RIGA TECHNICAL UNIVERSITY

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# SORPTION PROPERTIES OF CRYSTALLINE FERRIC HYDROXIDES (OXIDES) AND LATVIA'S CLAYS

Dr. habil. chem. theses

**SUMMARY**

**Riga**

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This work has been done at the Chair of Inorganic, Analytical and Physical Chemistry of the Faculty of Chemical Technology of the Riga Technical University within a period from 1964 to 1997.

Kind of work: Synopsis of published research works in chemistry, subdivision physical chemistry, for the degree of Dr. habil. chem.

Official opponents: Dr. habil. phys. **Juris Tiliks**
Dr. habil. chem. **Uldis Sedmalis**
Dr. habil. sc. ing. **Antanas Sadunas**

This work will be presented in May 14, 1998 at 14.00 during the open session of the Habilitation and Promotion Council in Chemistry at University of Latvia, room 21, 48 , Kr. Valdemara street, Riga.

The Synopsis and the Summary of this work is available in the Library of the University of Latvia, 4, Kalpaka boulevard, and Latvian Academic Library, 10, Rupniecibas street, Riga.

Chairman of the Council,
Dr. habil. chem., professor A. Zicmanis

## IMPORTANCE AND TOPICALITY OF THE PROBLEM

Properties of dispersed systems are essentially determined by the values of the specific surface area and by the pore structure parameters characteristic of the layered solid powders. The problem has been studied for years. Today it becomes important due to the rapid development of the material science and new technologies. As evidence for it serve the increasing number of articles, reviews and monographs, as well as the holding of national and international symposiums, the most important ones among them being the series COPS (Characterisation of Porous Solids) organised by IUPAC.

A lot of experimental methods are used to study the porous structure of solids. It is well known that the determination of adsorption and desorption isotherms is the most important and frequently used method. The Commission on Colloid and Surface Chemistry Including Catalysis of International Union of Pure and Applied Chemistry (IUPAC) has elaborated recommendations for reporting the sorption data with special reference to determination of the surface area and of porosity. The recommendations reflect the recent development of adsorption theory and the progress in studies of porous solids structure. The methodology of the present work was based on these recommendations.

The main idea of this research was to resolve certain problems of theory and practical application of highly dispersed systems with layered solid powders. The pore structure characteristics, the specific surface area, and their changes were studied. The studied materials are of great importance for Latvian economics. Ferric hydroxides, oxides and clays are widely found in Latvia as important components of soil where they participate in ion - exchange -adsorption processes. These compounds are significant also in other natural colloidal systems and mixtures. The surface of clay particles is frequently covered with hydroxicompounds of iron. Research of sorption capacity of these materials is an urgent problem for Latvia

especially now. It is connected with environmental protection problem and its improvement. In fact, mathematicians have worked on models on assessment of risks caused by outflow of oil (U. Buikis, 1989). The absence of sorption data for Latvian minerals (clays included) makes it difficult to fit the models to the actual situations. The soil remediation in former Soviet army missile bases is also an urgent problem. The knowledge on the surface phenomena occurring in the nature needs elucidation. It is important to investigate the possibilities of introducing the Latvia's clays into new, non- traditional areas of applications, such as sorbents or flocculates of water treatment, as bleaching material of vegetal or other oils, etc.

## AIMS AND OBJECTIVES OF THE RESEARCH

The aim of this work was to establish the relationship between the properties of specific highly dispersed solid powders and parameters of the surface characteristics. Two kinds of powders were studied:

- synthetic crystalline ferric hydroxides and products of their thermal decomposition, and
- natural and modified clays from several Latvian deposits.

The results of theoretical and experimental research have been presented in two chapters. A synopsis of study on $\alpha$ and $\gamma$ crystalline ferric hydroxide powders and their thermal decomposition products are reported in the first chapter.

The second chapter deals with the research results on sorption properties of Latvian clay samples. In such a way the principle "from the simple to the complex" was realised. At first, comparatively simple ferric hydroxides and oxides were studied. Then the properties of more complex objects - clay samples were elucidated. The contents of the first chapter have been dealt with the articles published from 1964 to 1993. The contents of the second chapter are based on articles published

from 1973 to 1997. Some articles have been submitted for publication in "Latvian Journal of Chemistry" and in "Journal of Applied Chemistry" ( Russia).

The main part of the experimental work was carried out in the laboratory of Faculty of Chemical Technology of Riga Technical University. Some experiments were performed in other laboratories both in Latvia and in Russia.

All the publications were written by the author. The opinions of the co-authors have been taken into consideration. Some contribution to this work has been made by professors L. Liepina and E. Gudriniece, assistant professor R. Buman, A. Raman and others.

The author has published 57 scientific publications, among them 30 are concerned with the present work.

The main results of the performed research are given and analysed in the synopsis of the work.

## OBJECTS AND METHODS OF RESEARCH

The sorption properties of crystalline ferric hydroxides (oxides) and natural, as well as modified Latvia's clay samples, have been studied. The clay samples were taken from several deposits (Liepas, Kupravas, Usmas, Lazhas, Rolavas, Ozolnieku, Akmens, Pampalu, Zanas, Vadakstes, Libertu, Strelu, Priekules and others).

The chemical analysis and other chemical and physical - chemical analysis methods (X - Ray, thermography, electron microscopy, photocolorimetry, ect.) were carried out to characterise the composition of the samples. The main attention has been paid to the measurement of the adsorption and desorption isotherms of nitrogen, argon, n-hexane, carbon tetrachloride, benzene, methanol and water vapours. IUPAC recommendations have been strongly followed. Adsorption of dyes from solutions was measured at constant temperature. The influence of several treatments ( thermal treatment, treatment with mineral acids) on surface properties and porosity was studied.

## CONCLUSIONS

**1.** For the first time in the history of the Latvian science a wide and systematic study of the sorption characteristics and porosity of the Latvia's clay samples was carried out. Specific surface area values,pore volume, pore size distribution curves and other data had been compiled in an electronic and printed form.

**2.** Calculation methods of standard parameters characteristic of surface and porosity, especially convenient for studied samples, have been elaborated.

**3.** After the results of different experiments had been gathered, the conclusion was drawn that sorption isotherms may be divided into two groups following the forms of the isotherms and the hysteresis loops. The crystalline structure of clay minerals is important in this respect. Samples with smectite structure are included in the first group. The samples of non swelling structure, such as illites or hydromices, are included into the second group. Significant for the isotherms of the first group samples is the parallel orientation of the hysteresis loop to the pressure axis and a shoulder on the desorption isotherm at $P/Po \approx 0.3$.

**4.** It has been proved experimentally that crystalline ferric hydroxides are active sorbents (according to Gregg's view point) increasing the value of the specific surface area as the thermal treatment temperature increases. The specific surface area of clay samples decreases after thermal treatment, but increases upon acidic treatment. The Latvian clay samples also should be included into the group of active sorbents, if Gregg's classification is improved.

**5**. A new pore structure model has been proposed by the author in order to develop the pore structure theory of layered solid corps. The model describes in full the complex pore structure changes during the thermal treatment of $\alpha$ ferric hydroxide. It explains both the pore structure changes of $\gamma$ ferric hydroxide during the thermal treatment and the pore structure changes of smectyte type clay samples occurring under action of mineral acids.

**6.** The pore structure model has been improved and used to calculate the standard isotherm of water vapour adsorption. The standard adsorption isotherm makes it possible both to estimate the volume of micropores and the value of the specific surface area of micropores as well as mesopores.

7**.** For the first time a new characteristic feature of sorbents i.e. the fractal dimension D of studied samples has been calculated.

**8.** On the basis of many experiments it has been concluded that treatment with mineral acids is one of the most important ways of changing the surface and the porosity of clays.

In general, the following trends in the specific surface area and pore structure changes have been established as the acid concentration increases:

- the values of the specific surface area pass through a maximum;
- continuous increase in the characteristic pore radius;
- increase in the total pore volume for the samples of smectyte type structure;
- initially the total pore volume increased, but then decreased for the samples of illite type structure.

These relations are basic for the preparation of sorbents with desired properties from Latvia's clays.

**9.** Some clay samples (from deposits Liepas, Usmas, a. o.) were found to give homogeneous adsorbents as the products of acidic treatment. The potential barriers between the adjacent adsorption positions on such adsorbents surface are low. They can be used in gas-adsorption chromatography as adsorbents or in gas-liquid chromatography as supports of the non-volatile phase.

**10.** The use of the studied clay samples for bleaching of vegetal oils may be considered as the most important contribution to the recent history of utilisation of Latvian clays. It was reported in "Latvian Journal of Chemistry" in 1993. It was shown by the author for the first time that local raw material may be successfully used in a new field of utilisation, in the field which is important for the further

development of Latvian economy. Now the obtained experimental data gives us hope to resolve the problems of optimising rapeseed oil production. The theoretical approach to the optimisation problem is based on the acidic treatment effects formulated by the author.

**11.** The new type sorbents obtained from the by-products of rapeseed oil bleaching may currently attract some attention. It should be considered as an example of waste-free technology. After bleaching the used sorbents contained 40 and more per cent of rapeseed oil, the separation of which was very difficult. The sorbents were thermally treated (coked) at several temperatures to $600^0$ C in the presence of air. A series of new type sorbent samples were obtained. The particles of the sorbents are composed from two parts: the core and the surface layer. The core was alumosilicate (matrix), which was covered with a coke layer (in a way similar to active charcoal). The synthesized new type sorbents have good adsorption capacity of organic compounds from the gas phase and high thermal resistance, which is important in regeneration for repeated use of sorbents.

**12.** The research on adsorption of cation-active dyes from water solution (methylen blue, methyl violet) has made it possible to show that Latvian clays may be used as cheap and efficient sorbents in paper, textile and similar production for waste water treatment. Great attention has been paid to the improving the experimental measurements for obtaining reproducible results.

It was observed that the time for attaining to the adsorption equilibrium sometimes is longer than mentioned in references. The measured adsorption isotherms were of the Langmuir's type. The ion exchange capacity has been calculated using the values of maximal adsorption of dyes. It was established that the ion exchange capacity depends on the concentration of mineral acid (sulphuric, hydrochloric) used for activation. Increasing the acid concentration decreases the ion exchange capacity.

**13.** The present research of highly dispersed powders enable us to conclude that both the pore structure and the surface characteristics of layered solids, allow to resolve important theoretic and practical problems. It may be supposed that a new prosperous theoretically interesting and practically significant trend has been initiated in the history of Latvia's clay research.

## APPROBATION

The reports on the current work results were regularly delivered at USSR conferences **(**Leningrad, 1971, Kosova, 1986), at international and national symposiums and conferences (IUPAC Symposium on Characterization of Porous Solids, COPS II, Alicante, Spain, 1990; World's Symposium of Latvian Science, Riga, 1991; IUPAC Symposium on the Characterization of Porous Solids, COPS III, Marseille, France, 1993; Latvian Workshop "Problems of the Pollution, Analysis and Methods", Riga, 1994; Fourth Euro Ceramics Society Symposium (ECERS IV), 1995, Italy; Colloquium on Pollution, Riga, 1995;
Fifth Euro Ceramics Society Symposium (ECERS V), France, 1997.).

The current work was examined in an open session of Inorganic, Analytic and Physical Chemistry Chair of the Riga Technical University Faculty of Chemical Technology, on 13th March, 1998, Report No.5, with favourable references and in an open session of Physical Chemistry Chair of the University of Latvia Chemical Faculty on 16th March, 1998, Report No.6, with favourable references and the decision to promote the work to the Habilitation and Promotion Council in Chemistry at University of Latvia as meeting the set requirements by content, volume and significance.