kinetic curves indicates that there exists a diffuse hindered stage of heterogeneous radiolysis of water in the presence of radium silicate at 300 K. The temperature effect on the rates of formation of molecular hydrogen during heterogeneous radiolysis of water was studied on the $(RaO)_x(SiO_2)_y + H_2O_s$ systems because in experiments on the radium silicate+ H_2O_l system in closed ampules the temperature cannot be increased.

It was found that at $T \geq 473$ K radium silicates possess the thermocatalytic activity in water decomposition [10]:



Data on the radiation-thermal and thermal hydrogen accumulation in radiation-heterogeneous decomposition of water can be obtained experimentally. For justifiable separation into components, the radiation-thermal and thermal decomposition of water was performed under identical conditions in the presence of radium silicate.

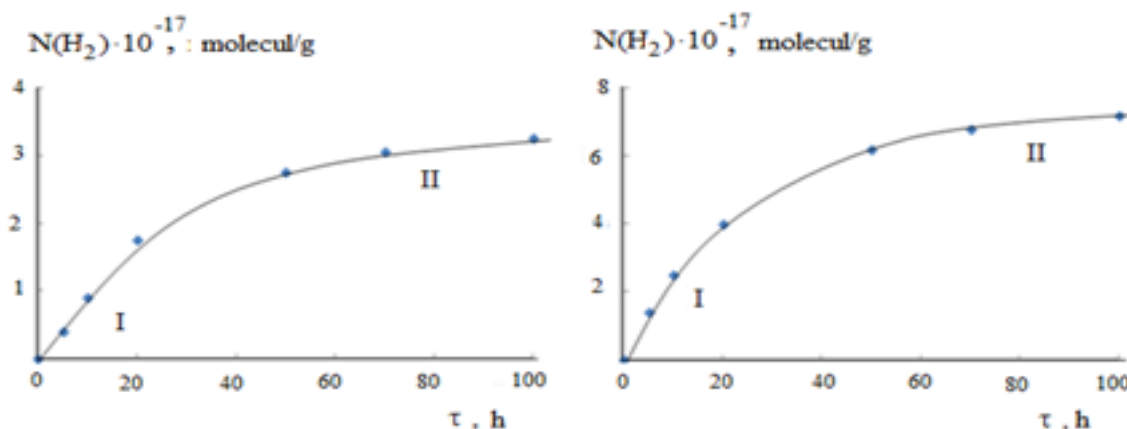


Fig. 1. Kinetics of molecular hydrogen formation in heterogeneous radiation decomposition of water in the radium silicate+H₂O_{ads}. ($\rho_{H_2O} = 5 \text{ mg/cm}^3$) (a) and radium silicate+H₂O_{liq} systems (b) ($m_{H_2O} = 0.02 \text{ g}$) at $T = 300 \text{ K}$ and $D = 0.28 \text{ Gy/s}$

Table 1. Rates and radiochemical yields of molecular hydrogen in heterogeneous radiolysis of water in two states at $T = 300 \text{ K}$

No	Irradiated systems	$W(H_2), \text{ mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$	$G(H_2), \text{ mol./100eV}$
1	Radium silicate+ H ₂ O _{ads}	$2.22 \cdot 10^{12}$	0.13
2	Radium silicate+ H ₂ O _{liq}	$0.83 \cdot 10^{13}$	0.47

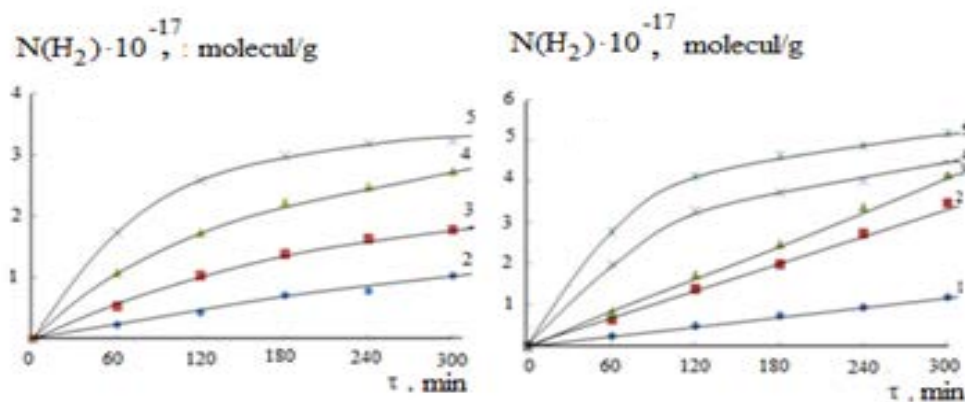


Fig. 2. Kinetics of molecular hydrogen accumulation in the thermal (a) and thermal radiation (b) decompositions of water on the surface of radium silicate at $\rho_{H_2O} = 5 \text{ mg/cm}^3$, $D = 0.28 \text{ Gy/s}$, and temperatures of 1 – 373; 2 – 473; 3 – 573; 4 – 623; 5 – 673 K

Table 2. Rates ($\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$) and radiochemical yields ($\text{mol}/100 \text{ eV}$) of molecular hydrogen in thermal radiation and thermal decompositions of water in the radium silicate + $\text{H}_2\text{O}_\text{s}$ system at different temperatures

T, K	$W_{\text{pt}}(\text{H}_2) \cdot 10^{-13}$	$W_{\text{T}}(\text{H}_2) \cdot 10^{-13}$	$W_{\text{p}}(\text{H}_2) \cdot 10^{-13}$	G(H_2)
1.373	–	–	0.42	0.18
2.473	1.75	0.06	1.69	0.85
3.573	3.05	0.11	2.94	1.12
4.623	5.28	2.78	3.00	1.34
5.673	8.61	4.44	4.17	1.63

The kinetic curves of radiation thermal and thermal water decomposition at $T = 373 \dots 673$ K are shown in Fig. 2. At increased temperatures, the second slow stage of hydrogen accumulation during radiation-heterogeneous radiolysis of water in the presence of radium silicate at $T = 300$ K was not observed. All the kinetic curves have a stationary region after a certain period of time. In the first approximation, the radiation component of the thermal radiation process is determined as the difference:

$$W_{\text{R}}(\text{H}_2) = W_{\text{RT}}(\text{H}_2) - W_{\text{T}}(\text{H}_2). \quad (2)$$

Using the rates of the radiation components of the thermal radiation decomposition of water, we determined the radiochemical yields. The resulting rates and radiochemical yields of molecular hydrogen are listed in Table 2. A comparison of molecular hydrogen yields during the radiation- heterogeneous processes in the radium silicate + $\text{H}_2\text{O}_\text{s}$ system in the range $300 \dots 673$ K shows that the temperature stimulates heterogeneous radiolysis, and the yield of hydrogen increases linearly from 0.18 to 1.63 mol./100 eV with temperature. The activation energies of the thermal radiation and thermal processes were determined from the temperature dependence of the reaction rates in the Arrhenius coordinates (Fig. 3) and proved to be the same within the accuracy of determination: $E_{\text{a}} = 13.45 \dots 15.4$ kJ/mol.

This indicates that the thermal component is a more energy-consuming stage of the thermal radiation process. To examine the effect of the radium cations on the radiation catalytic activity of the silicate in the course of water radiolysis, we synthesized pure silicate $\text{Si}(\text{OH})_4$ by reactions (1) and (2).

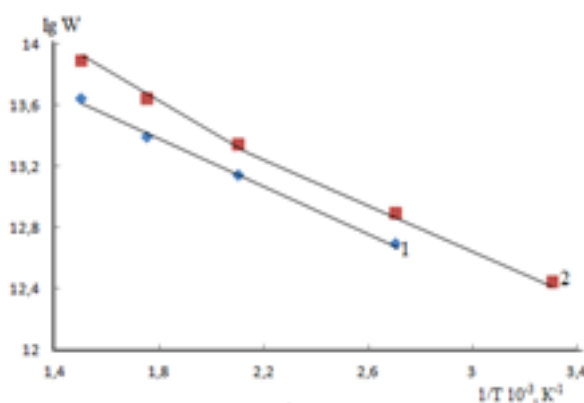


Fig. 3. Temperature dependences of hydrogen formation rate in the thermal (1) and thermal radiation (2) processes in the presence of RaO-SiO_2

The obtained samples were transformed into the stable silica gel form by thermal and thermovacuum treatment. As in the case of radium silicate, the experiments on radiation-heterogeneous decomposition of water were performed in two variants. In the first variant, water was in the adsorbed state ($\text{SiO}_2+\text{H}_2\text{O}_{\text{ads}}$) in the second, silica gel was in water ($\text{SiO}_2+\text{H}_2\text{O}_{\text{liq}}$). The kinetic curves of molecular hydrogen accumulation are shown in Fig. 4 for both systems.

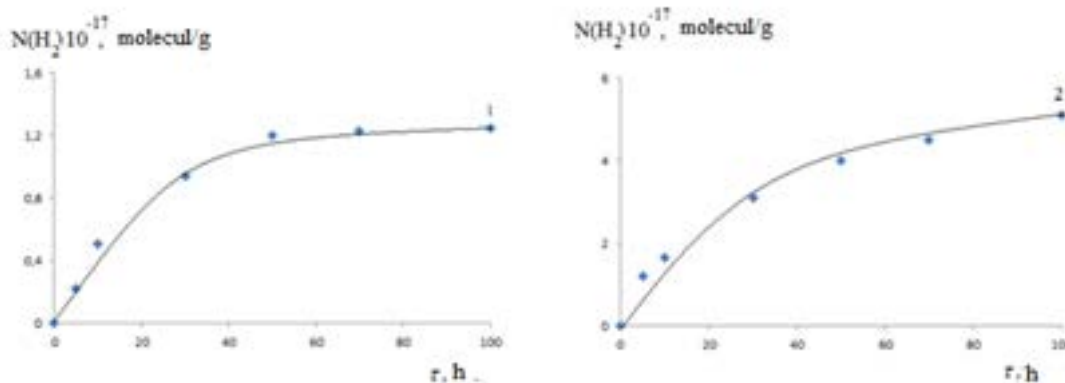


Fig. 4. Kinetics of molecular hydrogen formation in the catalytic radiation decomposition of water in the adsorbed ($\rho\text{H}_2\text{O} = 5 \text{ mg/cm}$) and liquid states ($m\text{H}_2\text{O} = 0.02 \text{ g}$) in the presence of SiO_2 at $D = 0.28 \text{ Gy/s}$ and $T = 300 \text{ K}$.

For comparison with radium silicate in the $\text{SiO}_2+\text{H}_2\text{O}_{\text{ads}}$ system, we studied the temperature effect at $T = 673 \text{ K}$. Fig. 5 shows the kinetic curves of hydrogen formation in radiation heterogeneous radiolysis of water in the presence of silica gel + $\text{H}_2\text{O}_{\text{ads}}$. Table 3 lists the rates and radiochemical yields of hydrogen.

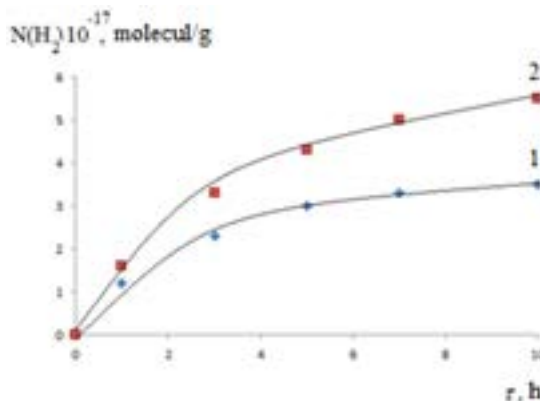


Fig. 5. Kinetic curves of molecular hydrogen formation in the (1) thermal and (2) thermal radiation decomposition of water in the presence of SiO_2 at $T=673 \text{ K}$.

Table 3. Kinetic parameters of heterogeneous radiolysis of water in the presence of SiO_2

System	$W(\text{H}),$ $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$	$W(\text{H}),$ $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$	$W(\text{H}),$ $\text{mol} \cdot \text{g}^{-1} \cdot \text{s}^{-1}$	$G(\text{H}_2),$ $\text{mol}/100\text{eV}$
$\text{SiO}_2+\text{H}_2\text{O}_{\text{ads}}(300 \text{ K})$	—	—	$1.11 \cdot 10^{13}$	0.61
$\text{SiO}_2+\text{H}_2\text{O}_{\text{liq}}(300 \text{ K})$	—	—	$5.8 \cdot 10^{13}$	3.2
$\text{SiO}_2+\text{H}_2\text{O}_\text{S}(673 \text{ K})$	$4.17 \cdot 10^{14}$	$3.47 \cdot 10^{14}$	$7.0 \cdot 10^{13}$	4.32

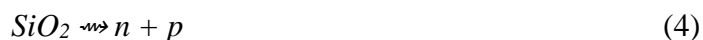
The silicate systems are dielectrics with a forbidden gap of $E_g = 10$ eV. The primary acts of interaction of gamma quanta with oxides form σ electrons with different energies [9, 13–15]. The energy of σ electrons is lost as a result of subsequent stages of interaction, and these processes continue until the energy of the new electron-generating generations is capable to initiate the formation of electron–hole pairs [16]:

$$E_{ge} = (3/5)E_{eh}, \quad (3)$$

where E_{ge} is the energy of σ electrons; E_{eh} is the thresh-old energy of the formation of electron-hole pairs, for dielectrics; E_{eh} is roughly evaluated to be $2 E_g$ [16]. As a result of the interaction of γ quanta with the silicate systems, electrons with an energy of $E \leq 12$ eV and approximately five or six electron-hole pairs with 100 eV form at the final stages of the cascades of elementary processes [9, 15-16]. For electron excitations with an energy of $E_{ge} = (3/5)E_{eh}$, the electron–phonon interaction is the main route of energy relaxation in dielectrics. The relaxation length in oxide dielectrics is $L \approx 10^2 \dots 10^3$ nm [15, 16]. Therefore, these electrons can interact with water molecules depending on the generation site and the particle size of the silicate systems [9, 15-17].

The electrons with an energy of $E_{ge} \leq 12$ eV can be emitted to the nearsurface space or create excited states in the silicates. According to the schemes, the number of these electrons also corresponds to ~ 5 particles per 100 eV. When these electrons quit the oxide surface, radiolytic processes involving low- energy electrons occur [8, 17].

In the silicate, an electron and hole pairs are generated:



They can be localized at localization sites, if any, in the bulk of oxide:

$$n + L_A + L_n \quad (5)$$

$$p + L_d + L_p \quad (6)$$

where L_A and L_D are the acceptor and donor localization sites, respectively; L_n and L_p are the localized states of electrons and holes. They interact if there are water molecules on the surface



by the recombination mechanism of water decomposition

$$G(H_2) = (1/2)G(n, p) \quad (9)$$

On the other hand, the excited states that form in the silicate systems can be involved in water decomposition:



In oxide systems with a disordered structure and various impurities, some of the nonequilibrium charge carriers can be localized or experience recombination decay in the bulk. The radium cations can serve as electron trapping centers and later, as their recombination centers.

The radiation catalytic activity of radium silicate, therefore, is lower than that of pure silicate [10–12].

A definite part of nonequilibrium charge carriers can be in the localized states in the radium silicate and silica gel particles. The proportion of particles that come out to the surface and hence the yield of hydrogen increase with temperature [9, 10]. As can be seen at defect migration temperatures ($T = 600...623$ K) in the structure of oxide compounds [10, 18], the yield of hydrogen corresponding to the number of formed nonequilibrium carriers in the oxide phases is $G(\text{H}_2) \approx 3.0...4.5$ mol./100 eV.

In the case of radium silicate and silica gel, all types of particles on the surface and in the bulk of water can be involved in water radiolysis. The generations of δ -electrons that quit the solid phase possess sufficient energy for excitation of water molecules in the dissociative level of water and initiation of radiolytic processes. Therefore, in heterogeneous radiation processes in the radium silicate + $\text{H}_2\text{O}_{\text{liq}}$, silica gel + $\text{H}_2\text{O}_{\text{liq}}$ systems, the yield of molecular hydrogen is higher than in heterogeneous radiolysis of water in the absorbed states. The observed high yield of molecular hydrogen can be explained by possible liberation of nonequilibrium charge carriers $G(n,p)$, excitons $G(\text{ex})$, and nonrelaxed and scattered electrons $G(e_{\text{ge}})$.

4. Conclusions

The kinetics of accumulation of molecular hydrogen at the system radiumsilicate + H_2O gamma radiolysis of water. It was found that the radiation-chemical yield of hydrogen for radiumsilicate + H_2O ($G(\text{H}_2) = 0,47$ mol./100 eV) more than, in the radiolysis of pure water ($G(\text{H}_2) = 0.45$ mol./100 eV).

The kinetics of accumulation of molecular hydrogen with radiation, the radiation-thermal and thermal ($T = 300...673$ K) processes radiumsilicate water.

It is shown that the formation of the surface-active centers and secondary electrons in the presence of radiumsilicate causes an increase in the saturation velocity of molecular hydrogen under thermal and radiation-thermal processes in the system radiumsilicate + H_2O .

References

1. В.М. Вдовенко, Ю.В. Дубасов. *Анали-тическая химия радия*. Л., 1973, 187 с.
2. Р.А. Кузнецов, П.С. Буткалюк, В.А. Тарасов и др. Выходы продуктов активации при облучении радия-226 в высокопоточном реакторе СМ // *Радиохимия*. 2012, т. 54, №4, с. 352-356.
3. IAEA1384 Nuclide Explorer tool for retrieving interactively detailed data on radionuclides properties. URL:<http://www.nea.fr/abs/html/iaea1384.html>.
4. И.Л. Буткалюк, П.С. Буткалюк, С.В. Томилин. Исследование взаимодействия соединений радия с конструкционными материалами // *Физика и электроника*. 2013, №4, т. 15, с. 1053-1057.
5. А.А. Garibov, Т.Н. Agayev, Z.A. Mansimov, S.Z. Melikova, К.Т. Eyubov. Investigation of radium orthosilicates by methods of FT-IR spectroscopy and derivatography // *J. Austrian of Technical and Natural Sciences*. 2014, N 7-8, p. 72-75.
6. I.L. Butkalyuk, P.S. Butkalyuk, S.V. Tomilin. *Examination of radium compounds interaction with structural materials*. Ulyanovsk State University, 2013.
7. Y.Y. Ebaid. On the use reference materials in gamma-ray spectrometric efficiency calibration for environmental samples // *Radional. Nucl. Chem*. 2009, v. 1, N 280, p. 21-25.

8. А.К. Пикаев. *Современная радиационная химия. Радиолит газы и жидкостей*. М.: «Наука», 1986, 440 с.
9. Я.Д. Джафаров, А.А. Гарибов, С.А. Алиев, С.М. Искендеров, В.Р. Красноштанов, Расчет поглощенной дозы гамма-облучения в оксидных диэлектриках // *Атомная энергия*. 1987, т. 63, в. 4, с. 269-270.
10. А.А. Гарибов. Радиационно-каталитическое действия оксидных катализаторов в процессе разложения воды // *Радиационно-каталитические процессы в дисперсных средах*: Сборник научных трудов / Под. ред. В.Н. Пармона. Новосибирск: «Наука», Сибирское отделение, 1992, с. 121-161.
11. А.А. Гарибов, М.Я. Бакиров, Я.Д. Джафаров, Г.З. Велибекова. Закономерности радиационно-каталитического действия систем Me^{2+} - SiO_2 в процессе радиолит воды // *Химия высоких энергий*. 1984, т. 18, №6, с. 502-505.
12. А.А. Гарибов, М.М. Меликзаде, М.Я. Бакиров, Г.З. Велибекова, М.Х. Рамазанова. Влияние катионов на каталитические свойства силикагеля при радиолит адсорбированных молекул воды // *Химия высоких энергий*. 1982, т. 16, №2, с. 130-134.
13. А.П. Овчинников. Расчет распределения поглощенной энергии у плоской границы раздела сред при гамма-облучении // *Физическая химия в микроэлектронике*. Красноярск: КГУ, 1976, с. 23-24.
14. А.Ф. Аккерман, М.Я. Грудский, В.Б. Смирнов. *Вторичные электронные излучения из твердых тел под действием гамма-квантов* М.: «Энергоиздат», 1986, 168 с.
15. В.П. Ковалев. *Вторичные электроны*. М.: «Энергоиздат», 1987, 9 с.
16. М.А. Эланго. *Элементарные неупругие радиационные процессы*. М.: «Наука», 1988, 15 с.
17. И.П. Каплан. Исследование первичных процессов радиолит воды методом математического моделирования // *Химия высоких энергий*. 1991, т. 25, №4, 29 с.
18. А.Р. Силинь, А.Н. Трухин. Точечные дефекты и элементарные возбуждения в кристаллах и стеклообразном SiO_2 // *Зинатне*. 1985, с. 206-214.

ГЕТЕРОГЕННЫЙ РАДИОЛИТ ВОДЫ В ПРИСУТСТВИИ РАДИЙ-СИЛИКАТА

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Резюме: Синтезированы радий-силикаты с различными активностями радия. Для сравнения изучены радиационно-каталитические активности радий-силиката (с активностью радия 6100 Бк/г) и исходного силикагеля в процессе радиолитического разложения воды. Гетерогенный радиолит воды изучен в адсорбированном и жидком состояниях в контакте с образцами радий-силиката и силикагеля. Выявлены влияния радий-катионов, состояния воды и температуры процессов на выход молекулярного водорода. Предложены механизмы гетерогенного радиолит воды с участием исследуемых образцов радий-силиката и силикагеля.

Ключевые слова: радий-силикат, гетерогенный радиолит, выход молекулярного водорода, γ -облучение, активность

RAD UM-SİLİKATIN İŞTİRAKI İLƏ SUYUN HETEROGEN RAD OL Z

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Xülasə: Müxtəlif aktivlikli radiumdan radium-silikat sintez olmuşdur. Müqayisə üçün suyun radiolitik parçalanma prosesində ilkin silikagelin radiasiya-katalitik aktivlikli (radiumun aktivliyi 6100 Bk/q) radium-

silikat t dqiql olunmuşdur. Radium-silikat v  silikagelin adsorbsiya olunmuş v  maye halında suyun heterogen radiolizi  yr nilm şdir. Radium-kationların, prosesin temperaturunun molekulyar hidrogenin  ıxımına t siri m  yy n olunmuşdur. T dqiql olunan radium-silikat v  silikagelin iştirakı il  suyun heterogen radiolizinin mexanizmi t klif olunmuşdur.

A ar s zl r: radium-silikat, heterogen radioliz, molekulyar hidrogenin  ıxımı,  -ş alanma, aktivlik