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SORPTIVE PROPERTIES OF FLUOR-HYDROXY-ALUMINIUM COMPLEXES OF MONTMORILLONITE

A b s t r a c t. When specific modification procedure is adopted, the introduction of fluor-hydroxy-aluminium polycations into the interlayer spaces of montmorillonite produces a rigid complex with a definite pore structure. The polymeric polycations undergo reversible rehydration at temperatures up to 550°C, whereas at higher temperatures they pass into unhydrating-aluminium oxyfluoride groupings. These properties have been documented by X-ray studies (Table 1). The increase in sorptive capacity (argon) relative to the untreated sample is due to the development of microporous structure (Table 2). Calcination brings about the decrease in sorptive capacity, attended by the decrease in micropore content in the total porosity of the sample.

INTRODUCTION

The interesting properties of montmorillonite complexes obtained by the introduction of complex hydroxy polycations of different metals into the exchange positions of this mineral (Brindley, Sempels 1977; Yamanaka, Brindley 1978; Shabtai 1979) are largely due to their specific sorption properties. The present studies were carried out on dioctahedral montmorillonite with fluor-hydroxy-aluminium polycations introduced into the interlayer spaces. The conditions of synthesis of polycations containing fluorine were described by Fijał and Olkiewicz (1983).

The sorptive properties of the resulting montmorillonite complexes and their porosity were determined from low-temperature argon adsorption and desorption, as well as from densimetric and porosimetric studies.

EXPERIMENTAL

Investigations were carried out on dioctahedral montmorillonite separated by sedimentation from the Chmielnik bentonite (< 10 µm fraction). Complex fluor-hydroxy-aluminium polycations were synthesized in solution at the ratio of Al:

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$(\text{OH} + \text{F}) = 1 : 2$. Montmorillonite suspension was then added to the solution at continuous stirring for 2 hours, whereby a montmorillonite complex with polycations at the exchange sites was formed. X-ray investigations were made to document the cation exchange and to demonstrate the enhanced thermal resistance of samples. Powder patterns were recorded with a DRON-3 X-ray diffractometer, using filtered $\text{CuK}\alpha$ radiation from a GPNT-1500 high-temperature camera.

The adsorption and structural studies included the determination of basal argon adsorption isotherms at $p/p_0 = 0.05$ —0.96 and isotherms at low relative pressures

Table 1

Positions of the 001 basal reflection of montmorillonite complex at different temperatures

Calcination temperature	d_{001} during calcination at specific temperature (\AA)	d_{001} after dehydration at room temperature
20°C	18.03—18.21	18.03—19.04
450°C	15.50	18.03
500°C	14.98	16.99
550°C	14.98	16.66

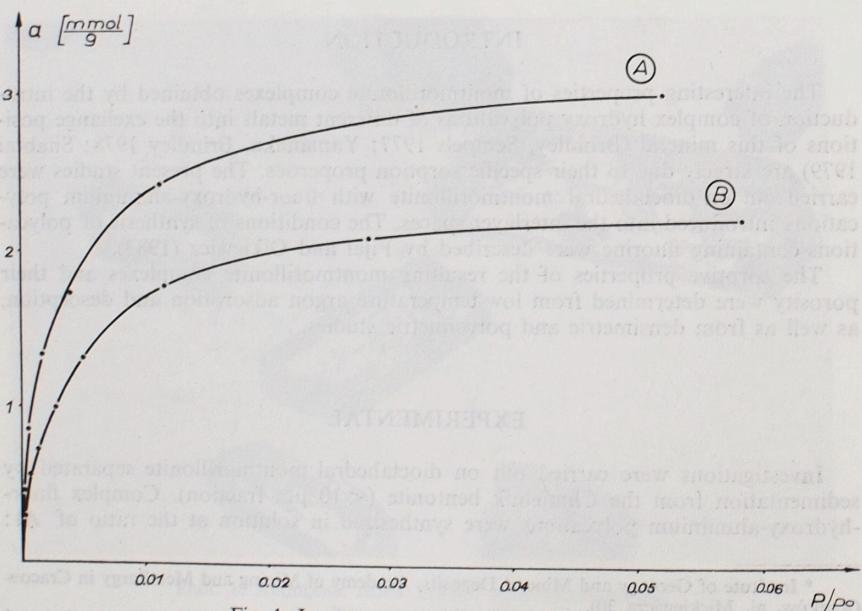


Fig. 1. Low-pressure argon adsorption isotherms
A — initial sample, B — calcinated sample

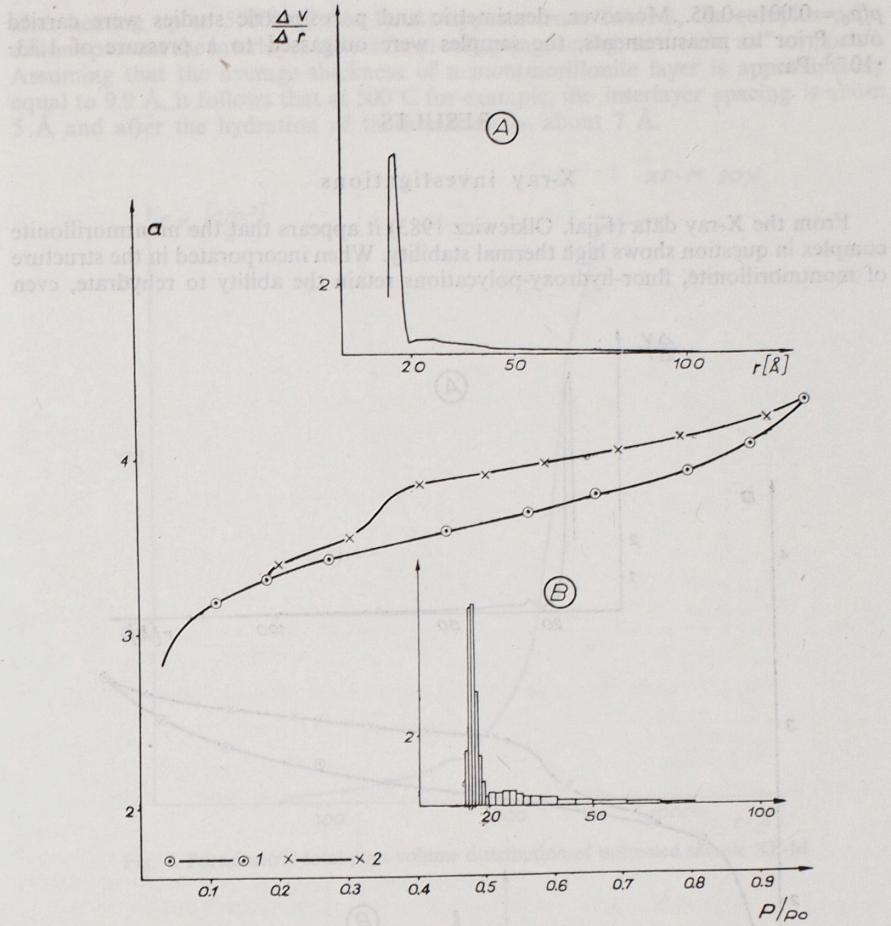


Fig. 2. Argon adsorption (1) and desorption (2) isotherms; total (A) and differential (B) pore volume distribution of untreated sample XF-M

Table 2
Porosity calculated from mercury and helium specific gravity. Characteristics of the pore structure of samples

Sample	d_{Hg} g/cm^3	d_{He} g/cm^3	V_{Hg} cm^3/g	V_{He} cm^3/g	V_s cm^3/g	V_{mic} cm^3/g	V_{mes} cm^3/g	V_{mac} cm^3/g	S_{BET} m^2/g
XF-M	1.651	2.593	0.606	0.386	0.220	0.084	0.012	0.124	227.2
XF-M calc.	1.861	2.549	0.537	0.390	0.145	0.063	0.011	0.071	170.6

$p/p_0 = 0.001\text{--}0.05$. Moreover, densimetric and porosimetric studies were carried out. Prior to measurements, the samples were outgassed to a pressure of $1.33 \cdot 10^{-3}$ Pa.

RESULTS

X-ray investigations

From the X-ray data (Fijal, Olkiewicz 1983) it appears that the montmorillonite complex in question shows high thermal stability. When incorporated in the structure of montmorillonite, fluor-hydroxy-polycations retain the ability to rehydrate, even

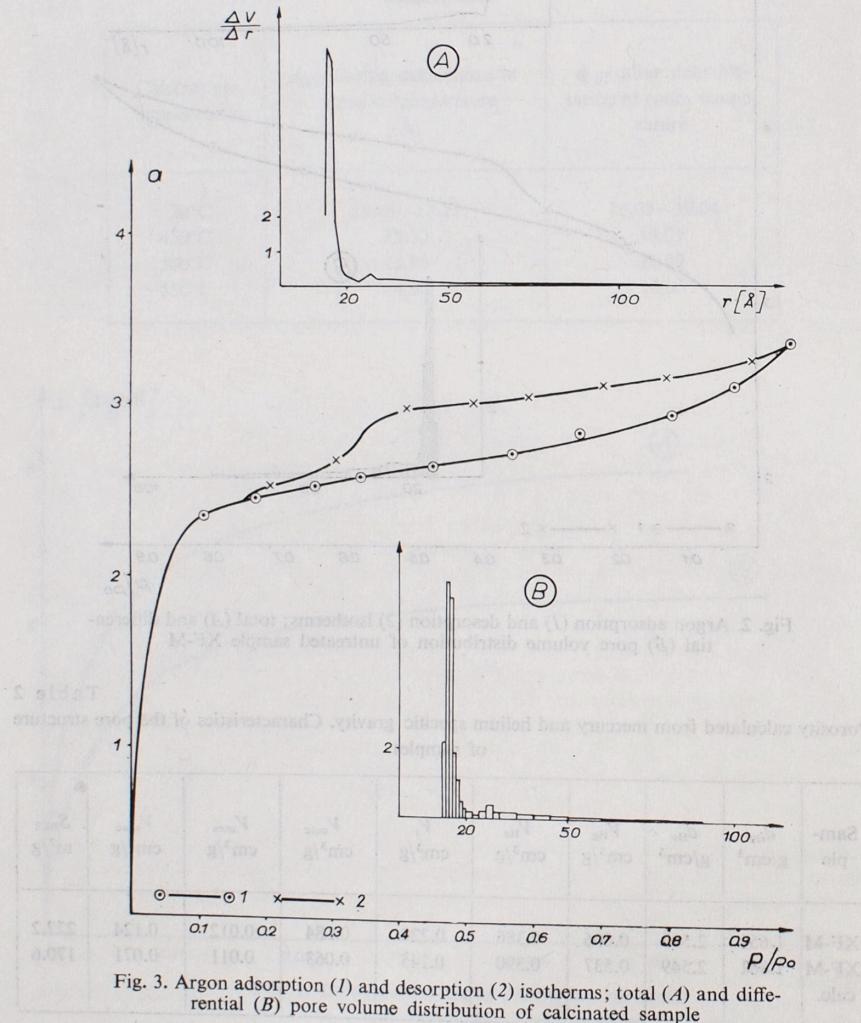


Fig. 3. Argon adsorption (1) and desorption (2) isotherms; total (A) and differential (B) pore volume distribution of calcinated sample

after heating up to 550°C (Table 1). As appears from Table 1, the complex polycations prevent the interlayer spaces from collapsing, acting, as it were, as "supports". Assuming that the average thickness of a montmorillonite layer is approximately equal to 9.9 \AA , it follows that at 500°C for example, the interlayer spacing is about 5 \AA and after the hydration of these cations — about 7 \AA .

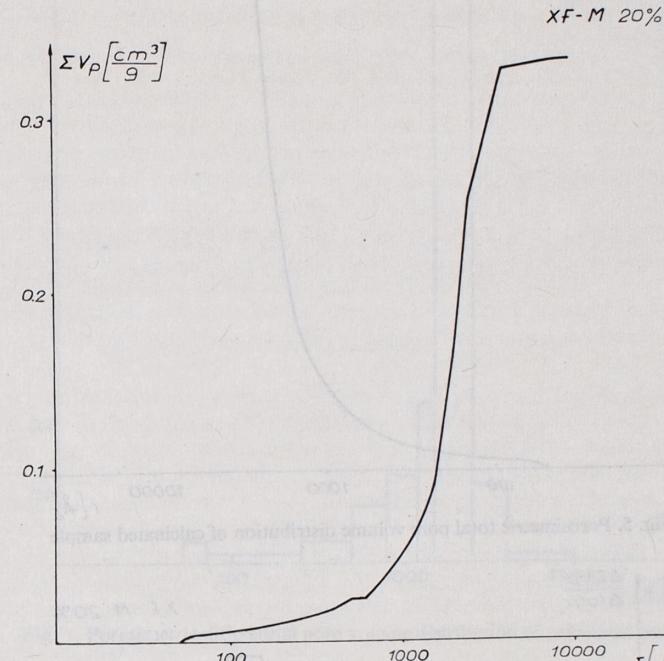


Fig. 4. Porosimetric total pore volume distribution of untreated sample XF-M

Adsorption investigations

Adsorption investigations were limited to measurements of argon adsorption at low relative pressures $p/p_0 = 0.001\text{--}0.05$ and over the whole range of relative pressures $p/p_0 = 0.05\text{--}0.98$, also including desorption isotherms. From low-pressure adsorption isotherms (Fig. 1) liquid argon volume W_o required for filling micropores was calculated, using Raduszkiewicz-Dubinin's equation ($\lg W = \lg W_o - D \lg^2 \frac{P_0}{P}$). The resulting values were regarded as indicating the micropore volume in the total pore volume of a sample. From desorption isotherms mesopore volume was calculated and their total and differential distribution against their pore radius was determined (Figs. 2, 3). The total pore volume V_s of the samples studied was determined from apparent (mercury) and true (helium) specific gravity. This parameter is the difference of mercury and helium volumes:

$$V_s = V_{Hg} - V_{He}$$

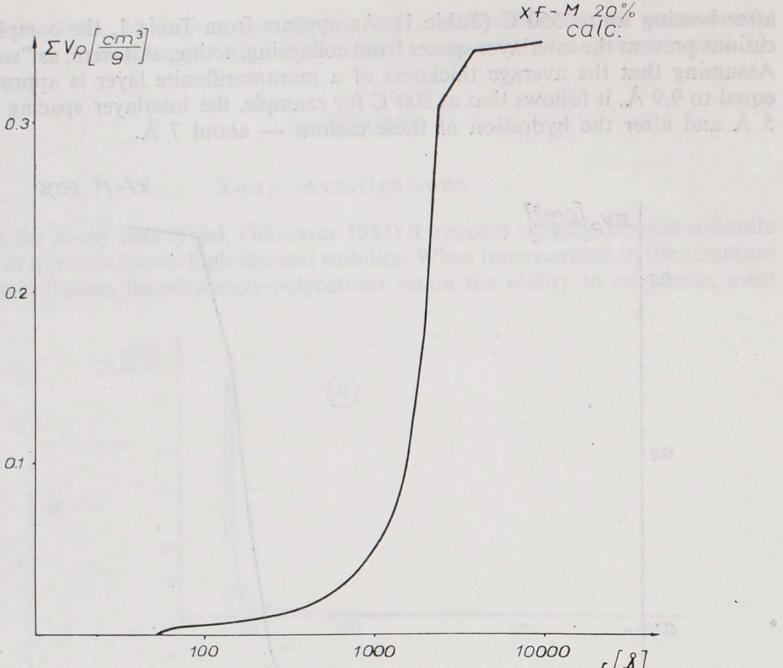


Fig. 5. Porosimetric total pore volume distribution of calcinated sample

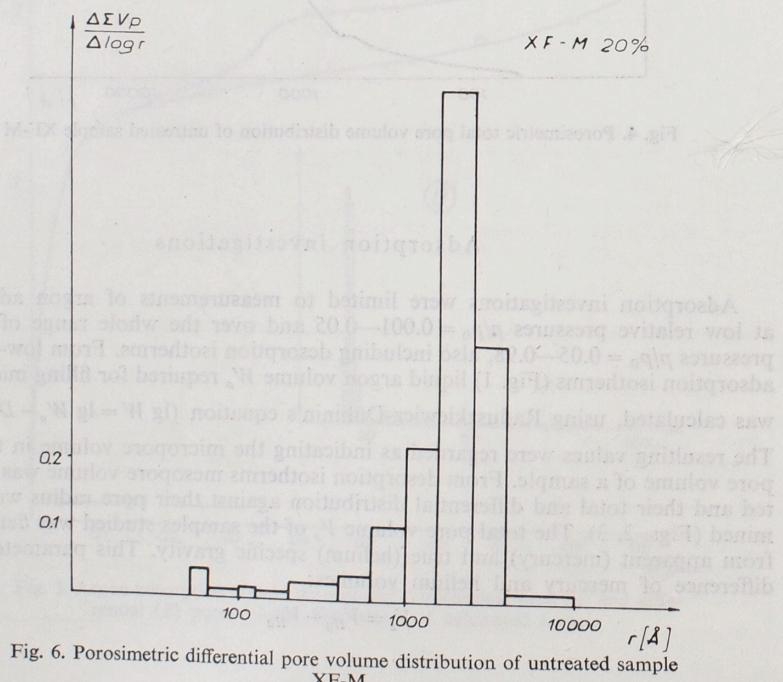


Fig. 6. Porosimetric differential pore volume distribution of untreated sample
XF-M

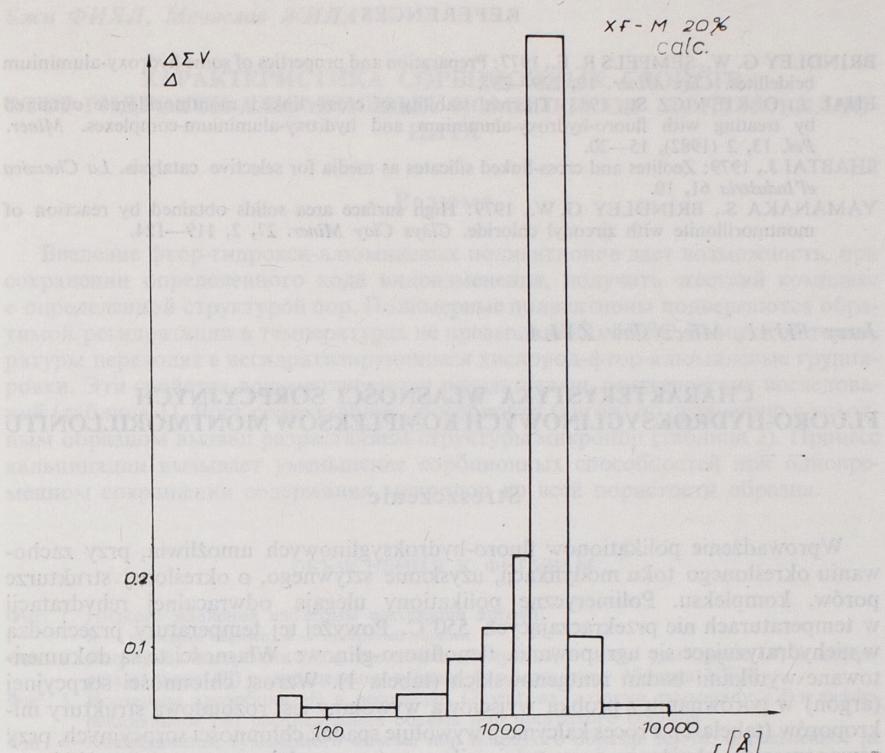


Fig. 7. Porosimetric differential pore volume distribution of calcinated sample

Some basal isotherms in the range of relative pressures $p/p_0 = 0.05$ — 0.35 were used to calculate the BET specific surface areas.

The calculated sorption-desorption parameters are presented in Table 2. It appears from the data that the content of micro- and macropores in the total pore volume is significant, while the percentage of transitional porosity (mesopores) is relatively low. From the differential pore volume distribution curves, determined from argon desorption isotherms, it is evident that the differences in mesopore volume distribution are insignificant. The results also indicate that during calcination of the sample XF-M, micropore volume decreases markedly, which fact is reflected in the change of specific surface areas.

Porosimetric results are presented in the form of graphs illustrating changes in the total and differential pore volume as a function of pore radius (Figs. 4—7). From the graphs it appears that the narrow pore volume maximum corresponds to pores of a radius of 100—600 nm. Calcination causes the pore volume maximum to shift to the interval of radius values of 200—600 nm.

It is worth noting that the montmorillonite samples with complex polycations acting as supports of montmorillonite layers show definitely better structural and sorption properties than untreated montmorillonite, yet they are inferior to synthetic zeolites of the 5A or 13X type.

Translated by Hanna Kisielewska

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CHARAKTERYSTYKA WŁASNOŚCI SORPCYJNYCH FLUORO-HYDROKSYGLINOWYCH KOMPLEKSÓW MONTMORILLONITU

Streszczenie

Wprowadzenie polikationów fluoro-hydroksyglinowych umożliwia, przy zachowaniu określonego toku modyfikacji, uzyskanie sztywnego, o określonej strukturze porów, kompleksu. Polimeryczne polikationy ulegają odwracalnej rehydratacji w temperaturach nie przekraczających 550°C. Powyżej tej temperatury przechodzą w niehydratyzujące się ugrupowania tlenofluoro-glinowe. Własności te są dokumentowane wynikami badań rentgenowskich (tabela 1). Wzrost chłonności sorpcyjnej (argon) w porównaniu z próbką wyjściową wywołany jest rozbudową struktury mikroporów (tabela 2). Proces kalcynacji wywołuje spadek chłonności sorpcyjnych, przy równoczesnym obniżeniu zawartości mikroporów w całej porowatości próbki.

OBJAŚNIENIA FIGUR

Fig. 1. Niskociśnieniowe izotermy adsorpcji argonu.

A — próbka wyjściowa, B — próbka wygrzewana

Fig. 2. Izoterna adsorpcji (1) i desorpcji (2) argonu oraz sumaryczny (A) i różnicowy (B) rozkład objętości porów próbki wyjściowej XF-M

Fig. 3. Izoterna adsorpcji (1) i desorpcji (2) argonu oraz sumaryczny (A) i różnicowy (B) rozkład objętości porów próbki wygrzewanej

Fig. 4. Rozkład sumarycznej objętości porów próbki wyjściowej XF-M wyznaczony z pomiarów porozymetrycznych

Fig. 5. Rozkład sumarycznej objętości porów próbki wygrzewanej wyznaczony z pomiarów porozymetrycznych

Fig. 6. Rozkład różnicowej objętości porów próbki wyjściowej XF-M wyznaczony z pomiarów porozymetrycznych

Fig. 7. Rozkład różnicowej objętości porów próbki wygrzewanej wyznaczony z pomiarów porozymetrycznych

Ежи ФИЯЛ, Мечислав ЖИЛА

ХАРАКТЕРИСТИКА СОРБЦИОННЫХ СВОЙСТВ ФТОР-ГИДРОКСИ-АЛЮМИНЕВЫХ КОМПЛЕКСОВ МОНТМОРИЛЛОНИТА

Резюме

Введение фтор-гидрокси-алюминевых поликатионов дает возможность, при сохранении определенного хода видоизменения, получить жесткий комплекс с определенной структурой пор. Полимерные поликатионы подвергаются обратимой регидратации в температурах не превышающих 550°C. Выше этой температуры переходят в негидратизирующиеся кислород-фтор-алюминевые группировки. Эти свойства документируются результатами рентгеновских исследований (таблица 1). Рост сорбционной способности (аргон) по сравнению с исходным образцом вызван разрастанием структуры микропор (таблица 2). Процесс кальцинации вызывает уменьшение сорбционных способностей при одновременном сокращении содержания микропор во всей пористости образца.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Низкого давления изотермы адсорбции аргона

A — исходный образец, B — прогретый образец

Фиг. 2. Изотермы адсорбции (1) и десорбции (2) аргона, а также суммарное (A) и дифференциальное (B) распределение объема пор исходного образца XF-M

Фиг. 3. Изотермы адсорбции (1) и десорбции (2) аргона, а также суммарное (A) и дифференциальное (B) распределение объема пор прогретого образца

Фиг. 4. Распределение суммарного объема пор исходного образца XF-M, определенное на основании порозиметрических измерений

Фиг. 5. Распределение суммарного объема пор прогретого образца, определенное на основании порозиметрических измерений

Фиг. 6. Распределение дифференциального объема пор исходного образца XF-M, определенное на основании порозиметрических измерений

Фиг. 7. Распределение дифференциального объема пор прогретого образца, определенное на основании порозиметрических измерений