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DIAGNOSTICS AND USE OF ECOLOGICAL MATERIALS

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Short description of the research activities

The aim of the study stay is to participate in the preparation and characterization of new ecological materials with tailored properties.

The management of hazardous waste is a recently developing field. The treatment of sorbents used for cleaning industrial waste streams containing hazardous toxic compounds (as radionuclides, heavy metals, etc.) consists in the immobilisation of hazardous species to obtain waste packages which can be safely disposed in the environment. Vitrification and ceramisation technologies have been used for this purpose. In present study optimal conditions for immobilisation of the waste in new sorbents were determinate. Processes taking place during thermal treatment of the prepared materials were investigated. Internationally recommended testing procedures such as Materials Characterization Center leach tests were used in testing chemical durability of radioactive waste forms.

Following materials were investigated in the frame of the project:

1) New planar sorbents (fibbers, tissue and felt) for cleaning industrial gases (e.g., flue gas of the incineration process) from hazardous pollutants.

Basalt planar sorbents used for uptake of acid gases, organic vapors and vapors of water from polluted air or natural gas. Chemical leaching basalt fibers by hydrochloric acid was used in the development of porous active surface of the basalt fibber. Planar sorbents made of the porous basalt fibers have advantages in comparison to other inorganic sorbents. They posses lower diffusion resistance and higher sorption ability towards H₂O, SO₂ H₂S, CH₄ and toxic organic compounds, such as phenol, methylphenol, 2-butanol, and dichlorethane than natural zeolite (clinoptiolite). Optimized conditions of the regeneration of sorbents were determine. Efficiency encapsulation radium-226 in a porous basaltic fibers was investigated. Testing of glassy matrices for encapsulation of hazardous waste was carried out.

<u>Coal planar sorbent for sorption of organic vapors, vapors of tritium water and radioactive</u> <u>rare gases.</u> Optimal conditions for activation of planar porous charcoal sorbents and for their regeneration after use were determined. Sorption isotherms for vapors of dichlormethane, 2butanol and methylphenol on the charcoal-fibers based planar sorbent were measured and the respective sorption capacities were calculated.

- Alumina pillared montmorillonite was investigated as a new class of microporous materials to be used as catalysts and adsorbents. Adsorption abilities of Al-MMT for radionuclides were measured. The prospects of use of materials for encapsulation of radioactive substances are considered
- 3) Perovskite based ceramics has been proposed as a matrix for partitioned trans-uranium waste. Effect of microstructure changes on mobility of radionuclides in simulated high level waste forms was investigated. Characterization of ceramic matrices as well as testing of chemical durability of the hazardous waste packages, namely heavy metals and radioactive waste was carried out. Advanced inorganic materials with photocatalytic and photovoltaic properties based on titanium and ruthenium oxide powders.
- 4) The mixed oxide TiO₂-RuO₂ system can be effectively used for catalytic reactions of technological and environmental importance. In this work the *in-situ* investigation was carried out in order to determine optimal conditions for the preparation of catalysts.

Methods of thermal analysis (such as thermogravimetry, differential thermal analysis and evolved gas detection), X-ray powder diffraction, electron microscopy, surface area measurements by nitrogen sorption/desorption, mass spectroscopy and others were used for the characterization of the materials. Diffusion structural analysis was used for the characterization of morphology changes of tailored inorganic materials under *in-situ* conditions of their heat treatment. Mathematical models of the processes taking place during thermal treatment of the investigated material were designed and used for the evaluation of the results of diffusion structural analysis.

The recommendations for manufacture and use of new materials are given.

The measurements by traditional methods of thermal analysis (thermogravimetry, differential thermal analysis), X-ray diffraction measurement, electron microscopy measurements and surface area determinations were carried out in the collaboration with the Institute of Inorganic Chemistry AS CR, Rez. The scientific level of the research work carried out at the NRI Rez was highly recognized by the international partners of NRI from Japan and Germany.

The results of investigation carried out during the study stay were presented in several national and international meetings, namely:

- International conference "Solid State Chemistry, Prague, August 20-28, 2000.

- The 4th NIMC (National Institute of Materials and Chemical Research) International Symposium on Photoreaction Control and Photofunctional Materials, Tsukuba, Ibaraki, Japan, 14-16, Mart, 2001, PCPM 2001, P-66, P. 234-235.

- Topical meeting on emanation thermal analysis held in Rez on August 9 10, 2000
- 2nd Czech-Japanese Workshop on advanced methods for characterization of inorganic materials held in Prague on September 8 – 9th, 2000.

The results of this research are used in the different chapters of the monograph: V.Balek, I.N.Beckman "Diffusion structural analysis of solids", and also for preparation of a new course of lectures "Ecological materials" for the students of Chemical department of MSU.

The detail description of the results obtained in the frame of this project and their detailed interpretation is given further in this report. The results of the research will be published in international journals. Therefore all the description given further should be considered as <u>CONFIDENTIAL</u>.

The experience and know-how gained during the research project will be used in the further research and teaching work an the Department of Chemistry, M. V. Lomonosov Moscow State University, Russia. Further collaboration between the NRI Rez and MSU is planned for the next period in order to continue the started activities.

Acknowledgement:

The financial support obtained in the frame NATO Science Fellowships Programme is highly acknowledged by the developer as well as the host institution. This acknowledgement will be written in the scientific papers prepared for publication in international journals.

1. General background of the research

Planar sorbents and apparatus of regular structure

The chemical process intensification is NOVEL DESIGN PHILOSOPHY where significant reductions in plant scale can be achieved by matching the chemical, and/or physical requirements with the FLUID DYNAMICS of a process. Resultant benefice can include reductions in capital and operating costs, and/or significant improvements in efficiency process yield, waste production and inherent safety. Applications include implementation of continuous processes, compact heat exchangers and separators, modification of chemistry and improved plant layout and control.

Traditional adsorption filters using granulated sorbents are not efficient enough for the treatment of gaseous waste streams in order to separate the toxic components. Therefore planar adsorption and chemically active filters have been developed to this propose. Main advantages of the planar sorbents in comparison with the traditional (granular) sorbents consist in:

- the higher efficiency of sorption,
- the possibility to achieve high technological flexibility and the optimization of the flux of mass
- heat transfer in the sorption modules. It is to note, that in the technological conditions a large amount of heat is formed due the chemisorption and this heat should be conducted out from the sorption module.
 - Main advantages of adsorption apparatus of regular structure are:
- high removal efficiency,
- small volume,
- simple operation,
- excellent scale-up ability, no entertainment, flooding or channeling.

Filtration through the active filters is a new process which easily combines adsorption, catalysis and filtration technology.

The aim of this study stay was to get acquainted with modern methods of the design and characterization of new materials for the treatment of waste streams in chemical industry. Special attention was be paid to the further development of regular structure apparatus with planar sorbents.

Possibility of design of integrated system included:

- Apparatus design;
- Tissue design;
- Fibrous material design.
- Adsorbent bad design
- Fibrous adsorbents for apparatus regular structure are
- Acids treatment basaltic fibers, tissue and felt;
- Active coal fibers, tissue and felt;
- Acid treatment glass fibers and tissue;
- Acids treatment basaltic fibers + active coal fibers

With the aim to develop the adsorption ability, porous basaltic fibers has been prepared by chemical leaching of the basalt fibers by hydrochloric. Basaltic planar sorbents to be used for the uptake of acid gases, organic vapors and water vapors from the air or natural gas streams, respectively. The planar sorbents made of the porous basalt fibres have advantages in comparison to other inorganic sorbents as they possess lower diffusion resistance and higher sorption ability towards SO₂ than e.g. natural zeolite (clinoptiolite). The sorption properties of the basalt based planar sorbents for SO₂, H_2S and CH_4 , involved in the natural gas were tested both for the dry and humid natural gas streams. Moreover, the sorption isotherms of this sorbent for toxic organic compounds, such as phenol, methylphenol, 2-

butanol, and dichlorethane, were measured and the respective sorption capacities were determined. Processes taking place during thermal treatment of the porous and non-porous basaltic fibers have investigated. Temperature range suitable for the regeneration of the chemically treated basalt planar sorbent was determined. For definition of the operational characteristics new sorbents, the tests of their mechanical properties in a mode repeated thermocycles were carried out. The dates necessary for designing of adsorption apparatus of regular structure, were derived from experiments on study a dynamic of gas filtration through a layer planar adsorbent.

Charcoal fibers were used for the manufacture of the charcoal based planar sorbents for uptake of organic vapours, and radioactive rare gases from waste steams. Planar sorbents involving both charcoal and basalt fibers were prepared and tested. The charcoal planar sorbents were tested for the sorption of organic vapors, tritium water vapors and radioactive rare gases. The optimized conditions for the activation of planar porous charcoal sorbents and for their regeneration after use were determined. The sorption isotherms of the charcoal-fibers based planar sorbent for vapors of dichlormethane, 2-butanol and methylphenol were measured and the respective sorption capacities were calculated. Processes taking place during thermal treatment of the porous charcoal fibers and felt have investigated.

Sorption modules containing planar sorbents made of various materials (coal and basalt) were tested. The advantage of apparatus of regular structure is provided with their flexibility (rearrangement), compactness, low consumption of materials and high power efficiency.

Alluminia pillared bentonite

Alumina pillared montmorillonite ("called pillared clays") – was investigated as a new class of microporous materials to be used as catalysts and adsorbents.

Now one of most effective adsorbents is zeolite. Its wide application is caused high porous (almost 100 %), that provides sorption capacity, identical sizes pores, that provides high selectivity, and availability of all volume of pores for adsorbtive (open porosity). However, for many vapors zeolite are inapplicable, as the small diameters pores do not suppose sorption of substances with rather high molecular weights and, hence, by large sizes of molecules. The similar molecules arise, for example, at incineration is high molecular substances. The processing any types of municipal and industrial wastes requires use adsorbents and carriers of catalysts, with high porosity and with "calibrated" pores, but with essential by the large diameter pores, than at zeolite.

In this connection perspective direction represents updating natural clays, by introduction in their structure special cations.

Pillared clays represent a new class of microporous materials that have potential for use as catalyst and adsorbent. Pillared clays are members of the smectite group of 0:2 layered silicates in which the gallery cations are robust species capable of preventing the collapse of the interlayer region upon dehydration. Advantage of these compounds is in the fact, that the pores formed between the cations can be systematically modified by varying the cation size, shape and spacing. Pillared clays exhibit interesting physico-chemical properties, i.e. basal spacing of about 1,8 nm, specific surfaces areas between 150 and 350 m g^{-1} , mean pore diameters of 0.7-0.9 nm, and the ability to absorb various substances, i.e. hydrocarbons. Three properties of pillared clays, acidity, shape selectivity and thermal stability, determine their potential usefulness as catalyst. Pillared interlayer clay compositions are inorganic structures with high thermal stability.

The impetus work was to create porous three-dimensional structures from twodimensional clay minerals. It was felt that, because smectite clays have a low layer charge and if an inorganic polymeric cation were chosen that had a high positive charge, pores greater than those available in zeolites would be obtained. The initial choice of polymer was the aluminum Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Surface and porosity of alumina-MMT was measured. The results of the sorption tests (for Cs, Sr and organic substances) were used in the design of a sorption unit to be used for the uptake of hazardous nuclides from accident waste from Czech and Russian Nuclear power plants. Thermal stability of porous structure Al-MMT was investigated.

Perovskite ceramics.

In the assessment of potential environmental risk of the final disposal of high level radioactive waste (HLW) forms, their chemical durability is an important property. The characterization of this property under repository conditions requests a detailed knowledge about the growth rate of an alteration layer and various processes taking place in this layer.

Now perovskite based ceramics is considered as the most perspective material for HLW matrices [1]. The basic advantage of such material consists in the high absorption ability for heavy metals and chemical durability. In present study microstructure changes in simulated HLW waste matrices (perovskite based ceramics –"as polished" and "as leached") containing Ce and Nd as simulated Trans-Uranium elements was investigated. Internationally recommended testing procedures such as Materials Characterization Center (MCC) leach tests were used in testing chemical durability of high-level radioactive waste forms. Thermal stability of initial and leached perovskite ceramics were determined.

*TiO*₂-*RuO*₂ photocatalyzes for degradation of pollutants.

Photocatalytic technology is becoming more and more attractive to industry today because global environmental pollution has come to be recognised as a serious problem that needs to be addressed immediately. In line with new approach, various people in industry are beginning to develop products to which photocatalytic functions have been added. Industrial activities in the future should offer products and services that are in harmony with environment. Titanium dioxides as a photocatalysts let photoactivity play a positive role: decomposing materials of our choice, e.g. dirt, prime, malodorous chemicals, irritants, toxic chemicals, smoke residue, bacteria, etc. [2]. Materials with photocatalytic properties based on titanium and ruthenium oxide powders can be used for degradation, condensations or polymerizations of different substances. Such reactions are applicable in variety of problems of environmental interest, water and air purification, especially in the elimination of toxic chemicals such as halogenated aliphatic and aromatic hydrocarbons from wastewater, soil and groundwater. They can also be successfully used in environmental control, destruction of bacteria and viruses, inactivation of cancer cells. Many of the reactions have already found interesting and important practical applications in production of goods for various fields of everyday life: self-sterilizing photocatalytic tiles, self-cleaning building materials, antifogging glasses, photocatalytic air cleaners, photocatalytic water purificators, films for automobile side-view mirrors.

With the aim to develop the photocatalytic material usable in broader wavelength region, RuO_2 -doped titanium dioxide with the composition $(TiO_2)_x(RuO_2)_{i-x}$ (x = 1, 0.9) has been prepared by sol-gel technique. In present study we have investigated processes taking place during thermal treatment of the prepared titania-ruthenia materials.

2. Instrumentation

The diffusion structural analysis (DSA) measurements were carried out using modified NETZSCH DTA404 equipment at the heating rate of 6K/min, in 50 ml/min of the carrier gas (argon, air). The resulting DSA curves are presented as temperature dependencies of the radon release rate E (in relative units); $E=A_{\alpha}/A_{total}$, where A_{α} is the α radioactivity of radon released in unit time from the labeled sample, and A_{total} is the total γ radioactivity of the labeled sample. The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(Tl) detectors were used for the α – and γ -radioactivity measurements, respectively.

TG, DTGA and DTA measurements were carried out using NETZSCH STA 404 Equipment, in an alumina crucible and heating rate of 6K/min.

The measures of surface area and pore size distribution were carried out using Coulter SA 3100 analyzer. The isoterm data of sorption of vapors of liquid nitrogen was subjected to a variety of calculation models to obtain surface area and pore size distribution results. The B.E.T. calculation was one model used for the determination of the sample specific surface area; the B.J.H. calculation yields the pore size distribution. The t-Plot method is used for the estimation of micropore volume and micropore area. It provides a way of characterisation and sizing the pore structure of a material. Date directly available from the t-Plot calculation are the surface area of the meso- and macropores, and the micropore volume. It used in conjunction with the BET surface to calculate the micropore surface area.

X-ray diffraction patterns (XRD) were recorded on Siemens D500 diffractometer using CuK_{α} radiation. The powder samples were pressed in a glass holder. The basal spacing and crystallinity of materials were investigated.

SEM micrographs were obtained with PHILIPS Equipment (Type XL 30CP).

3. Diffusion Structural Analysis of porous solids and solid-state reactions

In this work the emphasis is on development of foundations of diffusion structural analysis (DSA)/

The method of DSA is based on the measurement of the release of 220 Rn from samples which have been previously labelled by introduction of tracers of 228 Th- and 224 Ra- serving as parent isotopes of 220 Rn [3 – 5]. The release of radon atoms from the samples can be measured continuously, under *in-situ* conditions of the sample thermal treatment. It was experimentally demonstrated that the radon release rate depends on the surface area of the solid and on the radon diffusion parameters in the solid matrix.

The inert gas atoms are serving as the nanostructure probe of the materials. A high sensitivity of the DSA method towards order–disorder changes taking place during structure transitions, sintering, weathering of rocks or corrosion of solid surfaces has been advantageously used. The processes of the interaction of solids with gases, liquids or other solid components were investigated by DSA in numerous systems. Moreover, this method gives a supplementary insight in to processes of radiation damage, alteration and degradation of materials surfaces. The DSA results usually complement results of differential thermal analysis, thermogravimetry, X-ray diffraction, determination of surface area and porosity, or optical and electron microscopy characteristics of the samples.

In some cases, for example when carrying out longer lasting and/or high-temperature measurements of surface and morphology changes, it is necessary to introduce parent nuclides of the inert gas, e.g. radon, as a relatively permanent source of the labeled gas. Trace amounts of thorium ²²⁸Th can be introduced into the sample by co-precipitation during the sample

preparation from a solution or by adsorption on the surface of the sample. ²²⁰Rn is formed by spontaneous alpha decay according to the scheme

²²⁸ Th
$$\xrightarrow{\beta}$$
²²⁴ Ra $\xrightarrow{\alpha}$ ²²⁰ Rn $\xrightarrow{\alpha}$
T_{1/2} = 1.9 y T_{1/2} = 3.8 d T_{1/2} = 55

and can be introduced into the solid owing to the recoil energy (85 keV per atom). The above nuclear reactions which give rise to the radon nuclide, have also been used for the incorporation of the inert gas into the solid sample. Radon atoms penetrate several tens of nanometers, depending on the composition of the target materials.

3.1 Development of new model for diffusion structural analysis data

This section describes the basic theory of the DSA measurement. It also outlines the calculation models which are used in the DSA method. A fully detailed treatment of these calculations is not given.

The mathematical model describing the transport of inert gasses was developed to be used in the evaluation of the results of the diffusion structural analysis. The influence of thermal treatment of porous solids on the diffusion characteristics and diffusion conductivity of transport paths in the porous solids were considered in the model. The basic attention was paid to materials with complex porosity. For the description of diffusion of inert gasses used as a gas probe of the microstructure changes taking place during solid-state reactions and collapse of porous structure. The appropriate mathematical theory as the background for the model was developed. The influence of the basic parameters of model on the shape of the DSA - curve was demonstrated. The computer modeling was used in order to carry out the diagnostics of porous samples such as fibrous basalt, fibrous coal and alumina-pillared bentonite.

The diffusion of inert gases was used as a gas probe of the microstructure changes of the sorbent materials during their treatment was quantitatively described by the model. The influence of the basic parameters of the model on the character of the DSA curves was demonstrated.

The changes of emanating rate during heating can be expressed as:

$$E(T) = E_0 + E_D(T),$$

where E_0 is emanating rate temperature due to recoil, $E_D(T)$ is emanating rate due to diffusion.

Recoil effects and parameters for radon of diffusion depends on temperature and mechanisms of the solid-state processes.

In the model the temperature dependence of the emanating rate was expressed as the product of two functions: diffusion function ($E_D(T)$ or D (T)) and structural function, $\Psi(T)$, respectively.

$$E_{T}(T) = E_{D}(T) \bullet \Psi(T) \propto D(T) \bullet \Psi(T),$$

It was assumed that the character of the DSA curves depends on the number of diffusion paths serving for the gas release, on the $\Psi(T)$ function, characterising the microstructure changes in the solid samples and the D(T) function characterising permeability of the radon transporting paths.

The combination of various functions $\Psi(T)$ and D(T) was used in the modeling, for example:

$$D(T)=D_0 exp(-Q_D/RT)$$
$$D(T)=D_{10} exp(-Q_{D1}/RT)+D_{20} exp(-Q_{D2}/RT)$$

$$\mathbf{D} = \frac{\mathbf{D}_{20} \exp(-\frac{\mathbf{Q}_{2}}{\mathbf{RT}}) + \mathbf{D}_{10} \exp(-\frac{\mathbf{Q}_{1}}{\mathbf{RT}}) * \mathbf{K}_{0} \exp(\frac{\mathbf{Q}_{K}}{\mathbf{RT}})}{1 + \mathbf{K}_{0} \exp(\frac{\mathbf{Q}_{K}}{\mathbf{RT}})}$$
$$\mathbf{D} = \frac{\mathbf{D}_{20} \exp(-\frac{\mathbf{Q}_{2}}{\mathbf{RT}}) + \mathbf{D}_{10} \exp(-\frac{\mathbf{Q}_{1}}{\mathbf{RT}}) * \mathbf{K}_{0} * \Phi(\mathbf{T}) * \exp(\frac{\mathbf{Q}_{K}}{\mathbf{RT}})}{1 + \mathbf{K}_{0} * \Phi(\mathbf{T}) * \exp(\frac{\mathbf{Q}_{K}}{\mathbf{RT}})}$$

where Q_i is the activation energy of radon diffusion in the respective solid phase; D_{oi} - is the pre-exponential factor characterizing the respective lattice property, K_0 - constant rate of reaction of exchange of radon atoms between different diffusion paths, Q_K – heat of reaction.

For the structural function $\Psi(T)$ following expressions were used in the modeling:

$$\psi(\mathbf{T}) = \exp(-q\mathbf{T})$$

$$\psi(\mathbf{T}) = \mathbf{T}^{-\mathbf{m}}$$

$$\Psi(\mathbf{T}) = \frac{1}{1 + \left(\frac{\mathbf{T}}{\mathbf{T}_{\mathbf{m}}}\right)^{\mathbf{p}}}$$

$$\Psi(\mathbf{T}) = \frac{1}{1 + \exp\left(-\frac{\mathbf{T} - \mathbf{T}_{\mathbf{m}}}{\Delta \mathbf{T}}\right)}$$

$$\Psi(\mathbf{T}) = 1 - 0.5 \left[1 + \exp\left(\frac{1 - \frac{\mathbf{T}_{\mathbf{m}}}{\mathbf{T}}}{\frac{\sigma\sqrt{2}}{\mathbf{T}}}\right]$$

where q, m, T_m , ΔT and σ -are parameters. T - temperature, K. $\operatorname{erf}(\mathbf{z}) = (2/\pi^{1.2}) \int_{0}^{\mathbf{x}} \exp(-\mathbf{z}^2) d\mathbf{z}$ - Integral Gauss function, $\mathbf{z} = \frac{\mathbf{T} - \mathbf{T}_m}{\sigma^* \sqrt{2}}, \quad \sigma = \frac{\Delta \mathbf{T}}{3}, \text{ T is}$

the temperature corresponding to the maximal rate of the $\Psi(T)$ change, ΔT is width of the temperature range in which $\Psi(T)$ takes place.

In general, the following expression was proposed for the description of DSA curve

$$\mathbf{E}(\mathbf{T}) = \mathbf{E}_0 + \sum_{i=1}^n \mathbf{p}_i \mathbf{D}_{i0} \exp(-\frac{\mathbf{Q}_i}{2\mathbf{R}\mathbf{T}}) + \sum_{j=1}^m \mathbf{p}_j \mathbf{D}_{j0} \exp(-\frac{\mathbf{Q}_j}{2\mathbf{R}\mathbf{T}}) * \Psi_j(\mathbf{T})$$

3.2 Experimental

Radon atoms ²²⁰Rn were used as tracers making possible to characterize porosity and microstructure changes of solids. The labeling of the samples of the materials by ²²⁸Th and

 224 Ra was made by the surface adsorption of the water solution containing the above radionuclides. The samples have been stored before the experimental measurement of radon release for at least 1 moth to allow the radioactive equilibrium between 228 Th and 224 Ra is attained.

The measurement of ²²⁰Rn release rate from the sample of basalt fibers was carried out using the equipment of NRI. The measurement was performed every minute during heating at the rate of 1K/min. The temperature interval used for the heating was -10° C to 1300° C. After the sample heating its cooling to room temperature was carried out at the rate of 1K/min. Several heating runs in dry air or argon overflowing the sample were carried out. The air (or argon) flow was used to transpire the released radon from the sample into the detection chamber.

3.3 Evaluation of experimental data

The theoretical model, developed for the DSA has been be used in the frame of the research project for the evaluation of the experimental results and their comparison. Using the recently developed model for the evaluation of the DSA results, fine microstructure changes taking place in the solid matrix and the porous system were quantitatively described [6-8].

The computer treatment of DSA experimental curves with help of the designed models was used for calculate temperatures of the maximal rates of loss of adsorption water, dehydration sintering, temperature intervals of all processes and parameters of radon diffusion.

The DSA results have been used for the determination of the temperatures at which the active surface of the sorbents is formed, and, finally, for the determination of temperatures at which the collapse of the porous structure takes place.

4. Basaltic fibrous sorbents

4.1 Optimization of the conditions for the manufacture the designed basalt fibrous sorbents

New sorbents were prepared from non-porous basalt fibers by means of chemical leaching in two steps. The chemical composition of the virgin fibers (mass%): $SiO_2 - 48-54$, $Al_2O_3 - 10-15$, $Fe_2O_3 - 7.5-15$, MgO - 3-7, Na₂O and K₂O - 3%. The consecutive chemical leaching of the basalt fibers by sulphuric or hydrochloric acid was used in order to develop a porous active surface of the basalt fibers [9].

In the first step the fibers were treated for 20-50 min with 2-5 HCl at $92 - 95^{\circ}$ C under stirring, washed with distilled water and again treated with 0,25 - 3 N HCl for 4 - 8 h at the same conditions, and washed with distilled water. The samples were dried in air. Chemical composition of the porous basalt fibers was: 99,5% SiO₂.

4.2 Characterisation of surface and porosity of basaltic fibers

Surface area measurements were used for the direct characterization of basalt fibrous sorbent. N_2 adsorption-desorption isoterms were recorded on the Coulter SA 3100 apparatus. For nitrogen the BET surface area determinations, the cross-sectional area of the adsorbate molecule was assumed to be 0.162 nm². Several pretreatment conditions were tested. Prior to nitrogen physisorption, basalt fibers were degassed for 24h at 60^oC and 10⁻⁵Pa.



Fig. 1 Isoterm adsorption of N_2 on basalt fibers: Curve 1 – basalt initial; Curve 2 – basalt leached; Curve 3 – basalt industry leached; a – adsorption; d – desorption.

Table 1. Surface areas and pore volume determined with nitrogen sorption of porous basaltic

fibres.					
Basalt	BET surface area,	Total pore volume,	t-plot surface		
Materials	m²/g	cm ³ /g	area, m ² /g		
Initial fibers	8.051	0.0275	13.19		
Porous fibers	238.23	1.5765	254.41		
Porous felt	121.95	0.1341	129.16		

Pore Diameter (nm)	Pore Volume			
	cm ³ /g	%		
Under 6	0.0219	1.40		
6-8	0.024690	1.57		
8-10	0.03282	2.09		
10-12	0.04938	3.15		
12-16	0.06918	4.41		
16-20	0.12710	8.10		
20-80	1.22943	78.35		
Over 80	0.01466	0.93		
BJH Total	1.56915	100.00		

Table 2. Pore size distribution of basaltic fibrous adsorbent

The adsorption and desorption isoterms of N₂ for initial (non-porous) and acid treated (porous) fibres and felt are shown in **Fig.1**. Adsorption isotherms are type IV, i.e., typical of a multilayer adsorption on a mesoporous and microporous adsorbent. The hysteresis loop – H4 type according to the IUPAC classification – is due to capillary condensation in the mesopores. **Table 1** lists the surface area values determined by nitrogen adsorption (B.E.T. calculation and t-plot method) for basaltic fibers before and after leaching. B.E.T. specific surface area of porous basalt adsorbent is higher than initial (i.e. $S^{BET}_{leach}/S^{BET}_{init}=30$). t-plots allow one to estimate both the microporous surface area and the external surface area. The total (mesoporous and microporous) porous volume V_{total} was estimated from the adsorption

at P₀/P_s=0.95 (**Table 1**). The increase of V_{total} during the process of leaching (V_{leach}/V_{initial}=60) is due to the creation of micropores (adsorption active centres) and mesopores (transport paths for gas diffusion). **Table 2** list pore size distribution (calculated by BJH method) of the basalt fibrous adsorbent. The mean value of micropore diameter is $\overline{\mathbf{d}_{por}} = 3.7$ nm, the mean value of mesopore diameter is $\overline{\mathbf{d}_{por}} = 3.7$ nm, the mean value are presented in **Fig.2**.



Fig. 2 The pore size distribution of virgin (1) and porous (2) basaltic fibers (Schematic).

4.3 Sorption properties of basaltic fibers

The sorption properties of basalt based planar sorbents for SO_2 , H_2S and CH_4 involved in natural gas were tested both for dry and humid natural gas steams [10]. Moreover, sorption isotherms for toxic organic compounds, such as phenol, methylphenol, 2-butanol, and dichlorethane on this sorbent were measured and the respective sorption capacities were determined.

It was established, that the sorption capacity of H_2S and SO_2 on the porous, chemically treated basalt fibres is comparable with industrial zeolites and silicogels. At the increased temperature the sorption capacity decreased. The adsorption isotherm (see **Fig.3a** for H_2S and **Fig.3b** for SO_2) was evaluated on the Dubinin-Astahov equation:

$$A=a_0 \exp[-(A/E)^n]$$

A=RTln(p_s/p)

where a- is adsorption capacity, a_0 - limiting capacity, A - reduction of free energy of adsorption, E -characteristic energy of adsorption in a characteristic point, n - constant, R - gas constant, T - absolute temperature, p_s - saturation pressure, p - sample pressure. The constant n is determined by structure of a porous material - for microporous samples it is equal 2, for mesoporous sample - is equal to 1. The dependence of differential enthalpy of adsorption on the volume adsorbed was determined from the following equation:

$$\mathbf{q} = \mathbf{E}\left[\left(\mathbf{ln}\frac{\mathbf{a}_0}{\mathbf{a}}\right)^{\frac{1}{\mathbf{n}}} + \frac{\alpha \mathbf{T}}{\mathbf{n}}\left(\mathbf{ln}\frac{\mathbf{a}_0}{\mathbf{a}}\right)^{\frac{1}{\mathbf{n}}-1}\right]$$

where α - thermal coefficient of adsorbent expansion. The values of parameter n for the adsorption isotherms of H₂S, and SO₂ are given in **Table 3**.



Fig, 3. Effect of temperature on the sorption of H_2S and SO_2 of porous basalt fibers: a - H_2S adsorption; b - SO_2 adsorption; Temperature T=299 (1), 313 (2) ⁰C. Points –experiment, curve – calculation on Dubinin-Astahov equation

gases on porous basalt libres.					
Gas	Т, К	a ₀ , g/g	E, kJ/mol	n	
H_2S	304	0.723	4.375	1.00	
	320	0.401	4.186	0.87	
	335	0.355	4.465	0.93	
SO_2	299	0.356	7.095	1.14	
	313	0.273	7.001	1.30	

Table 3. Parameters of the Dubinin-Astahov equations calculated from sorption isotherms of gases on porous basalt fibres.

A model describing gas transport and sorption of hazardous compound was developed in order to characterize the planar sorbents. Two types of pores (macropores controlling the gas transport, and micropores controlling the sorption of hazarous components) were considered in the model. It was found that the gas transport and the heat flux conditions can be improved in the technological sorption modules using the planar sorbents.

Table 4. 2- Butanol adsorption capacities of basaltic sorbent.

Basaltic fibres					
Sample	Concent	Gas flow,	Breakthr	Amounts of	Capacity,
	ration,	mL/min	ough	adsorbate,	mg/g
	mg/mL		time, h	mg	
1	0.6486	50.336	1.10	2.155	26.033
2	0.6551	52.569	1.40	2.893	34.672
Average					30.353
Basaltic felt					
1	0.6573	54.508	2.70	5.804	63.087
2	0.6551	54.168	2.70	5.749	57.113
Average					60.100



Fig. 4 Thermoanalytical characterization of porous basaltic fibers heated in argon (heating rate 6 K/min): a) DTA (1), TG (2) and DTG - curve (3); b) Gas evolution method with mass-spectrometric detection; Curve 1 – thermodesorption of water; Curve 2 – released all gases and vapours.

Vapor of 2 – butanol used as test gas according to suitability of basaltic adsorbent for cleaning air from toxic hydrophilic organic substance. The experiment carried out on two samples: porous basalt fibers prepared in laboratory condition and industry porous basaltic felt. Isoterm adsorption measured by a chromatograph method, on column filled with basalt samples. Adsorption capacity measured on breakthrough time of test gas. Results are listed in **Table.4**.

4.4 Characterization of thermal stability of basaltic porous structure

(i) Thermal analysis.

TG/DTG and DTA results of the porous basalt fibers are shown on **Fig. 4a**. The sample was heated in argon up to 600 °C. In TG curve, continuous mass loss up to 800 °C was observed during the heating. This mass loss is due to the dehydration of the sample. As it can be seen from the TG/DTG curves (**Fig.4a**) registration, the water release took place in two subsequent steps. In the first step, physically adsorbed water was released from the sample surface with maximal mass loss rate at 90 °C. This stage of the dehydration was not accompanied be effect on the DTA curve. In the second step (250 - 450 °C) chemically adsorbed water, CO₂ and vapors of organic substances was released from pores. The destruction pores was reflected by the DTA curve as an slightly exothermic peak in the region 410 - 500 °C with maximum at 460 °C.

Sample	Stage	T_{min} , ${}^{0}C$	T_{max} , ^{0}C	Delta, %
1	1	20.8	185.9	-5.16
	2	186.2	549.7	-4.62
	In all	20.8	549.7	9.78
2	1	21.2	159.6	-8.29
	2	159.9	551.9	-6.32
	In all	21.2	551.9	14.61
3	1	21.0	192.3	-12.69
	2	192.3	545.5	-3.78
	3	21.0	545.5	16.47

Table 5.TG/DTG - effects for basaltic sorbents

Thermogravimetry method was used for investigated gas desorption from different basalt samples: fibres treated in laboratory condition (1), fibers treated in industry condition (2) and felt manufactured from porous fibers (3). Results are listed in **Table 5**. The TG/DTG method does not allow to determine composition of gases mixture escaping from solid during heating. For more detailed study of processes termostimulated gas release from virgin and treated basaltic fibers a thermodesorption method with mass- spectrometer detecting of gases was used. As an example, in the **Fig.4b** the curve temperature dependencies of rate of water release (curve 1) and all other gases and vapors (curve 2) from basaltic fibers, leached in laboratories conditions, are given. It is visible, that in a low temperature interval is water evolution, whereas other vapors are evolution mainly in a highly temperature interval.

(ii) Diffusion structural analysis

Thermal stability of macropores and micropores was determined experimentally by means of emanation-thermal analysis. The DSA was used for the characterization of morphology changes of the basalt sorbents under in-situ conditions of their heat treatment in argon in the temperature range 20-1300°C. The mathematical models were developed and used for the evaluation of the DSA results and their comparison with the results of other methods.

Virgin basaltic fibres.

In the course of heating of sample of virgin (initial) basalt the increase of radon release rate, E, observed in the temperature range 300-1350K (see curve 1 in **Fig. 5a**) can be considered as a consequence of temperature stimulated diffusion of radon-220 in near surface layer of non-porous basalt fiber. The decrease of radon emanation rate in temperature range 1400 - 1600K is directly related to sintering of fibres and decreasing of surface area available for radon evolution from solid. During the process of cooling the radon release rate monotonous decreased (Curve 2, **Fig.5a**).

DSA-results for virgin basaltic fibers were evaluated in the context of the model of parallel diffusion of radon on two independent channels with the subsequent sintering of fibers. The mathematical equation for the description of temperature dependence of radon evolution rate is:

$$\mathbf{E}(\mathbf{T}) = \left\{ \mathbf{P}1 * \exp\left(-\frac{\mathbf{P}2}{\mathbf{T}}\right) * \operatorname{Coth}\left[\mathbf{P}3 * \exp\left(\frac{\mathbf{P}2}{\mathbf{T}}\right)\right] + \mathbf{P}4 * \exp\left(-\frac{\mathbf{P}5}{\mathbf{T}}\right) \right\} * \left\{1 - 0.5 * \left[1 + \operatorname{erf}\left(\frac{\mathbf{T} - \mathbf{P}6}{\mathbf{P}7 * \sqrt{2}}\right)\right]\right\}$$
(6)

where
$$\mathbf{P}_1 = \frac{3\sqrt{\mathbf{D}_{01}}}{\mathbf{r}_0\sqrt{\lambda}}$$
; $\mathbf{P}_2 = \frac{\mathbf{Q}_{\mathbf{D}_1}}{2\mathbf{R}}$; $\mathbf{P}_3 = \mathbf{r}_0\frac{\sqrt{\lambda}}{\sqrt{\mathbf{D}_0}}$; $\mathbf{P}_4 = \frac{3\sqrt{\mathbf{D}_{02}}}{\mathbf{r}_0\sqrt{\lambda}}$; $\mathbf{P}_5 = \frac{\mathbf{Q}_{\mathbf{D}_2}}{2\mathbf{R}}$; $\mathbf{P}_6 = \mathbf{T}_{\mathbf{Sm}}$; $\mathbf{P}_7 = \sigma = \frac{\Delta\mathbf{T}_{\mathbf{S}}}{3}$

 D_{01} and Q_{D1} - are a pre-exponential factor and activation energy radon diffusion on lowtemperature range, respectively; D_{02} μ Q_{D2} - are a pre-exponential factor and activation energy radon diffusion on high-temperature range, respectively; T_{Sm} – temperature of the maximal of the sintering rate; ΔT_S – width of a temperature interval of sintering; r_0 – radius of fiber (As radon diffusion occurred an unbounded medium, at account occurred for r_0 length of a diffusion wave at maximal temperature of DSA-experiment, $r_0=10^{-4}$ cm), $\lambda=0.01272$ c⁻¹ – decay constant of radon-220.



Fig. 5 Diffusion Structural Analysis of basaltic fibers: a) Initial basalt; b) Basalt treated in HCl (porous basaltic adsorbent); Curve 1 – linear heating; Curve 2 – cooling.

The model assumes, that the experimental DSA-curve for virgin basalt reflects two processes: process I (temperature interval 200 – 800K), connected with radon thermodesorption from defects in the near surface layer (emanation power $E_1(T)$, and process II (temperature interval 800 - 1400K), connected with radon bulk diffusion on basalt lattice (emanation power $E_2(T)$). The modeling curve, E(T), represents as the sum: $E(T)=E_1(T)+E_2(T)$

In turn functions $E_1(T)$ and $E_2(T)$ are entered as product of two functions $D_i(T)$ and S(T):

 $E_1(T)=D_1(T)*S(T)$ and $E_2(T)=D_2(T)*S(T)$

Function $D_i(T)$ reflects temperature dependence of radon diffusion considering Arhenius law: $D_1(T)=D_{10}exp(-Q_1/RT);$

 $D_2(T) = D_{20} exp(-Q_2/RT).$

The functions D_1 and D_2 are characterized own activation energy of migration, Q_1 and Q_2 , resp. and the function S(T) is identical to both processes. The function S(T) reflects process of sintering of fibers. As the first approach believed, that the function kinetic of

sintering is symmetric and can be described by the integral Gauss function expressing changes of the surface area upon heating as an S-like curve

$$\mathbf{S}(\mathbf{T}) = \mathbf{S}_0 * \{1 - 0.5 * [1 + \mathbf{erf}(\mathbf{z})]\}$$

$$\mathbf{T} - \mathbf{T}_{\mathbf{m}} \qquad \Delta \mathbf{T}_{\mathbf{m}} = \mathbf{T}_{$$

where $\operatorname{erf}(\mathbf{z}) = (2/\pi^{1.2}) \int_{0}^{1} \exp(-\mathbf{z}^{2}) d\mathbf{z}$, $\mathbf{z} = \frac{\mathbf{z} - \mathbf{m}}{\sigma * \sqrt{2}}$, $\sigma = \frac{\Delta \mathbf{z}}{3}$, T is the temperature corresponding to the maximal rate of the S(T) change. AT is width of the temperature range is

corresponding to the maximal rate of the S(T) change, ΔT is width of the temperature range in which S(T) takes place.



Fig. 6 Experimental DSA results (points) compared with the DSA results of the mathematical modeling (curves 1 - 6) of the radon release from virgin basaltic fibers

The modeling of the DSA curve enabled us to obtain kinetic parameters characterizing the radon release from the non-porous basalt. The parameters used in the modeling are summarized in **Tables 6 and 7**. **Fig. 6** presents the experimental DSA results for heating of virgin basaltic fibers (points) as well as the results of the modeling. Curve 1 corresponds to the model DSA curve in the all temperature range 200 – 1600K. Curves 2 and 3 corresponds to model DSA curve ($E_1(T)$) for process I and to model DSA curve ($E_2(T)$) for process II, resp. The curves 4 and 6 describe temperature dependencies of $D_1(T)$ and $D_2(T)$, resp. Curve 5 is diffusion emanation power, $E_{D1}(T)$. Curve 7 in **Fig. 6** is derivatives of S-like shape functions describing the change of surface area of the virgin fibers on heating in the temperature intervals where the sintering of fibers take place.

The comparison of an experimental DSA-date with modeling curve demonstrates, that the offered model well describes experimental results in all the investigated interval of temperatures.

On **Fig.7a** the individual DSA-peak for low-temperature process I in virgin fibers (curve 1) and its components are submitted: D(T) (radon permeability of transport paths) and S(T) (number of transport paths for radon). On **Fig.7a** the structural function is submitted as dS(T)/dT, i.e. as derivative from S(T) on temperature. This function represents kinetic of fibres sintering. Thus, the **Fig.7** allows to compare kinetics of three processes: emanation, diffusion and sintering. The similar curves for high-temperature process II in virgin fibers are shown in a **Fig.7b**.

Basalt Initial Heated P1 P2 P3 P4 P5 P6 P7	186.59 138.76 0.146 18126 4899 1552 60	$\begin{array}{c} D_{10}=4.9*10^{-7} \ cm^{2}/s \\ Q_{D1}=2.27 \ kJ/mol \\ D_{20}=3.4*10^{-4} \\ Q_{D2}=81.41 \ kJ/mol \\ T_{m}=1552 \ K=1279^{\circ} \ C \\ dT=60^{\circ} \end{array}$	Basalt Leached P1 P2 P3 P4 P5 P6 P7 P8	$\begin{array}{c} 312.5\\ 327.3\\ 0.111\\ 1.04^{*}10^{5}\\ 1.05^{*}10^{4}\\ 848.4\\ 190\\ 9.18^{*}10^{6}\\ \end{array}$	$\begin{array}{c} D_{10}=1.38*10^{-6} \text{ cm}^{2}/\text{s}\\ Q_{D1}=5.4 \text{kJ/mol}\\ D_{20}=1.53*10^{5}\\ Q_{D2}=175 \text{ kJ/mol}\\ T_{m}=848 \text{K}=575^{\circ} \text{C}\\ \text{dT}=190^{\circ}\\ D_{30}=1.19*10^{3} \end{array}$
			P9	143911	Q _{D2} =239kJ/mol
Cooling P1 P2	2552 3949	$D_{C0}=9.2*10^{-5}$ $Q_{CD}=65.63$ kJ/mol	P1 P2	1.74*10 ⁵ 7963	D _{C0} =0.43 Q _{CD} =132.3kJ/mol

Table 6. Parameters characterising the processes of diffusion and sintering (determined byDSA) of initial and chemically leached porous basalt fibres

 Table 7. Parameters characterising thermal behaviour (determined by DSA) of the porous basalt fibre planar sorbent

Basalt	Basalt
initial,	Leached,
heating	Heating
$T_{m1} = 1382K = 1112^{\circ}C$	$T_{m1} = 657 K = 384^{\circ} C$
A _{m1} =1055	A _{m1} =889
T _{m2} =1462K=1189 [°] C	$T_{m2} = 1082 K = 809 C$
A _{m2} =593	A _{m2} =678
$T_{s}=1552K=1279^{\circ}C$	$T_{s}=848K=575^{0}C$
φ=4.85	φ=1.986
φ ₁ =0.829	φ ₁ =0.665
φ ₂ =0.171	φ ₂ =0.335

Parameters calculated from ETA – curve of virgin basaltic fibers listed in Table 6.



Fig. 7 Model DSA curves describing individual processes taking place on heating of the virgin basaltic fibres: a) Process I; b) Process II; Curve 1 – radon release rate; Curve 2 – radon diffusivity; Curve 3 – sintering rate.

Porous basaltic fibers.

Fig.5b shows the DSA results of basaltic fibers treated in HCl. The increase of radon release from porous basaltic fibers, observed in the temperature range 300-600K (see curve 1

in **Fig. 5b**) can be considered as a consequence of water release from the sample surface. On further heating from 600 to 1000K the radon release rate increased slowly characterizing the process of dehydration. On the sample heating above 1000 $^{\circ}$ C the collapse porous structure and sintering of fibres took place leading to the decrease of surface area. The process sintering ends under temperature 1350K. The heating after temperature 1400K involves an increase radon release rate as a consequence of temperature stimulated diffusion of radon-220.

The wide effect on the DSA-curve for porous basalt can be spread out on three elementary components. The first DSA-peak is connected with process of water escape from sample. At the further heating the radon flux from a material increased because of growth of diffusivity. However on this process is imposed other process - destruction of porous structure. The process of porous collapse results in reduction of a surface and, hence, causes essentially decreased of radon evolution rate. The total effect results in occurrence the second peak on the DSA-curve. The processes resulting in occurrence on DSA-curve of the third high-temperature peak are similar to second, but here decreasing the emanation power after short-term growth occurs because of reduction of a surface caused by sintering of fibers. At temperatures is higher 1350K radon evolution rate begins to be increased on the monotonous exponential law.



Fig. 8 Experimental DSA results (points) compared with the results of the mathematical modeling (curves 1 - 11) of the radon release from leached basaltic fibers.



Fig. 9 Temperature dependence of "structural function" for DSA of porous basaltic fibers: a) Integration form; b) Differential form; Curve 1 – process I; Curve II – process II; Curve III – process III.

A mathematical model was proposed for a more detailed description and evaluation of the processes characterized by DSA. The principles of the mathematical modeling are described here below. The modeling of the DSA curve enabled us to obtain kinetic parameters characterizing the radon diffusion from the porous basalt.

The model assumes, that the experimental curve reflects four processes: peak 1+peak 2+ peak 3+ exponential function. Process I (temperature interval 200 - 600K), connected with water thermodesorption (emanation power $E_1(T)$), process II (temperature interval 600 - 1000K), connected with radon termodesorption from microporous and subsequent collapse of porous structure (emanation power $E_2(T)$), process III (temperature interval 1000 - 1350K) connected with thermostimulated radon released from solid and subsequent sintering of fibers (emanation power $E_3(T)$, and process IV (temperatures above 1400K) connected with radon bulk diffusion on basalt lattice (emanation power $E_4(T)$. The modeling curve, E(T), represents as the sum:

$E(T)=E_1(T)+E_2(T)+E_3(T)+E_4(T)$

Function $E_i(T)$ for i = 1,2 or 3 is entered as product of two functions $D_i(T)$ and $S_i(T)$: $E_1(T)=D_1(T)*S_1(T), E_2(T)=D_2(T)*S_2(T)$ and $E_3(T)=D_3(T)*S_3(T)$,

where $D_1(T)=D_{10}exp(-Q_1/RT)$; $D_2(T)=D_{20}exp(-Q_2/RT)$, $D_3(T)=D_{30}exp(-Q_3/RT)$, $E4(T)=D4(T)=D_{30}exp(-Q_3/RT)$, $S_1(T)$, $S_2(T)$ and $S_3(T)$ are S-like shape function (Gauss law). S_1 – function of cover of surface by water, S_2 - function for pours collapse, S_3 - function for sintering fibers.

Fig. 8 presents the experimental DSA results for heating of initial basaltic fibers (points) as well as the results of the modeling. Curve 1 corresponds to the model DSA curve in the all temperature range 200 – 1600K. Curves 2, 3 and 4 corresponds to model DSA curve ($E_1(T)$) for process I, model DSA curve ($E_2(T)$) for process II, and model DSA curve ($E_3(T)$) for process III, resp. The curves 8, 9, 10 and 11 describe temperature dependencies of $D_1(T)$, $D_2(T)$, $D_3(T)$ and $D_4(T)$ resp. Curves 5, 6 and 7 are derivatives of S-like shape functions describing the change of surface area of the sample on heating in the different temperature intervals.

It follows, that a good agreement between experimental and theoretical results was obtained.

The temperature dependencies of structural functions are submitted in the **Fig.9a** and (integrated form) and **Fig.9b** (differential form). It is visible, that the maximal rates of change of a surface accessible to allocation of gas, for processes I and II are achieved practically at one temperature, whereas, maximal speed of sintering of fibers (the process III) is achieved at more highly temperature. The greatest intensity characterizes structural process III.

Two processes taking place during the cooling were observed (Curve 2, **Fig.5b**). The first one is attributed to volume radon diffusion (range temperatures 1550 - 1050K), second one is recoil emanation (range temperatures 1000 - 300K).

The parameters characterizing the basalt porous fibers planar sorbents were calculated from the DSA experimental results (see **Table 7**).

4.5 Optimization of the regeneration of the basalt sorbents.

Surface area measurements and scanning electron microscope were used for the direct characterization of "as virgin" and "as leached" basalt sorbents.

Temperature range suitable for the regeneration of the chemically treated basalt planar sorbent was determined. SO_2 and H_2O were used as adsorbtive. It was found that the temperature necessary for the regeneration of the porous basaltic sorbents is by 100 - $200^{0}C$ lower than that for natural zeolites. A significant energy saving can be achieved in the industrial scale, when using the planar sorbents units made of porous fibers.

In the study of the thermally stimulated release of H_2S from basalt fibers treated in two steps by HCl solutions the radioactive tracer method was used. The H_2S was labeled with ³⁵S. It was found that the character of the thermal desorption spectrum of $H_2^{35}S$ depends on the presence of water traces in the basalt porous fiber (**Fig.10**).



Fig. 10 Experimental $H_2^{35}S$ thermostimulated release curve for porous basaltic fibers, modelling curves, and difference between an experimental and theoretical curve: a) - Evolution H_2S in absence of water, b)- Evolution H_2S at the presence of water. 1 - experimental data, 2 - theoretical curve, 3, 4 - contributions the single a component, 5 - difference between curves 1 and 2, On a vertical - flux, rel. units, on horizontal - T, K



Fig. 11 Thermodesorption gases and vapours from basaltic industry leached fibres: H_20 -evolution; Evolution substances with M = 39 - 92 (M=48 - CO₂, M=92 - toluene).

For definition of optimum conditions of sorbents regeneration, studied processes of gas release from porous basaltic fibers for a long time stored in atmospheric air. Samples placed in the vacuum equipment and heated up. Composition of evolved gases determined by a mass-spectrometry method. Typical thermodesorption spectrum is given in a **Fig.11**. The gas evolution passes in two stages: in an interval of temperatures 80-150^oC water, vapors of some substances and partially carbonic gas escapes from solid. In an interval of temperatures 400-500 ^oC released CO₂ and vapors of organic substances (for example, toluene).

The temperature range suitable for the regeneration of the basaltic sorbents was determined. The temperature necessary for the regeneration of the basaltic sorbents is by 200°C lower than that for natural zeolites. Consequently, the significant energy saving can be achieved in the industrial scale, when using in the sorption modules the planar sorbents made of the chemically treated basalt fibers. Moreover, the DSA was used for the determination of the temperature range in which the porous materials are thermally stable. It was determined by the DSA that the porosity collapse of the chemically treated basaltic fibrous planar sorbents takes place in the temperature range of 800-1100°C. In this temperature range the encapsulation of hazardous elements in the porous basalt can be achieved.

4.6 Operational characteristics basaltic planar sorbents.

The porous structure of basaltic fibers begins to collapse at temperatures about 500° C. At temperatures up to 450° C adsorbent keeps serviceability for a long time.

For definition of the operational characteristics new fibrous sorbents the tests of their mechanical properties in a mode repeated thermocycles were carried out. The working elements on base of leached basaltic fibers subjected to cycles adsorption - regeneration in a temperature interval $-10 - 300^{\circ}$ C. It is revealed, that 1000 cycles do not render appreciable influence on mechanical properties of sorbents. Some attributes of change of mechanical durability of a fiber are shown after 2000 cycles. After 2500 cycles is formed a fine powder (in amount 10 weights %). Adsorption characteristics of the filter are worsened on 7 % after 3000 cycles of heating and cooling.

Thus, it is possible to recognize the operational characteristics porous basalt fibers satisfactory: they are at a level traditional industrial sorbents.

4.7 Diagnostic of basaltic adsorbent bad.

Planar adsorbents allow to realize the various circuits of spatial organization of transport processes in the adsorption equipment. Depending on a way of stacking generated as felts, cardboard etc. of adsorbent bad and direction of gas flux, the transport mechanism of an adsorbtive inside a sorbent bad can be as only diffusion (at current of gas along regular layers), and mixed convection - diffusion (at filtration of gas through layers). In the first case the major characteristic of adsorption system determining of kinetic of process, alongside with sorption isoterm is effective diffusivity D of an impurity through a sorbent bad.

(i) Adsorbent bad design.

Adsorption working elements on base of basaltic treated fibers represented:

1) Tissue from treated basalt fibers of various thickness

2) Tissue with variable alternation of virgin and leached basalt fibers, that provided the increased durability adsorbent.

3) Basalt wool compressed on half of its initial volume

4) Felt received by pressing of basalt wool up to pressure 500 kg*cm⁻²

5) Cardboard received by pressing of felt up to pressure 10 ton*cm⁻²

The working elements represented adsorbent, was placed between plates from porous ceramics. The elements had as flat form, and form of hollow cylinder.

(ii) Gas transfer characterisation of basaltic adsorbent bad.

Diagnostics of adsorption elements on the basis of a porous basaltic fiber carried out on SO_2 and H_2O . The filtration module allowing to determine of the transport characteristic of felt in a mode as diffusion, and filtration permeability (**Fig. 12**) was designed [**11**]. During experiment the control of difference of gas pressure on an input and output of the module, the volumetric flow of gas, density of packing of adsorbent and temperature in several points of sample surface carried out. Besides the filtration module, the equipment for definition of the transport characteristics planar adsorbents included differential gauge, the system of gas mixture on input module and the block of chromatographic detecting of the composition of a gas mixture on an output of the filter.

Diffusion experiments carried out at a room temperature on a sample of felt in diameter of 41 mm and thickness of 6 mm, with apparent density ρ =0.25 g/cm³. Before experiment a sample recycled within one hour at temperature 420K in a current of dry argon. After end of regeneration of sample in module was created flows of the gas-carrier (argon) both through the reservoir, and through the receiver. To some moment of time t₀ in the reservoir submitted a flow SO₂. Composition of a gas mix varied from 20 up to 40 vol. % SO₂.

The gases flows were selected by such, that the difference of pressure on the filter measured on differential gauge, was equal to zero. The SO_2 on an output from the module was detected, with automatic gas sampling through an interval of time by 1 mines.



Fig. 12 The schematic design of adsorption module: 1 - metallo-ceramic porous plate, 2 - heater, 3 - sorbent sample, 4 and 5 - plates for pressing of basaltic wood, 6 - lead-in of a cables for thermocouple and heater, 7 - flange, I – Stainless steel, II - Teflon

SO₂ diffusion permeability through basaltic planar adsorbent

At diffusion mode of experiment, the flux of SO_2/Ar -mixture on the entrance surface of the filter and the flux of Ar on the output surface of the filter chosen so that the difference of pressure on a working element was equal to zero (a membrane mode of experiment).

As was shown above, SO₂ adsorption on porous basaltic fibers is adequately described Dubinin-Astahov law at values of a parameter n by this isoterm close to unit ($n\approx1$). If n=1 we can used much more simple isoterm sorption – Freindlich isoterm, which is a special case Dubinin-Astahov isoterm at a parameter n=1:

$$a = kc^{m}$$

The processing of equilibrium experimental data on this isoterm has given the following values of parameters: k=0.23, m=0.43.

Kinetic model of gas diffusion through a fibrous material accompanying quasiequilibrium chemosorption on internal pores of fibers, in the assumption, that adsorbate is much greater adsorbtive, is described by the equations:

$$\rho \frac{\partial \mathbf{a}}{\partial t} = \mathbf{D} \frac{\partial^2 \mathbf{C}}{\partial \mathbf{x}^2}, \quad \mathbf{a} = \mathbf{k} \mathbf{c}^m,$$

$$\mathbf{C}(\mathbf{x}, \mathbf{t} = \mathbf{t}_0) = \mathbf{0},$$

$$\mathbf{C}(\mathbf{x} = \mathbf{0}, \mathbf{t} > \mathbf{t}_0) = \mathbf{C}^*$$

$$\mathbf{C}(\mathbf{x} = \ell, \mathbf{t} \ge \mathbf{t}_0) = \mathbf{C}^{**}(\mathbf{t})$$

$$\mathbf{V} \frac{\mathbf{d} \mathbf{C}^{**}}{\mathbf{d} \mathbf{t}} = -\mathbf{D} \mathbf{S} \frac{\partial \mathbf{C}}{\partial \mathbf{x}} \Big|_{\mathbf{x} = \ell} - \upsilon \mathbf{C}^{**}.$$

where a(x,t) - a mount of gas adsorption in internal pores of fibers, mole/g; C(x,t) - volumetric concentration of non-adsorbed gas in external porous space between fibers, mole/cm³; C* - initial concentration of gas in a reservoir; C** (t) - concentration of gas in a receiver; D - effective diffusivity, cm²/s; ρ - apparent density of a fibrous material; δ - thickness of a layer of adsorbent; x - distance from an entrance surface of a basaltic bad; S – surface area of the filter; t - time; t₀ - time of an establishment of a rectangular concentration signal in a reservoir; V - volume of the receiver; G - volumetric flow of the gas - carrier in the receiver.



Fig. 13 SO₂ permeability through basaltic felt (Membrane mode of experiment): Points – experimental dates, curve – theory. Parameters of model: $c^{*}=6,2^{*}10^{-6}$ mole/cm³, D=0,012 cm²/s, V=387 cM³, v=80 cm³/min, t₀=0 min (I), and $c^{*}=1,2^{*}10^{-5}$ mole/cm³, D=0,020 cm²/s, V=330 cm³, v=85 cm³/min, t₀=2,3 min (II).

The advanced model describes experimental data to a high degree approximation (**Fig.13**). The average value D for of kinetic curves was found to be $0,012 \text{ cm}^2/\text{s}$. The experimental value are less than expected SO₂ diffusivity in argon (0,11 cm²/s) calculated on the basis of the molecular-kinetic theory by factor 10. Since total porosity of felt (including meso- and micropores of fibers) is equal 0.87, the decrease of diffusivity is explained by two causes: 1) the through porosity of a felt is only a slight part of total porosity; and 2) the tortuous of transport pores is substantially higher.

Dynamics of SO₂ permeability through a layer of basaltic fibrous adsorbent.

The dates necessary for designing of adsorption apparatus of regular structure, were derived from experiments on study a dynamic of active filtration through a layer planar adsorbent [12,13].

The apparatus with planar porous adsorbent provides a possibility to choosing a type of regular packing adsorbent and, hence, a possibility to management of convection transport of separated substances. The filtration through layers of a porous felt represents two levels structure of transport which is carried out both on meso-pores of a fiber, and on macro-pores of felt. Increasing the total area of gas filtration through a material, it is possible to achieve rather low rate of filtration (at the high flow of gas through active filter). This brings the gases separation process to quasi-equilibrium sorption condition.

During experiment at first established the certain of argon flow through the filter, and then to a module entrance submitted SO_2 , creating in reservoir a gas mixture with

concentration 3 vol. % SO₂. In filtration mode in the receiver did not submit an auxiliary flow of the gas - carrier.

Adequate description of gas filtration through a layer of porous felt required development of new detailed model of sorption dynamics. Several dynamic parameters has to be taken into account. Believed, that the equilibrium in given adsorption system is described Freindlich isoterm. For the description of dynamics of absorption of an impurity in a filtrating adsorbent bad the following variants of models are proposed:

1. Equilibrium convection-diffusion model describing the migration of adsorbtive as process of convection diffusion through a fibrous material, accompanied quasi-equilibrium sorption in internal pores of fibers (Model I).

2. None-equilibrium model of ideal replacement (Model II).

3. Model of ideal replacement with the variously accessible adsorption centers (Model III).

Data treatment has shown, that the model III best describes permeability of gas through the active filter. Deviations experimental date from curves designed on simple models with unique kinetic parameter, is demonstration non-uniform character mass-transfer between adsorbtive and porous fibers. The reason of this non-uniformity consists in heterogeneity of porous structure, a consequence that is the heterogeneity of a field of filtration rates through felt and distinction in diffusion availability of different adsorption sites. Certain of the sorption active centers positioned near to basic transport pores. Its are rather easily accessible for gases. Therefore process of adsorption on such centers occurs very quickly, quasiequilibrium. Other centers are removed from basic transport pores, and mass- exchange to these centers occurs more slowly, none-equilibrium. The centers of the first type define in the basic initial stage of adsorption process, and the centers of the second type define process adsorption at the large times. At creation of model III assumed, that adsorption equilibrium on the centers of two types is described same isoterms.

The equations of such model look like:

$$\delta \rho \frac{\partial \mathbf{a}_1}{\partial t} + (1 - \delta) \rho \frac{\partial \mathbf{a}_2}{\partial t} = -\frac{\mathbf{G}}{\mathbf{S}} \frac{\partial \mathbf{C}}{\partial \mathbf{x}}, \quad \mathbf{a}_1 = \mathbf{k} \mathbf{C}^{\mathbf{m}},$$

$$(1 - \delta) \rho \frac{\partial \mathbf{a}_2}{\partial t} = \beta \left(\mathbf{C} - \left(\frac{\mathbf{a}_2}{\mathbf{k}} \right)^{1/\mathbf{m}} \right),$$

$$\mathbf{C}(\mathbf{x}, \mathbf{t} = 0) = 0; \quad \mathbf{a}_2(\mathbf{x}, \mathbf{t} = 0) = 0,$$

$$\mathbf{C}(\mathbf{x} = 0, \mathbf{t} > 0) = \mathbf{C}^*,$$

$$\mathbf{V} \frac{\mathbf{d} \mathbf{C}^{**}}{\mathbf{d} \mathbf{t}} = \mathbf{G}(\mathbf{C}(\mathbf{x} = \ell) - \mathbf{C}^{**}),$$

$$\mathbf{C}^{**}(\mathbf{t} = 0) = 0,$$

where $a_1(x, t)$ is equilibrium gas adsorption on the easily accessible centers, a(x, t) - is noneequilibrium gas adsorption on other centers, β - coefficient mass-transfer, s⁻¹. All other parameters are determined above. Amount adsorbate in the immobilization form assumed considerably large, than in the mobile form, i.e. a(x, t) >> C(x, t). The mode of ideal mixture of gas in the receiver is supposed.

Average values of parameters of models 3 designed from experimental data:

δ=0.28; =0.15; k=0.17; m=0.45.

The found values of parameters agrees well with their equilibrium values.

Dynamics of H₂O filtration through a layer of basaltic felt

Study of adsorption dynamics of water vapor carried out on apparatus allowing to release as drying of a gas flow, and adsorbent regeneration at a variation apparent ("bulk") density of a layer basalt wood by change of a degree of compression. During experiment

registered rate of a flow through the filter, humidity of gas on an entrance and exit of the filter, difference of pressure on the filter and temperature of the filter. During experiment registered a curve of dependence of humidity of a departing gas flow from time.

 H_2O adsorption isoterm on porous basalt fibers submits Langmuir law. Adsorption isoterms data have Type I characteristics. A Type I isoterm is obtained if the sample is a microporous material and is therefore characterized by a rapid rise in the volume adsorbed at very low relative pressures values. The mainly assumption with the Langmuir calculation is that only a monolayer is formed.

For realization of dynamic experiments used basalt wool, having the following parameters Langmuir isoterm sorption: $a_{\infty} = 8.6 \times 10^{-3} \text{ mole/g}$, $K=1.9 \times 10^{-3} \text{ mole/cm}^3$. The permeability curves of water vapor for three samples by values of "bulk" density of a layer $\rho = 0.23$, 0.36 or 0.43 g/cm³ in a range of change of the air volumetric flow 25 - 100 cm³/min were measured.

Processing results carried out within the framework of model of ideal replacement of gas in a adsorbent bad with the adsorption centers of a various degree of availability:

$$\delta \rho \frac{\partial \mathbf{a}_1}{\partial t} + (1 - \delta) \rho \frac{\partial \mathbf{a}_2}{\partial t} = -\frac{\mathbf{G}}{\mathbf{s}} \frac{\partial \mathbf{C}}{\partial \mathbf{x}}, \quad \mathbf{a}_1 = \frac{\mathbf{a}_\infty}{\mathbf{K} + \mathbf{C}},$$
$$(1 - \delta) \rho \frac{\partial \mathbf{a}_2}{\partial t} = \beta \left(\mathbf{C} - \frac{\mathbf{a}_2 \mathbf{K}}{\mathbf{a}_\infty - \mathbf{a}_2} \right),$$
$$\mathbf{a}_2 (\mathbf{x}, \mathbf{t} = 0) = \mathbf{a}_0, \qquad \mathbf{C} (\mathbf{x}, \mathbf{t} = 0) = \frac{\mathbf{a}_0 \mathbf{K}}{\mathbf{a}_\infty - \mathbf{a}_0}$$
$$C(\mathbf{x} = 0, \mathbf{t}) = \mathbf{C}^*$$

where $a_1(x,t)$ - equilibrium adsorption on the easily accessible centers, mole/g; $a_2(x,t)$ – nonequilibrium adsorption on less accessible centers; C(x,t) - volumetric concentration of nonadsorbing gas in externally porous space between fibers, mole/cm³; a_0 - residual amount adsorbing substance after regeneration of adsorbent before realization of dynamic experiment; C_0 - equilibrium with a_0 initial concentration of gas; C* - concentration of gas on an entrance filter; ρ - apparent density of a fibrous material ("bulk" weight), g/cm³; a and K - parameters of Langmuir isoterm.

The model contains parameters C_0 , C^* , G, S, which can be measured directly at realization of experiment; the isoterms parameters a_{∞} and K, which can be independently found from equilibrium experiments, and also effective macro-kinetic parameters δ and β , determined only during the decision of the appropriate task at evaluation experimental curves.

The results of evaluation of experimental curves are given in Table 8.

ρ,	G, 3	$a_{x}x10^{2}$,	$\mathrm{Kx10}^{7}$,	δ	β, s^{-1}
g/cm ³	cm /min	mole/cm ³	mole/cm ³		
0.23	25	1.0	3.5	0.19	0.046
	50			0.19	0.13
	100			0.14	0.35
0.36	25	1.0	2.7	0.15	0.071
	42			0.14	0.11
	100			0.15	0.32
0.43	25	1.1	6.9	0.29	0.075
	50			0.25	0.17
	100			0.28	0.17

Table 8. Parameters designed at processing of curves of permeability of water through felt manufactured from of porous basaltic fibres



Fig. 14 Water vapours filtration through basaltic porous felt (filtration mode of experiment). Points – experiment, curve – theory. Parameters: $\rho=0,23$ r/cm³, G= 25 (1), 50 (2) and 100 (3) cm³/min.



Fig. 15. The dependence of coefficient of mass-transfer β from linear rate of gas in the experiment on the study filtration H₂O (curve 1) and SO₂ (curve 2) through basaltic porous felt.

In a Fig. 14 the experimental and modeling curves for a sample of basaltic porous felt with "bulk" weight ρ =0.23 are represented.

The experiments have not revealed appreciable influence of a degree of compression of a fibrous material on kinetic parameters of model. Mass-transfer coefficient β grows with increase of linear rate of a flow (**Fig. 15**). It is unaffected by ρ . For waters vapor the average value δ for three investigated samples is equal 0,20.

4.8 Immobilization of radionuclides with help porous basaltic fibers.

In present study the prospects of use of basaltic porous fibers for vitrification radioactive metals are investigated. In a course experiment a 226 Ra- solution in water passed through a layer of basaltic felt. Filter dried, and then was heated at temperature 550^oC within 3 hours. Efficiency encapsulation radium in a SiO₂-matrix supervised by measurement of emanation ability on 222 Rn. For testing durability of this glass towards hydrolytic corrosion, basaltic fibers containing Ra-Rn were leached in acids or alkalis. An essential escape radium it is not revealed. Use of porous fibers allows to receive a fibrous material containing an enough high amount of isotopes, at rather low temperatures thermal treatment. At more temperatures (1000^oC) fibers sintering with formation of a compact material. It is obviously possible to recommend porous basalt fibers as the SiO₂ matrix for hazardous waste immobilization.

5. Charcoal fibrous planar sorbents.

5.1 Preparation of charcoal fibers and tissue

Planar sorbents made of charcoal fibers (diameter 20 microns) and tissue were prepared to be used as sorbents for vapors of organic substances. The charcoal fibers were manufactured by the heating of polymers at high temperatures without access of air. The pore surface of the charcoal fibers increased when the products were processed by the hot water vapors [14,15].

5.2 Sorption properties of charcoal fibers

Surface area and microstructure of the charcoal fibers prepared under optimized conditions were determined by means of nitrogen sorption measurement and scanning electron microscopy. The sorption isotherms for vapors of dichlormethan, 2-butanol, and toluene on the planar charcoal fibrous sorbents were measured and the respective sorption capacities were determined (See **Table.9**)

compounds			
Compound	Sorption capacity		
	[mg/g]		
Dichlormethan	57.03		
2-Butanole,	112.4		
Toluene	129.1		

Table 9. Adsorption capacities of charcoal fibrous sorbent for three organic volatile

As follows from **Table 9** equilibrium adsorption capacity of charcoal fibers is comparable to capacity best granular coal sorbents, but dynamic adsorption capacity is obviously higher at coal fiber in comparison with granular sorbents.

5.3 Characterization of thermal stability of charcoal fibers.

(i) Thermal analysis

For the additional characteristic sorbent methods of the thermal analysis: DTA, TG, DTG and thermostimulated gas evolution (with a mass - spectrometer detecting of gases, escaped from a sample) were used. The analysis was carried out in a regime of linear heating in an atmosphere of nitrogen. Heating rate is 5^{0} C/min. Interval of temperatures is $20 - 550^{0}$ C.



Fig.16 Thermal analysis of charcoal porous fibers: 1 – TG; 2 – DTG; 3 – DTA.

Process	T _{min} , C	T_{max}^{0}, C	ΔΜ, %
	TG		
1	21.6	165.7	-9.23
2	165.7	528.8	-1.43
	DTG		
	78		
	DTA	80.8	

Table 10. Results of thermoanalysis of charcoal fibers

The DTA, TG and DTG curves of charcoal fibers are given in a **Fig. 16**, the parameters of main effects are assembled in **Table 10**. The appreciable loss of weight (evolution H₂0 vapor) occurs at temperatures $50 - 90^{\circ}$ C, and some decreasing of weight monitoring in a wide interval of temperatures with peak at 400°C, connected with evolution of CO₂ (is possible because of oxidation coal by traces of oxygen in nitrogen). The DTA-curve registers exo-effect at 100° C and endo-effect at 450° C.

(ii) Diffusion structural analysis of charcoal fibers.

The experiments carried out with charcoal fibers by a diameter 20 microns, are fabricated by application of pyrolysis of polymeric fibers without access of air with the subsequent processing of a graphite product to the hot water vapor with the purpose of development of a high specific surface. Fibers processed in a powder. An equilibrium mix Th and Ra entered into a material by a method of impregnation. DSA-curve was recorded in regime of linear heating (rate of heating 5 $^{\circ}$ C/min) and subsequent cooling of a sample in an atmosphere argon. Two consecutive heating run of the same sample (first heating - up to 500 $^{\circ}$ C, second - up to 750 $^{\circ}$ C) were carried out.

DSA-curves of heating (both first, and second) had the S-like form ("effect of exhaustion") characteristic for material with high emanation ability (**Fig. 17**). At cooling after the first heating, rate radon evolution decreases on curve, convex concerning an axis of temperatures. Thus the curve of cooling lays above by curve of heating. The cycle has resulted heating - cooling in essential (three times) increase of emanation ability coal at a room temperature.

The given example evidently demonstrates opportunities of a DSA from the point of view of diagnostics of process of development transport pores and their clearing of a various sort of impurity, adsorbing on their surface. It is known, that in pores charcoal, taking place the long time in contact to atmospheric air, is present significant amount of various substances retarded the radon diffusion. During heating in an atmosphere of dry inert gas (argon) adsorbed vapors escaped and the effective surface accessible for radon diffusion increased, as is shown in increase of emanation ability charcoal.

The parameters of radon diffusion in charcoal fibers calculated from the experimental DSA curve are given in **Table 11**. It is obvious that after heating of charcoal fibers up to 500^{0} C the activation energy of radon diffusion (Q) has decreased more than twice (from Q = 8.3 up to Q=1.8 kJ/mole, resp.), which indicated that radon diffusion on open pores was enhanced. Simultaneously, the value pre-exponential factor of radon diffusion was enhanced (from D₀=0.017 up to D₀=0.29 cm²/s), that apparently corresponds to the increase of number of transport paths during thermal treatment. The optimized conditions for preparation and further treatment of the planar sorbents based on porous charcoal fibers were recommended.



Fig. 17. Experimental DSA results (points) compared with the results of the mathematical modeling (curves 1 - 4) of radon release from charcoal fibers: Curve 1 - first heating; Curve 2 - first cooling; Curve 3 - second heating; Curve 4 - second cooling

Regime of thermo	А	D cm/s	Q, kJ/mole
treatment		$D_0, cm 75$	
First heating	1.47×10^{4}	0.017	8.35
First cooling	2.46×10^{3}	0.029	1.82
Second heating	89	0.324	2.64
Second cooling	525	6.675	59.64

Table 11. Radon diffusion parameters in charcoal fibers.

During the second heating of charcoal fibers up to 750° C emanation ability in all range of temperatures remains rather high. The rate of change of radon rate evolution during heating is significant at low temperatures, but in range of high temperatures essentially decreases, so in the field of temperatures 400-500°C the rate of radon evolution practically does not depend on temperature, and is higher 700° C even decreases a little. The energy of activation radon diffusion during the second heating is much higher, than during first, but is a little bit higher, than was during the first cooling. Thus pre-exponential factor of diffusion has grown more, than on the order.

The results show, that during the second heating is achieved high emanation ability, at which mask solid-state processes connected to reorganization of porous structure of adsorbent (effect of "exhaustion" - all formed radon-220 during life, formed, to escape from a sample). The reduction of bandwidth of the transport channel at high emanation ability not affected on form DSA-curve (as it would be at low values of emanation ability), as all volume of a material is accessible for diffusion. The pores reorganization, occurring during thermal processing, resulting to reduction of an effective diameter of pores, is expressed not in fall radon evolution rate (though at the end of heating emanation ability nevertheless begins to fall), and in increase of effective energy of activation of radon diffusion.

The made conclusion about process of intensive reorganization of pores system in charcoal fibers occurring in a narrow interval of temperatures $(700 - 750^{\circ}C)$ during the second heating and proceeding during subsequent cooling, verified by result of mathematical treatment of a DSA-curve of the second cooling. This curve has typical for bulk diffusion on a nonporous material the exponential shape, that distinguishes it from three previous curves

having the shape, characteristic for emanation ability high porous material (the similar curves are always convex concerning an axis of temperatures). The energy of activation of radon diffusion at the second cooling essentially has increased and has reached value Q=59.6 kJ/mole, that specifies sintering pores, resulting to reduction of an effective diameter pores (macro- and mesopores pass in micropores). Simultaneously growth the value pre-exponential factor of radon diffusion up to value $D_0=6.7$ cm²/s specifies increase of common number micropores, having access to a surface.

Thus, the emanation-thermal analysis has allowed to receive the important information on the transport characteristics pores and about their changes during thermal influences. This reflects processes plugging and opening of transport channels in a course sorption and desorption vapors, accordingly, and collapse of porous structure during sintering. It is necessary to emphasize two basic advantages of use of a method of a radioactive inert gas probe to diagnostics of solids: the opportunity of investigation of processes of evolution of porous structure adsorbent is direct during external influence on a material and opportunity of the continuous separate control of change of diffusion resistance of pores (determined in such parameters, as length and diameter pores) and number of open pores (more exactly - a surface area accessible for gas diffusion).



Fig. 18 Thermostimulated organic vapours release from charcoal fibers (linear heating): Curve 1 – 2-butanole; Curve 2 – toluene; Curve 3 - dichlormethene

5.4 Optimization of the regeneration of charcoal fibers.

Optimal conditions for the activation of planar porous charcoal sorbents and for their regeneration after use were determined.

The procedures of regeneration of charcoal fibers chose by study of processes of thermustimulate gas evolution of organic substances from this adsorbent samples, previously saturated of organic vapours (mixture dichlormethane, 2-butanole and toluene.

Prior to the beginning of thermodesorption experiments, the coal fibers at first have been held in vapors of all three mentioned above substances. Proceeding from tabulated values of partial pressure these vapors, taking place at a room temperature in equilibrium with a liquid, ratio of concentration vapor in a gas phase of a mixture CH_2Cl_2 : 2-butanole: toluene 37.87 % is equal: 37.58 %: 25.19 % or 1.5: 1.49: 1. If fibers from charcoal to place in this atmosphere, the ratio vapors, adsorbate will make CH_2Cl_2 : 2-butanole: toluene 16.24 % is equal: 38.30 %: 45.45 % or 1: 2.36: 2.8, i.e. if in a gas phase dichlormethane is abundant, on adsorbent - toluene prevail. The given ratio of concentration vapors at a charcoal can be considered as initial in all subsequent applications of methods of the thermal analysis for the analysis of fibers.



Fig19 Mass-spectrum of gases, released from charcoal fiber at the temperature of 100 °C.

The thermodesorption curves in a regime of linear heating of a sample are given in a **Fig. 18**. It is visible, that the various organic vapours are released in various intervals of temperatures: the maximal rate butanole release is achieved at 130° C, toluene - at 250° C (is registered of mass-spectrometer as the large and wide peak), and dichlormethane - at 280° C, (can be registered only on a rather sensitive range of the device). The mass - spectrum at 100° C is given in a **Fig. 19**. The peaks of water (M=18), nitrogen (M=28), oxygen (M=32), CO₂ (M=44) and toluene (as two fragments of a molecule: M=91 and M=92) are well visible. The peak butanole (M=74) is swept hardly up, and the peaks dichlormethane (M=84 and 86 - because of presence at a molecule of two different isotopes of chlorine) practically are absent.

Received in the present work high porously charcoal fibers have in relation to organic substances vapors adsorption capacities comparable to world analogues, but have the best dynamic characteristics. The cleaning coal from different vapors requires different temperatures $(130^{\circ}C \text{ for 2-butanole both } 250^{\circ}C \text{ toluene and dichlormethane})$. On the basis of charcoal fibers and tissue the planar elements for adsorption apparatus of regular structure intended for clearing of air from vapors of toxic organic substances are manufactured.

6. Design of apparatus of regular structure with planar sorbents.

As was already mentioned, adsorption devices with planar adsorbents have two building blocks: transport channels and micropores – adsorption active centers. The rather large transport channels provide delivery of the necessary amounts of fluids, and the adsorption process is carried out in narrower "reactionary" channels [16].

In a **Fig. 20** the distribution of gas flows is schematically submitted at a stochastic arrangement spherical granules of sorbent (**Fig. 20a**) and at a regular arrangement planar sorbents (**Fig. 20b**). Two levels the structure similar the provision of system of carry of blood in of the man body: the wide channels (artery) provide effective submission of an initial mixture, and the narrow capillaries cause its effective separation.

In the spatially organized equipment the management of thermal flows is more effectively. In apparatus of regular structure working temperature of elements remains constant during all process. The devices are rather compact, that essentially expands sphere of their application. The apparatus of regular structure allow to save as constructional materials, and adsorbents, and reduce consumption of energy. Because of low dynamic resistance the expenses for compressors are reduced. Other source of economy – decrease energy expender on maintenance of constant temperature in the equipment during its regular operation. At last, the third source of economy – decrease consumption of energy at regeneration adsorbent. Therefore, despite of large cost of works on designing of similar devices, they appear economically by more favorable in comparison with stochastic arrangement of sorbent.

At creation of equipment for processing mixtures of gases the idea of two-level systems is used three times. The porous materials (phase design), working elements (modular

design) and adsorber construction (hardware design) - everyone concern to a class of regular structures. Already from one type of design it is possible to expect essential progress in development of similar systems intended for clearing of industrial wastes, and at use of all three types the achievement of effect of positive synergetic is possible.



Fig.20. Schematic diagram of the distribution gas flows in adsorbtion apparatus different structure: a) Accidentally arrangement of spherical granules of adsorbent. δ) Regular arrangement of planar adsorbent.

Important feature of the device with planar adsorbents - opportunity of use in one device of different types sorbents (for example, from porous basalt and from charcoal).

In a Fig. 21 the diagrams of two types apparatus of regular structure are submitted: the device with one kind sorbent (Fig. 21a) and integrated system with two (or more) kinds of sorbents (Fig. 21b).

The advantage of apparatus of regular structure is provided with their flexibility (rearrangement), compactness, low consumption of materials and high power efficiency.

The flexibility first of all is determined used adsorbent (or adsorbents). Within the framework of the present work are used adsorbents of a various chemical nature intended for clearing of various types of wastes (gas, liquid) from various impurities (vapor of water, sour gases, vapor of organic substances, ions of heavy metals etc.). Thus the transition from one system to another does not require essential reorganization of the equipment: the change of standard modules (technological designer) suffices.

The flexibility on adsorbent is provided with an opportunity of a variation over a wide range of spatial microstructure of sorbent. The porous structure can be changed or by increase of the sizes micropores (defects) as in modified bentonite, or by creation by porous sorbents with an optimum combination adsorption-active and transport pores, as it takes place in leached basaltic fibers.

The active filters allow in one module to combine layers of various types sorbents, for example, to alternate layers of a basalt fiber to layers activated charcoal. Thus the active filters within the framework of one module are easily combined with usual aerosol filters and with selective membranes. The combined filters with a layer of the non-porous basalt (clearing of aerosols), layer of porous basalt (clearing from hydrophilic pollutants), layer charcoal (clearing from hydrophobic pollutants) and polymeric asymmetric membrane with a continuous (not porous) working layer (clearing from bacteria and microbes) can find application for clearing air and water from different pollutants.



Fig 21. Schematic diagram of adsorber regular structure with planar adsorbent. a) Active filter, manufactured from single adsorbent; b) Active filter, manufactured from different adsorbents.



Fig. 22. Schematic diagram of the adsorption modules in the apparatus of regular structure

The designs of devices suppose use of working modules of various geometry (planar, cylindrical etc.) and with a various type of their spatial arrangement, that allows to operate flows in its of substances and heat. The optimization on removal of heat allocated in a course adsorption is especially important. Heat evolution results in uncontrollable increase of temperature of sorbents and, hence, to reduction of its adsorption capacity.

In work are tested flat bay elements with consecutive alternation of filters and gas backlashes. Is shown, that the achievement of unique decrease of volume of the device is possible. Thus is reduced of construction materials consumption and expenses of energy (at regeneration sorbent warming up of the small module to carry out much more easy, than large column with granulated sorbent). The active multielement filter by thickness 1 cm is see equivalent a adsorption column with stochastic granulated sorbents in height 1.5 m. However, because of complexity of a design flat bay elements, cost of their manufacture is higher, than cost traditional adsorbers.



Fig, 23 Schematic diagram operation of adsorption module.

In attempt of simplification of a design, were developed adsorbers of regular structure with cylindrical working elements. (**Fig. 22**). The device for clearing and/or drying of gases consist of one or several tubular (**Fig. 23**) of adsorption elements, which represent a set of hollow cylindrical blocks from the compressed fine or ultra thin basalt fiber previously treated by a mineral acid, superimposed on punched pipe. Punched gas permeable pipe is supplied on the ends elements compressing blocks up to density of a basaltic bad 0.1-0.5 g/cm³. The device is supplied with dividing washers established between cylindrical blocks.

The preliminary tests of the adsorber have shown, that used sorbent and apparatus (at the expense of a way of stacking fibrous adsorbent in the separate block and regular arrangement of elements in the device) allow in processes drying and/or of clearing of gases at small gas-dynamical resistance to achieve higher dynamic of sorption capacity in comparison with a stochastic adsorbent. The insignificant resistance to a gas flow results in significant decrease of power expenses at sorption, and the low heat sorption allows to lower energetic consumption at a stage of regeneration sorbent.

In work the adsorber of a similar design, but intended for using the several sorbents in series was tested. The equipment is used for clearing of air from vapor of volatile hydrophilic and hydrophobic pollutants of air.

7. Alumina pillared montmorillonite

Advantage of pillared clays is in the fact, that the pores formed between the cations can be systemetically modified by varying the cation size, shape and spacing. The preparation of pillared clays consists in ion-exchanging charge-compensating cations with large polyoxocations or with colloidal particles. The compounds of aluminum, zirconium, chromium, iron and titanium can be used as pillaring agent. Pillared montmorillonite (MMT) is usually prepared using bentonite with a montmorillonite content above 90%. (Montmorrillonite is a clay mineral in which substitution of Al^{3+} by Mg^{2+} in the octahedral sites predominates).

The ionic modification of the bentonite clay on base MMT schematic is given in a **Fig. 24**.



Fig.24 Schematic depiction of the pillared process

7.1 Preparation of alumina pillared montmorillonite (alumina-MMT).

The alumina-MMT were prepared by the intercalation of large inorganic cations (such as the hydroxyaluminium Keggin ion $[Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}]^{-1}$ into layered montmorillonite structure yielding alumina pillared montmorillonite. Following conditions were used for the preparation of the alumina pillared MMT: The as received montmorillonite clays were treated with dilute acid to remove CaCO₃ and sedimented to separate the clay from other minerals, such as quartz. The wet clay were suspended in the water containing approximately 5% of the clay. The solutions used for the pillaring were prepared separately. The 0.2 M solution of AlCl₃·5H₂0 was titrated to pH 4.5 and stirred overnight. This solution was then mixed with portions of the clay solution in different ratios and held at 80°C for 4-10 hours. The solid part was then filtered off with distilled deionized water and then calcined at 500°C.

Tabl.	12. Cher	nical con	nposition	of Al-N	1MT
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	H_20
58.89	28.82	2.51	3.48	0.15	1.54

The final alumina-MMT products obtained after the thermal treatment of the intermediate products were characterized by means of XRD, surface area measurement, pore volume and pore distribution measurements by nitrogen adsorption-desorption method. The thermal behavior was tested by differential thermal analysis, thermogravimetry, and diffusion structural analysis, resp.

The process of modification of clay results in increase of the area of a surface (from 43 up to 270 m²/g), growth of a specific surface mesopores (in 2.5 times) and increase of specific volume mesopores (in 10 times). The modification opens an internal surface (increases specific volume micropores), that can be important for adsorption, but the structure of a solid on itself remains former. The Al-MMT represents a microporous material, thermostable up to temperatures is higher 500° C.

The analysis of chemical composition has shown, that the basic components of Al-MMT are silicon and aluminum with impurity of iron, magnum and calcium (see **Table 12**).

7.2 Characterisation of surface and porosity of Alumina-MMT

The adsorption-desorption isoterms of N₂ were used for surface area measurements. The surface area value determined for the Al-pillared MMT was 205 m²/g, the surface area determined from the t-plot is 78 m²/g, the micropore surface area is 127 m²/g, the total pore volume and the micropore volumes were determined as 0.16 and 0.06 cm³/g, resp.

7.3 Sorption properties of Al-MMM

The main attention was paid to materials suitable for the uptake of hazardous metal ions and organic molecules from effluents originating from the chemical industry, metallurgical industry and nuclear power plants, taking into account that the hazardous species might be accidentally released into the environment. The following metal ions were considered in the waste effluent: Cs and Sr. The following organic compounds were considered: dichlorphenol as a representative of chlorinated phenols and Bengal red, dye representing aromatic molecules possessing several different functional groups. The modified clay materials ("pillared clays") were tested as sorbents of metal ions and organic compounds present in operational waste streams of the WWER type nuclear power plant.

The results of the sorption tests were used in the design of a sorption unit to be used for the uptake of hazardous nuclides from accident waste from Czech and Russian Nuclear power plants.

Basic radionuclides, which should be removed from solutions of nuclear waste are 137 Cs and 90 Sr. In the present work the different types clays tested by way of them of adsorption activity concerning these isotopes. Target parameter served K_d, determined as

$$\mathbf{K}_{d} = \left(\frac{\mathbf{C}_{0} - \mathbf{C}_{e}}{\mathbf{C}_{e}}\right) \mathbf{V} / \mathbf{m}$$

where C_0 initial concentration nuclides in a solution; C_e – equilibrium concentration; V/m=27 - volume of a solution, divided on weight adsorbent.

The results of measurement of adsorption efficiency of cesium and strontium on Al-MMT, modified chromium, zirconium and aluminium, are given in **Table 12**. As solutions of isotopes used real liquid wastes of a nuclear power plant with WWR reactor, containing besides taken metals boric acid, KOH, Na ions and strong complexing agents. It is revealed, that some of clay have very high values K_d for Sr^{2+} , but not for Cs^+ . K_d about 2000 cc/g is considered sufficient for clearing a solution. In process of increase of concentration complexing agents and ions Na⁺ in a solution adsorption decreases.

solutions simulating factorer to traste							
Sorbent	d-Spacing, A	Distribution	coefficient	Surface area,			
		K _d [ml/mg]		m^2/g			
		⁸⁵ Sr	¹³⁷ Cs	-			
Saponite-Cr43 C	21.3	2231	15.4	123			
Saponite-Cr31 H	24.3	4290	10.2	78			
Saponite-Zr3 N	25.4	13560	4.2	278			
Saponite-Zr13P	21/5	6767	3.9	252			
MontmorilloniteAl30	19.1	972	15.8	273			

Tabl. 13. Sorption properties of different pillared layered sorbents for Cs and Sr from test solutions simulating radioactive waste

Tab. 14	. Sorption	property	of different	inorganic	clays for	Cs, Sr,	Pu and	l Eu	uptake	from
simulat	ed accider	nt waste so	olution							

Sorbent	Distribution coefficient K _d [ml/g]				
	Cs ⁺	Sr ²⁺	Pu ⁴⁺	Eu ³⁺	
Montmorillonite					
aluminia pillar	1200	3700	163	53	
Synthetic Mordenite	>105	230	1202	13	
Natural clinoptilolite/					
titania gel	2600	8600	5540	5980	
Hydrated titania	1550	<105	26.860	6.4	
Synthetic philipsite	12000	550	1730	540	

The results testify to high selectivity Al-MMT to of strontium adsorption listed to **Tables 13 and 14**). As follows from **Table 14**, Al-MMT can be successfully applied for extraction Sr and Cs from liquid emergency resets of nuclear power plant.

7.4 Characterization of thermal stability of Al-MMT.

(i) Surface and porosity measurements

The thermal stability of the porous structure of Al-MMT was investigated by means method of nitrogen adsorption. Samples previously were annealed within 3 hours at temperatures 150, 300, 500 and 900°C. The surface area up to temperature $250^{\circ}C$ does not change. After heating to temperatures $300^{\circ}C$ begins collapse of porous structure and sintering. The surface and porosity monotonously decrease, and the maximal rate of sintering is achieved at $850^{\circ}C$ (see **Table 15 and Fig. 25**).

(ii) Thermal analysis.

Thermogravimetry (TG) indicated that the total mass loss of 19%. was measured on Al-MMT heating from 20 to 1300 °C. The curve of loss of weight fixes two processes: loss of adsorbed water, which occurs in an interval of temperatures $20-500^{\circ}$ C to the maximal rate achievable at temperature 110° C, and water evolution during reaction dehydration, occurring in an interval of temperatures $500-650^{\circ}$ C and reaching maximal rate at temperature 620° C (**Fig. 26**). The mass loss of 8.5% was observed in the range from 50 to 150° C. We supposed, that the water molecules were situated within the newly created pores of the pillared clay. At higher temperatures the hydroxyl groups formed as the result of thermal decomposition of the Keggin were released.



Fig. 25 Adsorption isoterms N_2 on Al-MMT annealed for 3 h on different temperatures: Temperature annealing: T=150(1), 500(2), 700C(3) and 900(4) $^{\circ}$ C; Adsorption Desorption

Fable 15. Surface area and	d pore volume of all	umina-pillared N	MMT as d	epending on t	he
tempe	rature of heating (he	eating time was	3 hrs)		

Temper	BET	Total pore	Micropore	Micropore
ature,	surface	volume,	surface area	volume,
^{0}C	area, m ² /g	cc/g	m^2/g	cc/g
150	204,75	0.1571	126.88	0.05674
300	191.86	0.1556	100.70	0.04502
500	132.90	0.1214	71.01	0.03183
900	49.909	0.0899	10.76	0.00458



Fig.26 Thermal analysis result (TG and DTA) of Al-MMT



Fig.27 XRD patterns of Al-MMT heated in Ar. Temperature of annealing: 200(1), 500(2), 700(3), 900(4), 1100(5) and 1350° C.

On reimersing the heat treated alumina pillared MMT into water for 24 hours and drying as before the TG revealed that approximately 70% of the lost weight had been recovered. It was observed that the alumina pillars may partially dehydrate and behave as a hydrated aluminium oxide. Our results were in agreement with the general assumption that the negative charge of the layers is compensated after heating by H^+ ions split out from the pillars.

The DTA precisely two processes: endo-effect at 113° C and exo-effect at temperature 923° C. Besides are observed of the extremely insignificant exo-effect at temperatures $557 - 717^{\circ}$ C of a not clear nature.

Tabl. 16 the Basic reflexes Al-MMT at different temperatures 200^oC: 18.462 (basic); 4.4741; 2.5332 500^oC: 18.592; 4.4857; 2.5141 (basic) 700^oC: 18.684; 4.4655; 3.3731; 3.1632 (basic) 895^oC: 10.075; 3.3438; 3.2051; 1.8503 - all peaks - small amplitude 1087^oC: 5.3725; 4.2777; 4.1216; 3.3983 (basic); 3.2202; 2.8951; 2.7016; 2.5530; 2.4496; 2.2988; 2.2156; 2.1304; 2.0272 1350^oC: 8.4892; 5.4050; 4.8966; 4.1030 (basic); 3.3926; and other insignificant peaks down



• Fig.28 Effect of the annealing temperature on crystal lattice parameter D_{001} for Al-MMT

(iii) X-ray power diffraction.

Change taking place in the Al-MMT during 3h heating were monitoring by XRD measurements carried out at 200, 500, 700, 900, 1100 and 1350^oC, respectively (XRD pattern see **Fig. 27**). The given method has found out a several alternating processes occurring in Al-MMT heated to different temperatures (**Table 16**).

The temperature dependence of a crystal lattice parameter d_{001} from temperature annealing modified Al-MMT is given in a **Fig. 28**. It is visible, that the structure Al-MMT remains steady up to 400° C, then begins to collapse, and the greatest rate of reduction of a constant crystal lattice is achieved at temperature about 1100° C.

<u>(iv) DSA</u>.

to 1.4263

The powders of porous bentonite heated up with rate 5 $^{\circ}$ C/min in a flow of air in an interval of temperatures from 16 up to 1300 $^{\circ}$ C. Thus 5 peaks - effects were registered at temperatures: 100, 570, 800, 920 and 1180 $^{\circ}$ C and two exponential portions of the DSA-curve (**Fig.29**). It is revealed, that peak best is expressed at 550, the peak at 929 is expressed poorly. Radon evolution rate at cooling is described monotonously decreasing curve and is well described by one exponent. The comparison DSA-curve of heating with the data of other methods of the thermal analysis is carried out in a **Fig. 30**. Only DSA- curve fixes all processes. None of the method of thermal analysis not fix all processes, but the set of methods fixes the same four effects. Solid-state processes in the range of temperatures above 1000 $^{\circ}$ C (decomposition hydroxides) is supported by DTA, TG and DTG; peak at 800 $^{\circ}$ C - data on annealing of a surface (sintering), and peak at 950 $^{\circ}$ C - data of the XRD measurement (destruction of a crystal lattice of a material).

DSA-curve of bentonite processed by a method of the least squares with use of various mathematical models. Model Peak 1 + Peak 2 +Peak 3 + Peak 4 + Peak 5 + Exp 1 + Exp 2

was used [17 - 21]. The Fig. 29 show a good fit of the equation in the date. In result, the complex process radon release was divided on elementary components.



Fig. 29 Experimental DSA results (point – heating, cross – cooling) compared with the results of the mathematical modeling of radon release (curves 1 - 7) from aluminum pillared bentonite (Al- MMT).

The parameters of radon diffusion in the Al-pillared MMT calculated from the experimental DSA curve were used for the determination of the optimised conditions for the thermal treatment the intermediate products during the preparation of the alumina pillared MMT. The diffusion parameter of radon (atom size 0.4 nm) was used for the characterization of the transport properties of the sintered samples after heating to high temperatures.

Heating	$D_0, cm^2/c$	Q, kJ/mol	T _m ,K	dJ, K	A _{sJ}	T _{mS} , K	dT _s , K
Peak1	3.23*10 ⁻⁶	2.521	1141	1322	0.853	1238	71
Peak2	$1.37 \text{x} 10^4$	231.7	1199	166	0.373		
Exp	6.17×10^{10}	434.7					
Cooling							
Exp	1.92×10^{5}	270.1					

Table 17. Diffusion parameters of radon in alumina-pillared montmorillonite.

The samples of Al-MMT subjected repeated thermal cycling: to heating from room up to a highly temperature with the subsequent cooling up to a room temperature. In each subsequent cycle maximal temperature increased: first heating carried out up to temperature 500° C, second - up to 700° C, third - up to 900° C, fourth - up to 1100° C and fifth - up to 1300° C. The DSA curves of heating and cooling are given in the Fig. 31a-e. The diffusion and structural parameters calculated from DSA – results for Al – MMT listed in **Tables 17, 18 and Fig. 31**.

Thus, the diffusion structural analysis has allowed to find out during thermal processing Al-MMT five effects at temperatures 120, 550, 750, 950 and 1200° C. Most important represent effect in area 550°C, where the process of destruction of microporous structure of a material begins. This process determines thermal stability of a porous material and sets a temperature range of its operation as adsorbent, catalyst and carrier of the catalyst.

From the DSA results the optimal temperature for the thermal treatment of the alumina pillared MMT was determined. The heating at 500° C for 3 hours was used. The materials

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prepared by this heat treatment were characterised by means of nitrogen sorption-desorption isotherm.

Regimes	D_0 , cm ² /s	Q, kJ/mole	T_{m} , C	ΔT , C	AssE	T_{mS} , C	σ
Heating 1							
Peak	104.1	48.71	220	109	1.84	88	144
Exp	$1,24 \times 10^{-3}$	11.67					
Cooling							
Exp 1	3.69×10^{-4}	7.32					
Exp 2	204	110.3					
Heating 2							
Peak 1	56.4	39.14	78	122	0.009	66	119
Peak 2	$1.23*10^{-3}$	13.75	558	554	0.295	724	252
Cooling							
Exp1	$1.x10^{-4}$	5.11					
Exp2	380.4	148.3					
Heating 3							
Peak 1	6.33*10 ⁻⁵	18.95	694	1025	0.458	964	268
Peak 2	6.89×10^{-3}	54.33	852	437	0.186		
Cooling							
Exp 1	1.37×10^{-4}	38.04					
Exp 2	6.75×10^{20}	571.7					
Heating 4							
Peak 1	1.1*10 ⁻⁵	2.88	890	1088	0.761	1019	105
Peak 2	9.65×10^4	241.5	988	164	0.19		
Exp	1.42×10^{6}	262.7					
Cooling							
Exp 1	0.268	116.9					
Exp 2	1.107×10^{19}	612					
Heating 5							
Peak 1	3.23*10 ⁻⁶	2.521	1141	1322	0.853	1238	71
Peak 2	1.37×10^{4}	231.7	1199	166	0.373		
Exp	6.17×10^{10}	434.7					
Cooling 5							
Exp	1.92×10^{5}	270.1					

Table 17 Emanation parameters of Al-MMT

Table 18. Contribute of different processes in radon release from Al-MMT.

Heating	$K_E = maxE_1/maxE_2$	F_1	F_2	$KF = F_1/F_2$
2	0.3	0.066	0.934	0.07
3	1.7	0.66	0.34	1.94
4	1.2	0.866	0.134	6.47
5	0.2	0.551	0.449	1.23

The diffusion information taken from processing DSA-curve of Al-pillared bentonite (21 parameters), is submitted on the diagram $\log D_0 - Q_D$ (**Fig. 32**). It is visible, that at thermal processing of a material of energy of activation radon diffusion changed on three order, and a pre-exponential factor - on 30 orders! The results demonstrate compensatory effect. If in usual

kinetic, at a derivation of the Arhenius law for temperature dependence of a constant of reaction rate the complete independence frequency factor and energy of activation from each other is supposed, in processes desorption and diffusion frequency factor D_0 and energy of activation Q_D depend one another on the exponent law.



Fig.30 Results of diffusion structural analysis (DSA) of Al – MMT compared with the results of the methods thermal analysis: 1 - DSA; 2 - DTA (schematic); 3 - TG; 4 - Rate of surface annealing (schematic); <math>5 - Change of the crystal lattice parameter D₀₀₁ (schematic).



Fig 31 Experimental DSA results (point – heating, cross – cooling) compared with the results of the mathematical modeling of radon release (curves 1 and 2) from aluminum pillared bentonite (Al- MMT). a - First heating and cooling; b - Second heating and cooling; c - Third heating and cooling; d - Fourth heating and cooling; 2e - Fifth heating and cooling.

In half-logarithmic scale the diagram $logD_0 - Q_D$ represents a straight line with factor of regress (0.94) close enough to unit. If to take only values for cooling (i.e. for more or less stable structures), factor of correlation is even higher (0.98). For DSA-curve heating, i.e. for radon diffusion in conditions of solid-state processes, factor of regress is lower, but too is high enough (0.83). **Fig. 33** shows the shape of S(T) function, describing the change of the surface area of the sample resulting from dehydration, in comparison with experimentally found surface area values calculated by BET method. It follows that a good agreement between experimental and theoretical results was obtained.



Fig 32. Dependence of the values $log D_0$ factor on activation energy Q_D of the radon diffusion calculated for Al-MMT



Fig. 33 Values of "B.E.T. surface area" obtained experimentally (dots) for samples of Al-MMT heated to various temperatures compared to "DSA surface area values" (full lines) determined from the theoretical curves.

The agreement of curve change of a surface determined by different methods, can not be casual. It proves as validity of model fixed in a basis of processing DSA-curve (a hypothesis about symmetry of process annealing and the description of change a surface by integrated function of errors), and correctness of account of parameters. Simultaneously becomes clear, that radon release in a course of dehydration copes by reduction of a all surface of pores (instead of their volume, diameter pores etc.), and at first radon release is controlled by a surface all pores, and at more temperatures - on collapse of volume micropores. From the point of view kinetic of annealing of a surface, DSA and B.E.T. for considered here process give the equivalent information, but DSA gives also other extraordinary important information, in particular about permeability pores on test gas. It is possible to judge evolution of this parameter during thermal processing on of energy of activation and pre-exponential factor of radon diffusivity.

7.5 Immobilization of toxically wastes with help Al-MMT

The extraction of dangerous substances from radioactive or industrial waste water by precipitation them on adsorbents is only first stage of waste management. The second stage is immobilization of pollutants and transmutation them (for example, by solidification) in the corrosion-resistant form, suitable for a long burial. Within the framework of the present work two ways immobilization of volatile radionuclides in a matrix adsorbents are offered:

- Thermal treatment spent sorbents, containing radionuclides, with formation of not porous and chemically proof ceramics;

Ceramification of spent adsorbents in a mix with easily fusible glass additives with formation non porous of the chemical-resistant forms.

The experiments on capsulation of radionuclides carried out with Al – pillared bentonite. Process of evolution of volatile substances from the glass additives recorded by a method of mass-spectrometry. In a temperature interval $870 - 1015^{\circ}$ C the escape of substance, for which relation M/Z=64 (apparently, zinc) was observed.

The ETA has been used in order to determine optimized conditions for the waste encapsulation. DSA-curve of a mix reflects processes of interaction Al modified bentonite with glasses beginning at temperatures higher 800⁰C. These processes accelerate capsulation of adsorbed substances.

As a result of the carried out research the opportunity effective immobilization of dangerous substances concentrated on Al-pillared bentonite was is shown by sintering its with special glass additives. The additives essentially reduce temperature solidification, that reduces energetic consumption of process. The received product corrosion-resistant and can be used it for a long burial of waste.

8. Perovskite ceramics.

8.1 Preparation of perovskite ceramics samples containing Ce and Nd as TRU similants

A bulk perovskite sample was prepared by hot pressing at the temperature of 1250 °C / 29 MPa for 2 hours. The nominal chemical composition of the perovskite samples is $Ca_{0.98214}(Nd_{0,00790}Ce_{0.00996})Al_{0.01786}Ti_{0.98214}O_3$, where Nd and Ce were used as simulant for Cm and Pu, respectively. The Nd and Ce rare earth elements were assumed to be trivalent and to be incorporated in the Ca site via an $A1^{3+}$ substitution on a Ti⁴⁺ site.

The ceramics samples were subjected to the leach test according to the MCC-1 protocol in a pH=2 buffer solution (0.05M KCl + 0.013M HCl) at 90°C for 2 months over four 7-day leach periods and a 28-day leach period.

The dissolution of perovskite is supposed to proceed according to the following scheme:

 $CaTiO_3 + 2H^+ \longrightarrow Ca^{2+} + TiO_2(anatase) + H_2O$

The "as polished" (virgin) and "as-leached" (altered) samples were labeled for the DSA measurements using 228 Th and 224 Ra in the acetone solution.

8.2 Characterization of perovskite ceramics and its alteration products

Annealing of polishing defects in the "as-polished" (virgin) perovskite was revealed by the decrease of radon release rate in the temperature range of 300 - 560°C. The decrease of the radon release rate in the range of 880 - 1200°C corresponded to the densification of the samples due to annealing of remaining latent pores (see **Fig. 34a**, curve 1). The DSA curve measured during sample cooling characterized the radon diffusion properties in the perovskite sample heated to 1200°C in argon containing 6 % of hydrogen. According to the SEM micrographs the "as-polished" sample microcracks due to polishing were observed on the sample surface [22 - 24]. The "as leached" perovskite sample a grain size of 0.2 µm for the crystallites forming the surface layer was determined. From the XRD patterns of the respective perovskite ceramics samples titanium dioxide (anatase) was formed on the sample surface as the results of the leaching. According to SEM – EDX results the surface inside the micropores of the "as-leached" surfaces was enriched by Nb and Ce.

The thickness of the altered anatase containing layer was estimated (using the amount of Ca in the leachate) to be approx. 40 μ m, the near surface part of the altered layer being labeled by radon atoms for the DSA measurements. From the radon release rate measured during sample of "as leached" (altered) perovckite heating (**Fig.34b**) we can conclude that the polishing defects observed in the "as-polished" samples were eliminated in the course of the hydrothermal treatment. The decrease of the radon release rate in the temperature range of 800-1000°C indicated the anatase - rutile phase transition. The DSA results of the "as-leached" sample implies that the annealing of remaining latent pores takes place on heating above 1000°C.

A mathematical model was used for the evaluation of the experimental data of radon release from the both virgin and altered perovskite samples.

By means of the mathematical model theoretical DSA curves of the altered and virgin perovskite ceramics, respectively, were calculated. The model is based on the assumption that two independent diffusion paths for radon exist and the radon release by recoil takes place.

A good agreement was found between the experimental DSA data and DSA theoretical curve obtained as the result of the modeling of radon release from perovsckite based ceramics (see **Fig.34a** and **b** for regime of heating, and **Fig.34c** for regime of cooling).



Fig. 34 Experimental DSA results (point) compared with the results of the mathematical modeling of radon release (curves 1-4) from perovskite based ceramics. a - Virgin perovskite, heating; b - Altered perovskite, heating; c - Cooling

Two independent annealing processes were considered to take place in the near surface layers of altered perovskite ceramics, namely in the temperature 340–600 and 600–980 °C, respectively (**Fig.34b**). The exponential increase of radon release rate obeying the Arhenius law was used for description of the diffusion behavior of radon in altered perovskite after heat treatment from 1000 - 1200 °C.

Equation of mathematical models for treatment of DSA-curves of virgin and altered perovskite ceramics listed in **Table 19**. Peak parameters calculated from DSA curves are summarized in **Table 20**. The values of activation energy of radon migration in the near surface layers of the virgin and altered perovskite calculated for the above temperature ranges using the proposed mathematical model are represented in **Tables 21a and 21b**. It is obvious that the DSA results gave supplementary information about annealing of the near surface layers of the perovskite ceramics before and after leach test following MCC-1 protocol and about the migration of radon atoms in the perovskite matrix for TRU immobilization. Moreover the results of REM enabled us to assess the availability of the ceramic matrix for

radon atoms, serving a noble gas probe (atom size 0.4nm). Grain boundaries, micropores and others are supposed to served as channels along which the radon atoms can migrate in the ceramic matrix.

Heating

Table 19. Equation for treatment of ETA-curve of virgin and altered perovskite **INITIAL**

1. Peak 1:

E₁(T) = U₀₁ * exp(
$$-\frac{Q_1}{R*T}$$
) * exp($-q_1 * T$)
2. Peak 2:
E₂(T) = U₀₂ * exp($-\frac{Q_2}{R*T}$) * exp($-q_2 * T$)
3. Peak 3:
E₃(T) = U₀₃ exp $\left(-\frac{Q_3}{RT}\right) \left\{1 + 0.5erf\left(\frac{T - T_{m3}}{\sigma_3\sqrt{2}}\right)\right\}$
4. Peak 4:
E₄(T) = U₀₄ exp $\left(-\frac{Q_4}{RT}\right) \left\{1 + 0.5erf\left(\frac{T - T_{m4}}{\sigma_4\sqrt{2}}\right)\right\}$
E_c(T) = E₁₈ + U_{co1} exp $\left(-\frac{Q_{c1}}{RT}\right) + U_{co2} \exp\left(-\frac{Q_{c2}}{RT}\right)$
LEACHED

Heating

1. Peak 1: 1. Peak 1: E₁(T) = U₀₁ * exp($-\frac{Q_1}{R*T}$) * exp($-q_1 * T$) 2. Peak 2: E₂(T) = U₀₂ * exp($-\frac{Q_2}{R*T}$) * exp($-q_2 * T$) 3. Peak 3: E₃(T) = U₀₃ exp $\left(-\frac{Q_3}{RT}\right) \left\{1 + 0.5erf\left(\frac{T - T_{m3}}{\sigma_3\sqrt{2}}\right)\right\}$ 4. EXP: E₄(T) = U₀₄ * exp($-\frac{Q_4}{R*T}$)

$$E_{C}(T) = E_{18} + U_{CO1} \exp\left(-\frac{Q_{C1}}{RT}\right) + U_{CO2} \exp\left(-\frac{Q_{C2}}{RT}\right)$$

Table 20. Peak parameters of DSA-curve (heating) for altered and virgin perovskite ceramics.

	Virgin				Al	tered		
	T _{max} , K	T_{max} , ${}^{0}C$	Asymmetry	Width	T _{max} , K	T_{max} , ^{0}C	Asymmetry	Width
Peak 1	422	149	0,634	138.7	372	99	0.173	116.1
Peak 2	586	313	-0,036	517.2	893	620	-485	245.2
Peak 3	1146	873	0,772	744.6	1050		0.149	806
Peak 4	1283	1010	0,316	526.8		1021	-0.232	1632
dS 3	1226	953	-0,043	138.6	1294			
dS 4	1356	1083	-0.011	637.4				

Virgin			Altered			
	$U_0, cm^2/s$	Q, J/mole		$U_0, cm^2/s$	Q, J/mole	
Heating			Heating			
Peak 1	$2.7*10^{21}$	$1.239*10^{5}$	Peak 1	$1.3*10^{26}$	$1.57*10^{5}$	
Peak 2	$5,7*10^{6}$	$2.804*10^4$	Peak 2	$4.76*10^3$	$6.342*10^3$	
Peak 3	$1.13*10^4$	$1.024*10^4$	Peak 3	$7.04*10^3$	$1.861*10^4$	
Peak 4	$8,68*10^4$	$6.029*10^4$	Exp	$1.25*10^{5}$	9.164*10 ⁴	
Cooling			Cooling			
Exp 1			Exp 1			
Exp 2	$1.25*10^{5}$	$1.29*10^{5}$	Exp 2	$4.5*10^{5}$	$1.26*10^5$	

Table 21a Parameters of DSA-curve of perovskite samples

9. TiO₂-RuO₂ photocatalyzes

9.1. Preparation of titania and ruthenium containing titania.

Reagent grade TiCl₄ and RuCl₃ xH₂O were used as starting materials [25 – 27]. For the preparation of hydrous titania by hydrolysis the following solutions were used: TiCl₄ diluted with the same volume of 1 mole/l HCl and consequently with distilled water so that the concentration of Ti⁴⁺ was about 0.7 mole/l calculated as TiO₂. To this solution a 2 mole/l ammonia was added drop by drop. For the ruthenium component, a 1 mole/l ruthenium chloride solution was prepared by dissolving RuCl₃ xH₂O in 0.1 N hydrochloric acid. The ruthenium content was determined gravimetrically using RuO₂ as the species determined gravimterically. The mixed solution in the molar ratio Ti:Ru = 9:1 was prepared by mixing the dissolved Ti and Ru chlorides in the respective overall ratio. To this solution the 2 mole/l ammonia was added dropwise in an abundant amount. The precipitate obtained was subsequently washed, filtered and dried at 120°C.

Virgin		Altered		
Temperature range	Activation energy	Temperature range	Activation energy	
[°C]	[kJ•mol ⁻¹	[°C]	[kJ•mol⁻¹]	
Heating run		Heating run		
100 - 150	124	100 - 150	157	
340 - 600	28.04	340 - 600	6.34	
600 - 980	10.24	600 - 980	18.61	
980 - 1200	60.29	980 - 1200	91.64	
Cooling run		Cooling run		
400 - 1200	129.00	400 - 1200	126.00	

Table 21b. Activation energy of radon migration in perovskite

9.2 Characterisation of initial samples.

From the XRD patterns it can be seen that the hydrous TiO₂, resulting after hydrolysis and drying at 120 °C, consisted of poorly crystallised anatase. In the coprecipitated oxides of the molar composition, Ti:Ru=0.9:0.1, a mixture of poorly crystalline anatase and an amorphous solid solution of ruthenia and titania was present. According to the photomicrographs of the initial samples obtained by TEM, the TiO₂nH₂O (where n=0.66) sample consisted of 1-5 μ m large agglomerates composed of nanosize grains (~5 nm). Surface area of this sample was determined as S=173 m²/g. The microstructure of the mixed hydrous oxide (TiO₂)_{0.9}-(RuO₂)_{0.1}nH₂O (where n=1.30) sample was similar to that of hydrous titania: the agglomerates were composed of slightly smaller primary grains than 5 nm. Surface area of the mixed oxide samples was S=213 m²/g **[28].**

9.3. Thermal behaviour of hydrous titania.

From TG-results follows that the hydrous titania (TiO₂nH₂O) losses water continuously from 60 to 400 °C (the total mass loss is 12.9 %). As it follows from the TEM photomicrographs, the primary grains of the titania samples heated to 300°C did not change in size, as compared with the feed sample, nevertheless the TEM photomicrographs indicated that water adsorbed on the surface and intergranular space was released. The surface area of the sample heated to 300 °C was S=148.4 m²/g. At the temperature of 400°C a partially crystalline anatase phase was detected by XRD. In the sample heated to 500°C the size of primary grains increased. The surface area of this sample decreased (S=89.7 m²/g), as compared with the sample heated to 300°C. A partially crystalline anatase phase was present in the sample heated to 500°C. In the titania sample heated to 800°C, well developed crystals of anatase of the size ~0.1 μ m were observed. The surface area of the sample heated to 800°C was S=41.6 m²/g. In the sample heated to 1000°C the crystal size increased to 1 μ m. The presence of rutile was detected by XRD in the sample heated to 1000°C.

The microstructure changes of the titania sample during heating were characterized by means of DSA (**Fig. 35**). The increase of Rn release rate in the temperature interval 300-600K reflected the process of the surface liberation from water under *in-situ* conditions of heating. The DSA results are in agreement with the surface area and TEM characteristics of the microstructure of titania heated to selected temperatures in the range 400-800°C. The annealing of surface was monitored by means of DSA under *in-situ* conditions of sample heating. At further heating above 1150K the radon release rate increase due to the diffusion of Rn in the rutile structure was measured.

Mathematical model Peak + Exp was used for treatment of DSA – results for $TiO_2*0.58H_2O$. A good agreement between the proposed models and the experimental DSA curves was obtained. The parameters characterising the kinetics of the microstructure changes during preparation of titania- based materials by heating of their precursors were determined (**Table 22a**). In addition, the determined diffusion structural parameters make it possible to predict the transport properties of the titania- based materials at increased temperatures.

Regimes	$D_0, cm^2/s$	Q,	T_{mS} , C	σ
		kJ/mole		
Heating				
Peak	1.10*10 ⁻⁷	7.39	706	273
Exp	$1.70*10^{-8}$	170.2		
Cooling				
_	4.4.9.4.94			
Exp	4.18*10*	31.8		

Table 22a Parameters of DSA-curves of TiO₂ *0.58H₂O

Table 22b Param	neters of D	SA-curves	of (TiO ₂	$)_{0.9}$ -(RuO ₂) _{0.1} *nH ₂ O
$D_{\rm o} \ \rm cm^2/s$	0	$T_{\alpha}^{0}C$	¢	

Regimes	D_0 , cm /s	Q,	I_{mS}, C	σ
		kJ/mole		
Heating				
Peak 1	3.38*10 ⁻⁶	12.1	399	152
Peak 2	$4.15*10^4$	204.9	610	47
Exp	$5.46*10^2$	231.3		
Cooling				
Exp	$8.18*10^{6}$	336.4		



Fig.35 Experimental DSA results (point – heating, cross – cooling) compared with the results of the mathematical modeling of the radon release (curves 1 - 3) from TiO₂*0.58H₂O

In the **Fig.36** the comparison of structural function, S(T), designed from DSA method, with experimental data of a B.E.T. method for $TiO_2*0.58H_2O$ is carried out. It is visible, that temperature dependence of the experimentally determined «B.E.T. surface area» agree with «DSA surface area values» calculated from the theoretical curves.



Fig. 36 Values of "B.E.T. surface area" obtained experimentally (dots) for samples of $TiO_2*0.58H_2O$ heated to various temperatures compared to "DSA surface area values" (full lines) determined from the theoretical curves.

9.4. Thermal behavior of hydrous titania containing 10% of ruthenia.

The thermal behavior of hydrous titania containing ruthenia in the molar ratio Ti:Ru =9:1 differs from that of hydrous titania, described in the previous paragraph. As indicated by the TG results, the mass loss taking place in the temperature range 60-400°C represents 20 % of the initial sample mass. From the TEM photomicrographs of the sample heated to 400°C it follows that the primary grain size did not practically differ from that of the initial hydrous sample. Loss of water from the surface and intergranular space was observed. On further heating of the sample, significant growth of the grains takes place resulting in the fully crystalline solid solution of ruthenia – titania with the rutile structure. This statement is supported by XRD patterns as well as by an exothermic DTA effect observed in the temperature range 430-480°C, corresponding to crystallisation [**29** – **31**].



Fig.37 Experimental DSA results (point – heating) compared with the results of the mathematical modeling of the radon release (curves 1 - 4) from $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ *nH₂O

From the DSA results for $(TiO_2)_{0.9}$ -(RuO₂)_{0.1} presented in Fig. 37 differences in the kinetics of the microstructure changes between hydrous titania containing 10% ruthenia and hydrous titania were monitored under heating. In the temperature interval 330-500 K a more intense initial increase of radon release rate was observed as compared to hydrous titania. This increase of emanation power corresponds to the liberation of the surface initially covered by water molecules, and to a free surface area increase due to the dehydration of the sample (the mass loss being more intense with the titania containing 10% ruthenia that hydrous titania only). Consequently, the decrease of radon release measured upon the sample heating above 600°K corresponds to the surface area decrease. At 670 the onset of the crystallisation was determined as the temperature of a change in the slope of the DSA curve. By DTA, the crystallisation interval was determined as 700-920K, corresponding to the crystallisation in the bulk. The intense decrease of Rn release rate continuing to 800K, followed by the slower decrease in emanation power up to 1100K. The increase of radon release rate observed on further heating above 1100K indicated the temperature of the onset of the diffusion release of Rn from the sample. In the temperature range 1100-1300K, a more intense increase in emanation power takes place with the $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ sample as compared to the TiO₂ sample [32]. The differences in the diffusion mobility of Rn atoms reflected the different dynamic properties of the respective samples in this temperature range.



Fig.38 Values of "B.E.T. surface area" obtained experimentally (cross) for samples of $(TiO_2)_{0.9}$ -(RuO₂)_{0.1}*nH₂O heated to various temperatures compared to "DSA surface area values" (full lines) determined from the theoretical curves.

Mathematical model Peak 1 + Peak 2 + Exp was used for treatment of DSA – results for $(TiO_2)_{0.9}$ - $(RuO_2)_{0.1}$ *nH₂O under heating. A good agreement between the proposed models and the experimental DSA curves was obtained. The parameters characterising the kinetics of the microstructure changes during thermal treatment of material and activation energy of radon migration were calculated (**Table 22b**).

The temperature dependence of structural function, S(T), for $(TiO_2)_{0.9} - (RuO_2)_{0.1}*nH_2O$ is shown in the **Fig.38**. It is visible, that the character of change of theoretical function during linear heating corresponds to the values of «B.E.T. surface area» method received determined during isothermal annealing of samples

10. Conclusion

In the present work the basic attention is given to development of complex system of diagnostics of solids and solid-state transformations occurring during thermal and chemical processing of substance. The basic problem of study of solid-state processes such as dehydration and sintering which is carried out in a regime of linear heating, is the absence of direct methods of the control of dynamics of change of an open surface of a sample. The modern methods of measurement of a surface are realized at low temperatures and essentially are static. A unique method, which could give the information about kinetic of a surface change directly at thermal treatment and without interruption of reaction, is the method of the diffusion-structural analysis. The application of a radioactive inert gas probe (radon-220) is capable to ensure the continuous control of change during structural transformation as of diffusion resistance of a material, and external surface of a sample. However, till now to realize this opportunity it was not possible because of assence of a sample. The spore of a surface are realized at DSA - curves.

In this study the methods of decomposition of a complex curve of theromostimulated radon release on elementary components with the subsequent account for each process diffusion and structural functions are offered. The DSA was used for *in-situ* monitoring of microstructure changes during heating of sample. In result the quantitative control of change of a surface of a sample time is carried out directly during such processes, as loss of adsorbed water, dehydration, crystallization, the phase transitions, sintering, collapse of porous structure etc. The change of diffusion resistance of a material determining of fluxes from a sample, as inert gas probe, and gaseous products of solid-state reaction was simultaneously measured. The DSA is tested on various classes of substances and types of solid-state processes. Its high sensitivity and resolution was demonstrated.

As a result of the carried out researches with use DSA it was possible to reveal temperature range of the basic processes. Temperatures the beginning collapse of porous structure of adsorbent and sintering of fibers in particular are revealed. The recommendations for optimum conditions of thermal treatment of materials are given. On an example basalt planar adsorbents all cycles of design (molecular, phase, modular and hardware) are carried out, and the recommendations for development of a design of the apparatus of regular structure are given. Alumina pillared montmorillonite is recommended as a substrate for catalysts of reactions of thermal decomposition of high molecules substances. The Al-MMT, besides are recommended for extraction of radionuclides from liquids waste of the nuclear plants. The porous basalt fibers are offered for vitrofication of radioactive substances with the purpose of their subsequent long time burial. The perovskite based ceramics are offered for ceramization of high level radioactive wastes. Durability of products intended for an encapsulation of radionuclides, tested on an example of perovskite subjected of thermochemical treatment. The new materials, created because of use of DSA, will be transferred on system of suppression of radioactivity of a nuclear power plants of Czech and Russia, and photocatalysts on a basis of titanium oxide will be recommended for photocatalytic technology of water treatment and air purification in Russian industry.

The information received within the framework of the present work is used in three chapters of the monograph: V.Balek, I.N.Beckman "Diffusion-structural analysis of solids". Scientific material used in the course of lectures for the students of chemical department of MSU on a topic "Materials for environment cleaning". Five papers are directed to a scientific journals and four reports at the International scientific conferences was made.

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