

THE SURFACE PROPERTIES AND Cs ADSORPTION OF NATURAL AND ACID-MODIFIED MONTMORILLONITES

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Bentonite (montmorillonite) clays is widely used in various industries, including nuclear power and particularly radioactive waste management as a component of engineered barrier systems for the radioactive waste disposal (Sellin and Leopin, 2013). During a long term operation of radioactive waste disposal site, engineered barriers based on bentonite may be exposed to thermochemical effects

The aim of this research is to assess the mechanism of montmorillonite's structure and the adsorption properties transformation in the process of the long-term interaction with a nitric acid solution.

Objects: Dashkovsky deposit (Moscow region) and Tagansky deposit (Kazakhstan)
Experiments: 10M HNO₃, 90°C, 1-5 hours; ¹³³Cs and ¹³⁷Cs adsorption.

Methods: XRD (Rigaku Ultima-IV, CuKα), FTIR (Bruker, Vertex 80v), XRF (PANalytical, Axios mAX), ICP-MS (Thermo, X-Series7); SEMy (Carl Zeiss, LEO 1450VP, sample preparation by the vacuum freeze-drying), Sbet (Quadrascorb SI/Kr); CEC (by methylene blue).

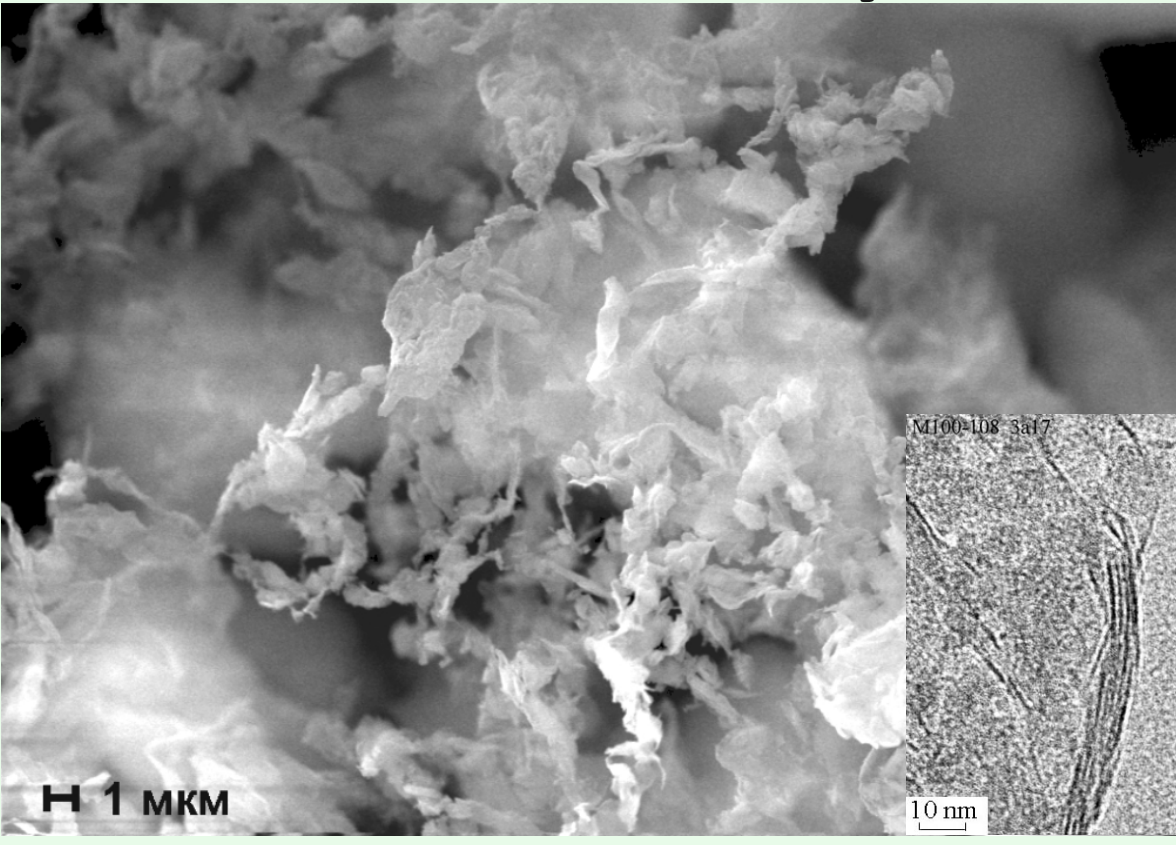
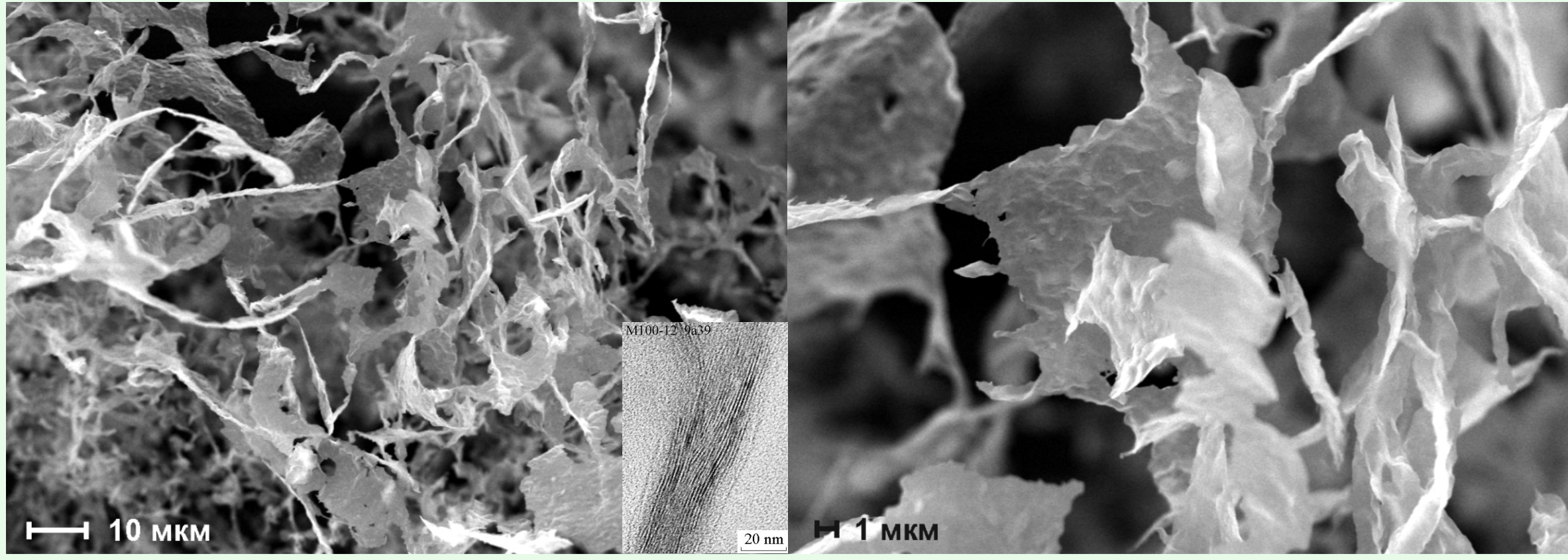
ACID MODIFICATION

Modification of smectites' particles interaction

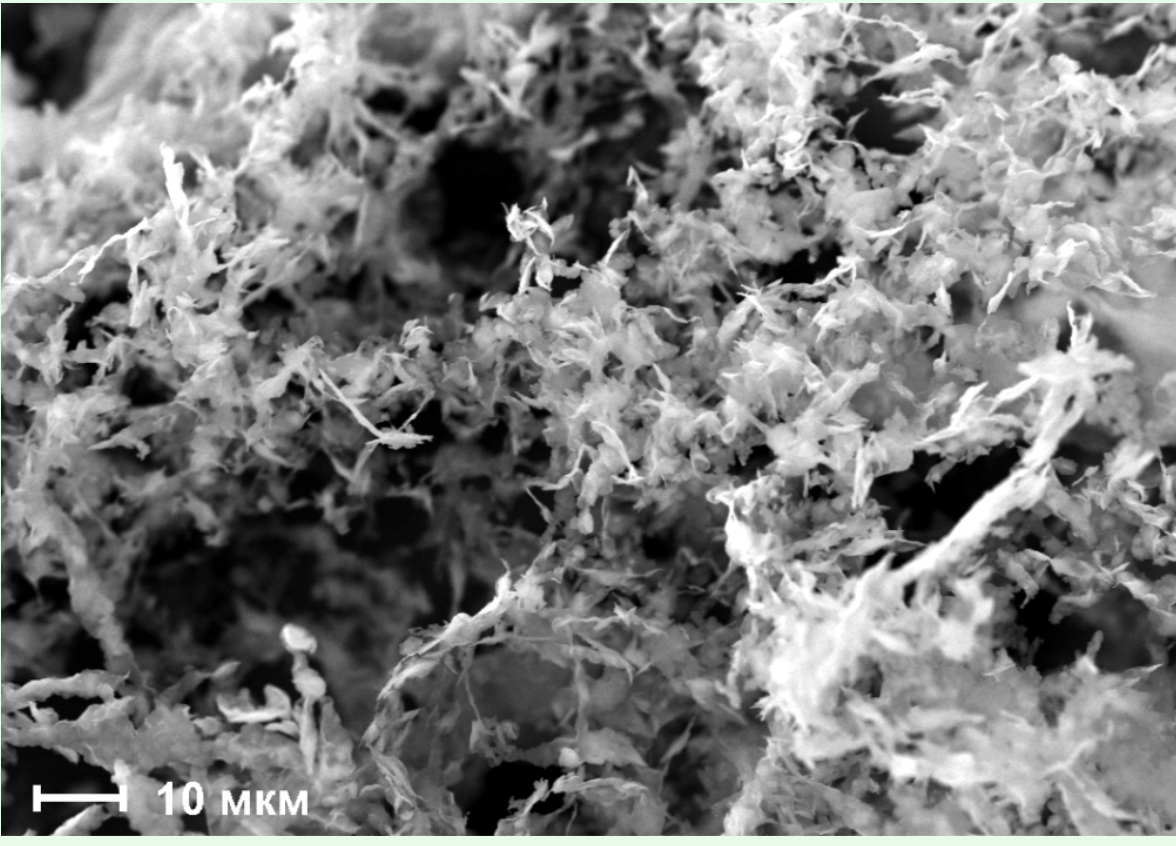
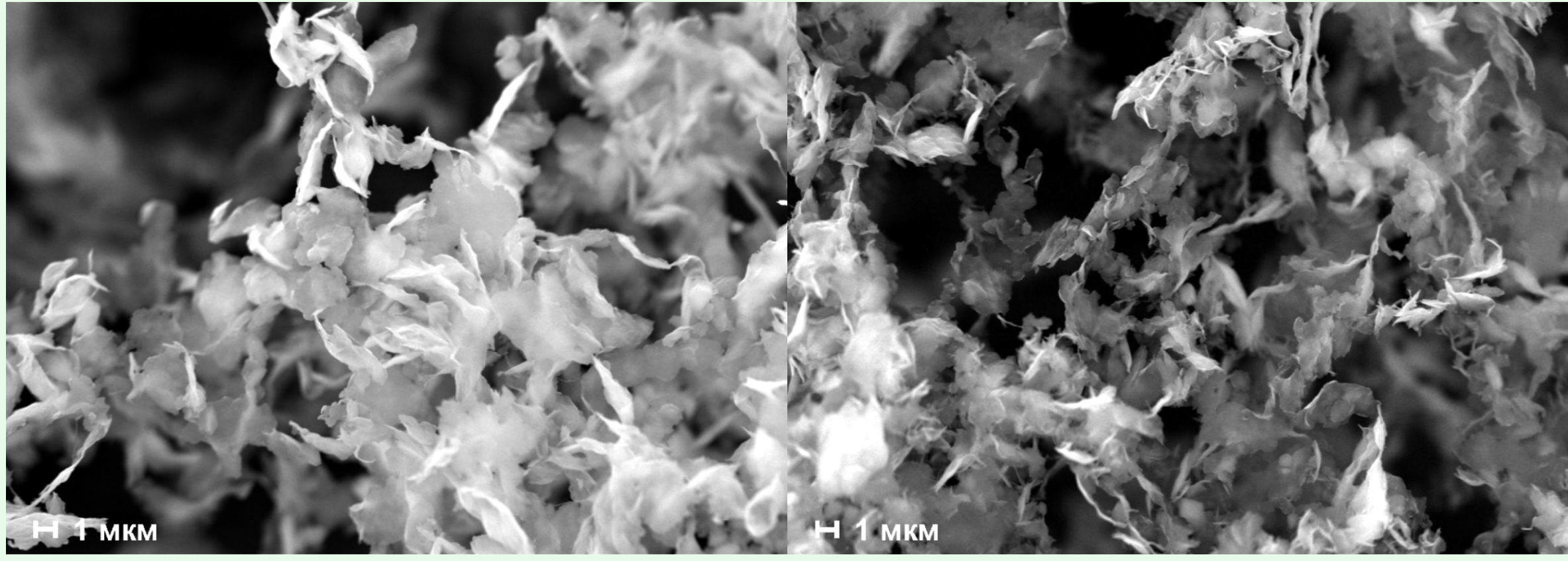
SEM Images of natural clays

Acid-modified clays

Taganskiy Mont



Dashkovskiy Mont



The suit of methods allows us to simulate the mechanisms of structural transformations of montmorillonite as a result of exposure to nitric acid, which are expressed in the leaching of interlayer cations, partial interlayer protonation (substitution of interlayer cations to oxonium ion), leaching octahedral cations of the positions, partial destruction of the layer 2:1 structure. It was noted by other authors (Timofeeva *et al.*, 2015, and others) that Fe and Mg are less stable to leaching than Al. Thus, montmorillonites with mainly Al in octahedral sheet and a small amount of Mg substitution, are more resistant to thermochemical treatment compared to montmorillonites with a significant degree of Fe to Al substitution.

Dashkovskiy montmorillonite has a 10-20% of tetrahedral charge and shows greater stability to acid treatment. A significant reduction in the charge layer in Taganskiy montmorillonite leads to the formation of pyrophyllite-like structures with a layer charge close to 0.

Transformation of structural characteristics, and, primarily, reduction of the charge and its redistribution between tetrahedral and octahedral sheets resulting thermochemical effects modifies the interaction of montmorillonite particles in pore space, that can be visualized by changes of the bentonite suspension microstructure using a scanning electron microscope. The reduction of the Tagansky montmorillonite layer charge after acid treatment demonstrates completely lose particles ability to interact with each other. In turn, the Dashkovsky montmorillonite particles retain the ability to form microaggregates which are characteristic for smectites even after treatment.

The absorption capacity of the interlayer is determined mainly by the layer charge and its distribution between the octahedral and tetrahedral sheets. Montmorillonite is typically characterized by localization of the layer charge in octahedral sheets due substitution of Al to Mg, Fe, and others.

Acid treatment - change of chemical composition

		Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	LOI	Wg, %
I - Taganskiy	Natural	1.10	3.75	16.29	61.61	0.22	1.42	6.67	7.97	9.24
	10 HNO ₃ , 1 h	0.16	2.92	14.62	68.65	0.13	0.06	4.31	8.22	22.53
	10 HNO ₃ , 5 h	0.10	1.28	7.79	80.93	0.12	0.05	1.89	6.82	23.65
II - Dashkovskiy	Natural	0.24	2.89	18.13	58.28	3.09	1.47	6.33	8.76	8.60
	10 HNO ₃ , 1 h	0.17	2.45	18.65	62.24	2.99	0.06	5.05	7.63	6.44
	10 HNO ₃ , 5 h	0.14	2.49	17.79	62.89	2.98	0.05	4.86	8.10	6.01

Tagansky montmorillonite belongs to this type. In some cases, a small proportion of isomorphous substitutions of Si to Al gives rise to a tetrahedral charge, respectively. Overall, the amount substitutions of this kind for montmorillonite is low, but very important for the adsorption of cations, in particular Cs⁺. The obtained data on the adsorption of Cs-137 shows that at low concentrations, the process is mainly determined by the absorption of Cs into tetrahedral sheets, creating a stronger field near the layer surface. Thus, the adsorption capacity for Cs-137 is larger for Dashkovsky montmorillonite which has about 20-30% of the tetrahedral charge whereas Tagansky has the layer charge localized in octahedral grids and therefore the lower adsorption capacity for Cs-137. However, the total amount of adsorbed Cs-133

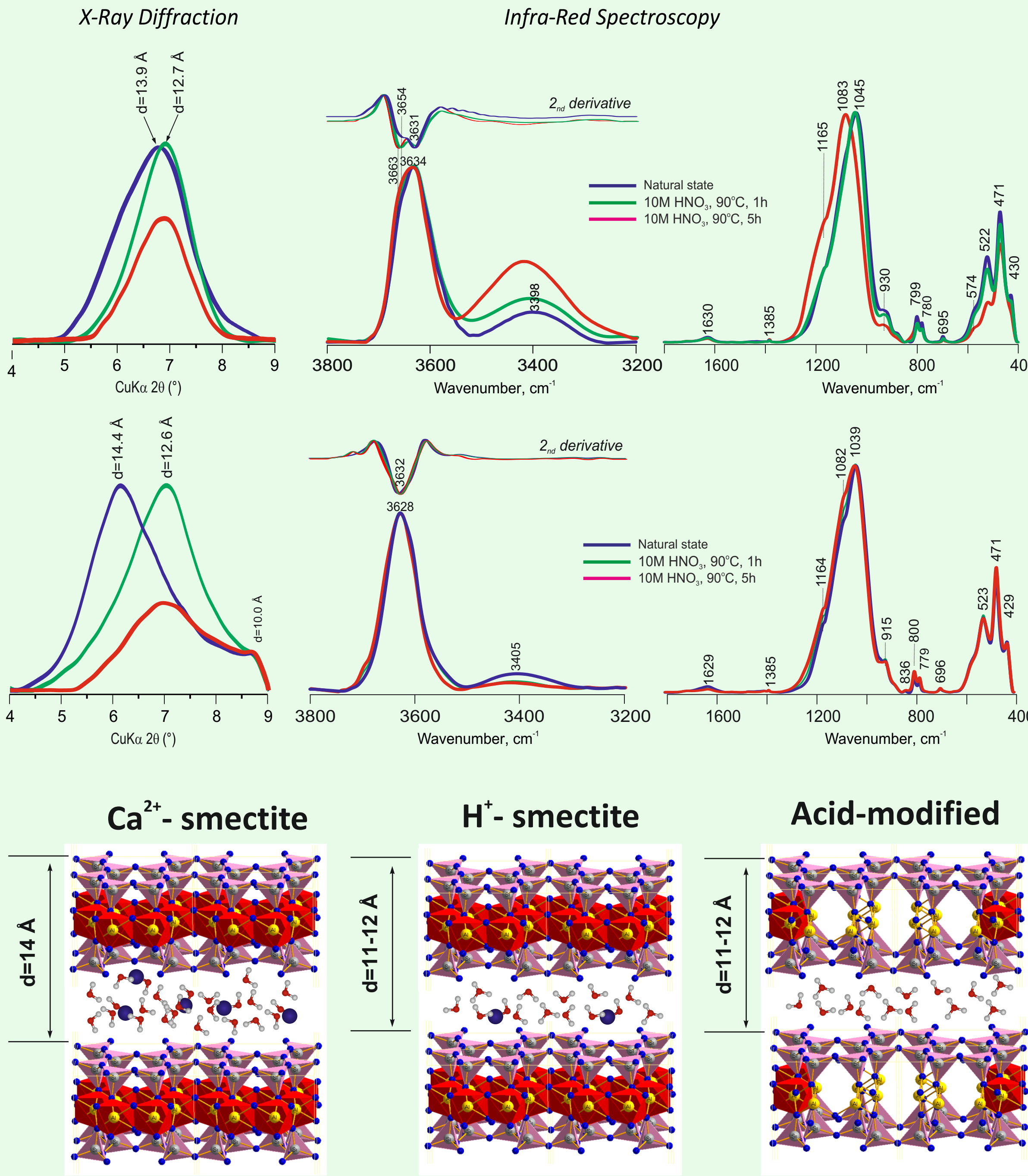
is determined by the overall cation exchange capacity, which is higher for Tagansky montmorillonite due to a lower layer charge. Partial protonation of the bond couple of octahedral Al3+ converts it from 4 to 6-coordinated (He *et al.*, 2015), together with leaching of the octahedral cations when exposed it creates a specific pore structure, associated with an appearance of nano-porosity and increasing micro and meso-porosity. In conjunction with the partial destruction of the structure which was also observed using a scanning electron microscopy, this leads to a significant increase of the specific surface area (up to 150-200% of the initial value). At the same time, as described earlier leaching of the octahedral cation, leads to a reduction of the layer charge, which results in decrease of cation exchange capacity.

Change of the adsorption properties

		Taganskiy Mont			Dashkovskiy Mont		
		natural	10M HNO3		natural	10M HNO3	
			1 hour	5 hours		1 hour	5 hours
Hygroscopic weitness Wg, %		11.2	22.4	24.9	8.5	7.3	7.3
Cation exchange capacity	CEC, mmol*eq/100 g	85	26	19	44	34	31
	CEC, % from natural MM		31%	22%		79%	71%
	Lost CEC, % from natural MM		69%	78%		21%	29%
Specific Surface Area	S _{BET} , m ² /g	110	125	178	64	80	135
	S _{BET} , % from natural MM		114%	162%		125%	211%
	Increased S _{BET} , %		-14%	-62%		-25%	-111%
Decontamination factor, 137Cs		36	117	164	195	203	287

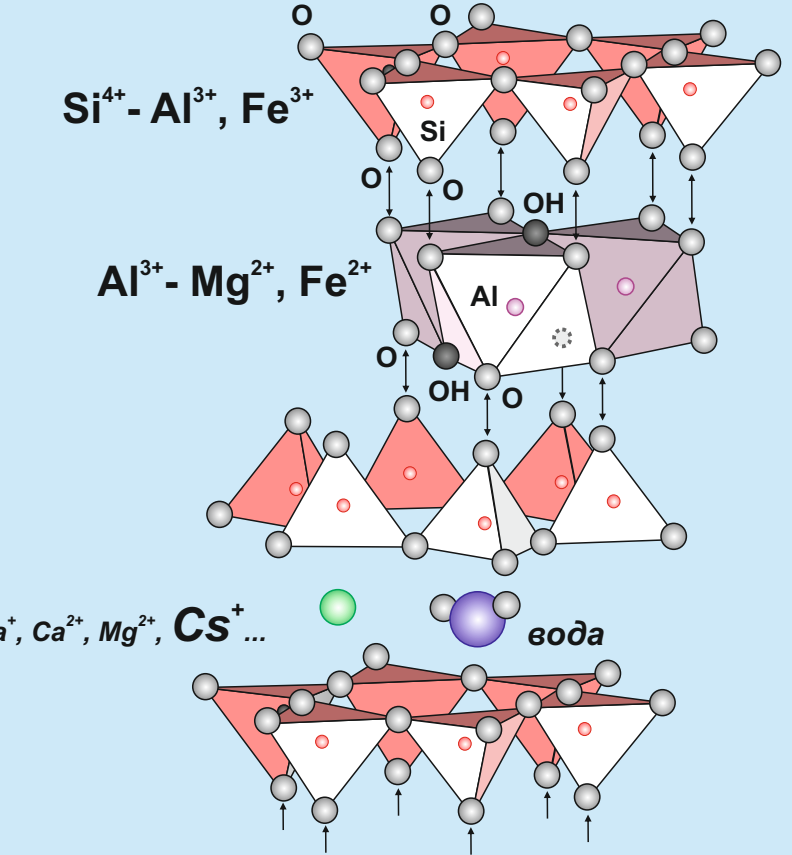
$$\text{Decontamination factor, } ^{137}\text{Cs: } K_{dec}(^{137}\text{Cs}) = \frac{A_{specific, initial}}{A_{specific, final}}$$

Structure modification due to acid treatment

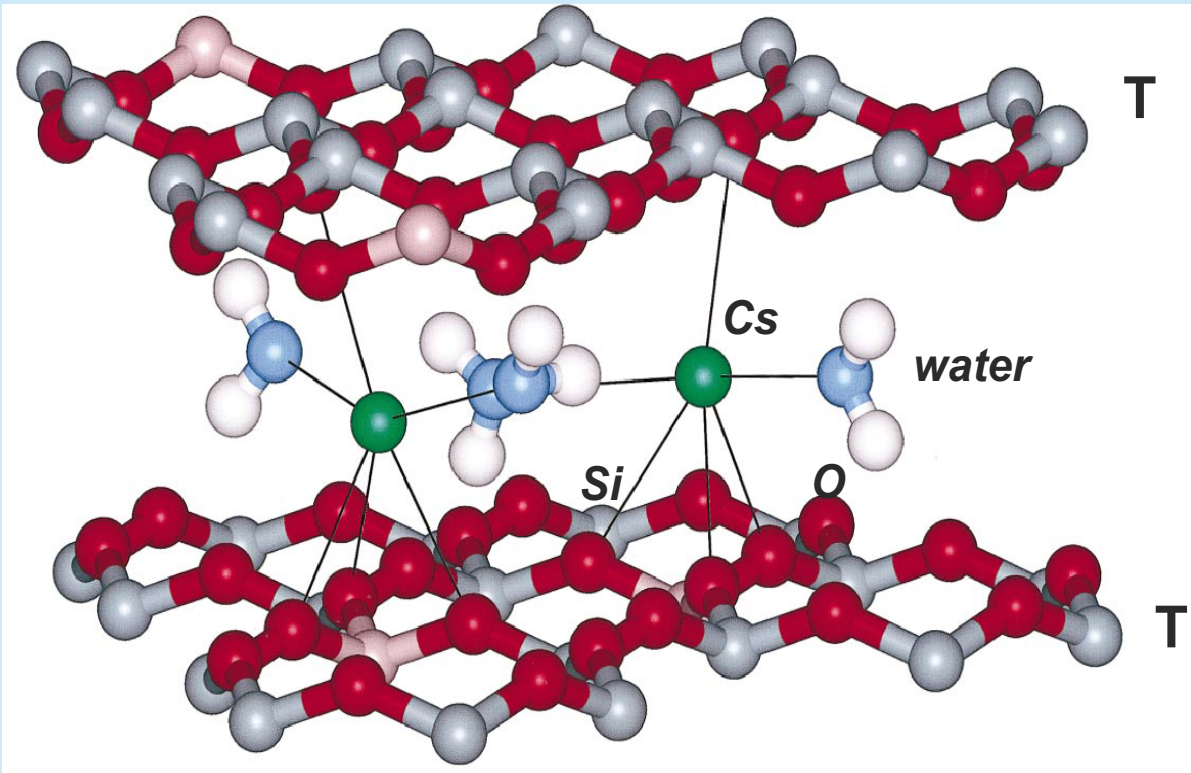


Cs ADSORPTION

Sheme of smectite structure

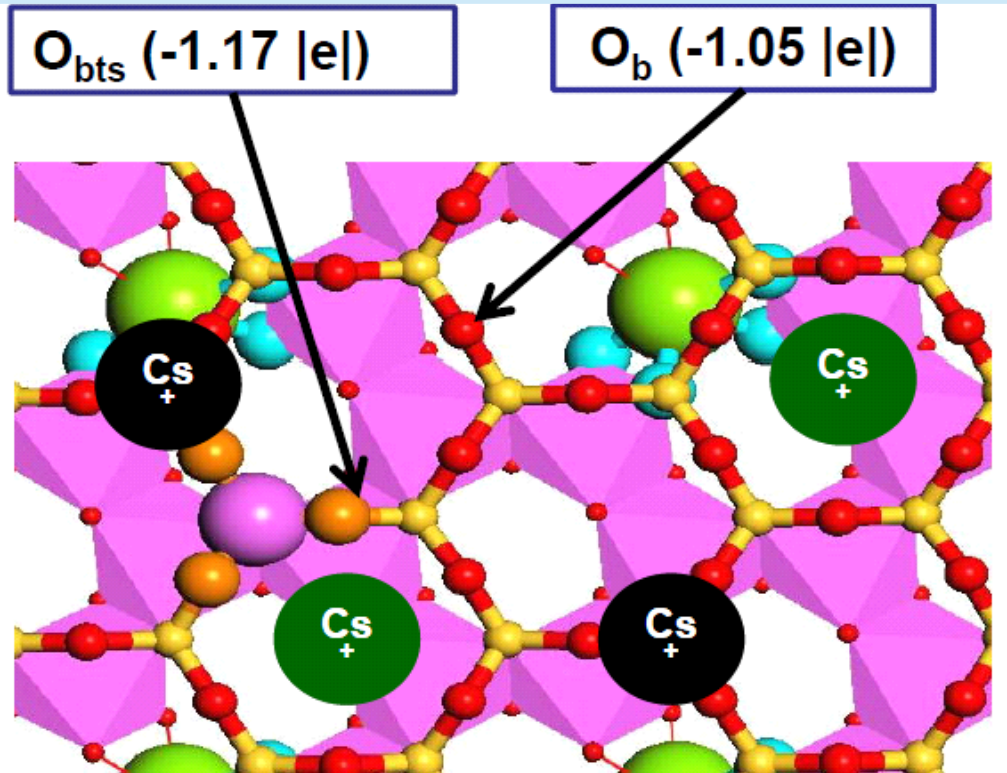


Cs behavior in the interlayer space



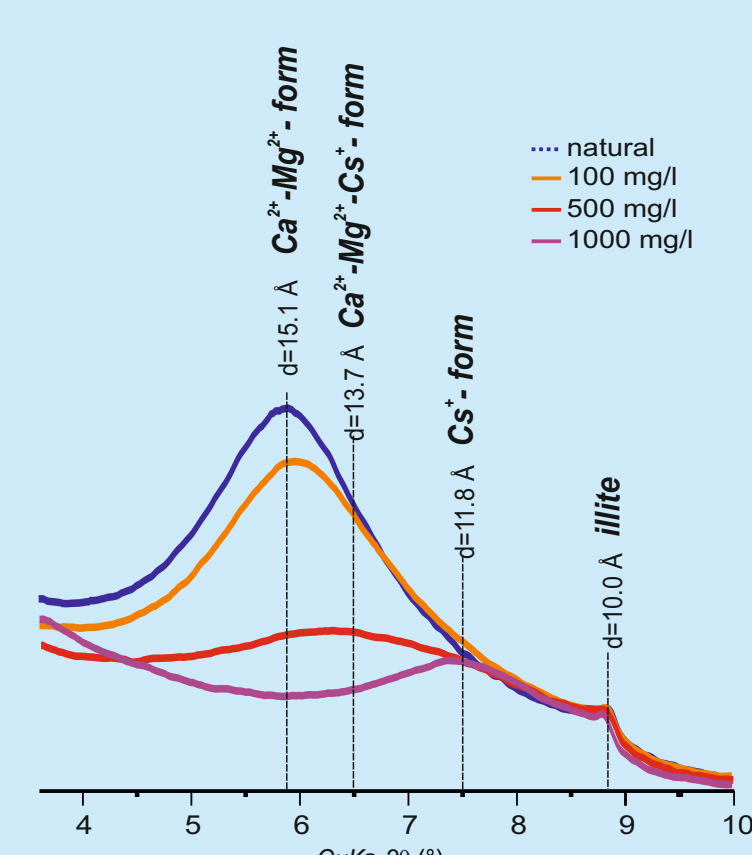
(by Sutton and Sposito, 2001)

Cs behavior on the surface

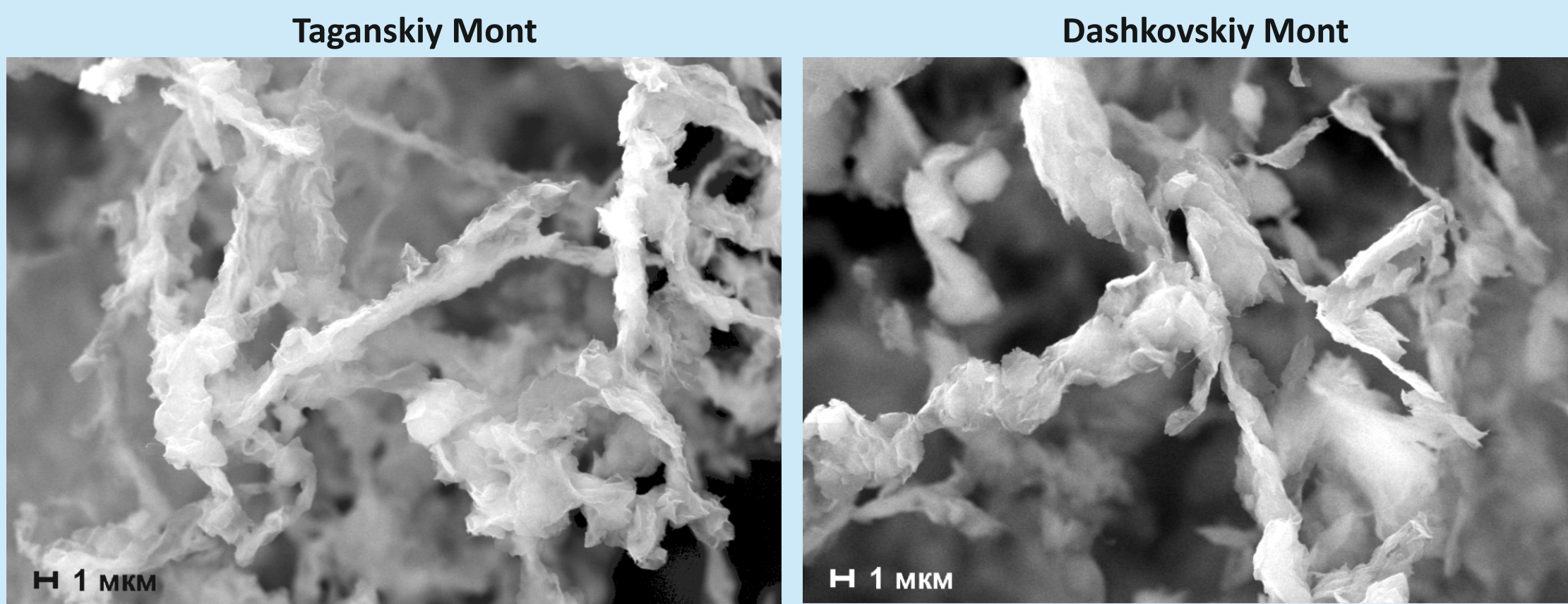


(by Ngouana and Kalinichev, 2014)

XRD-patterns of Cs-forms

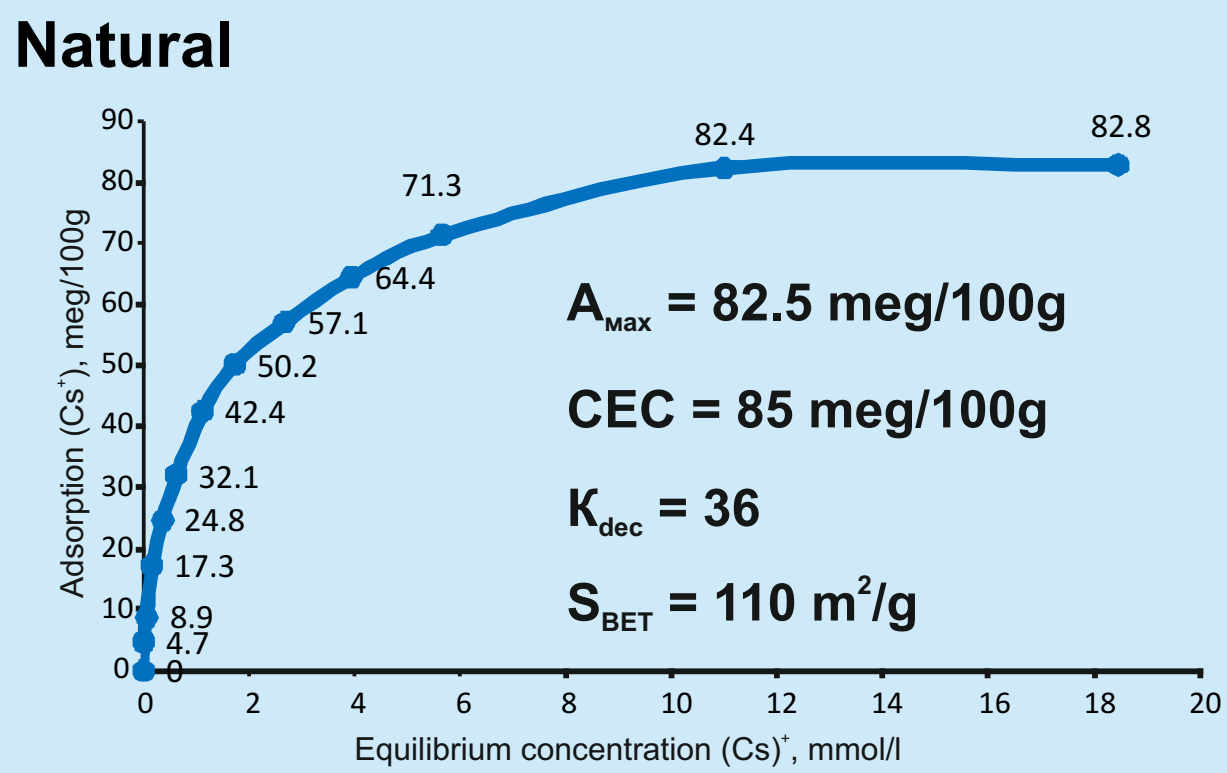


SEM-images of Cs-montmorillonites

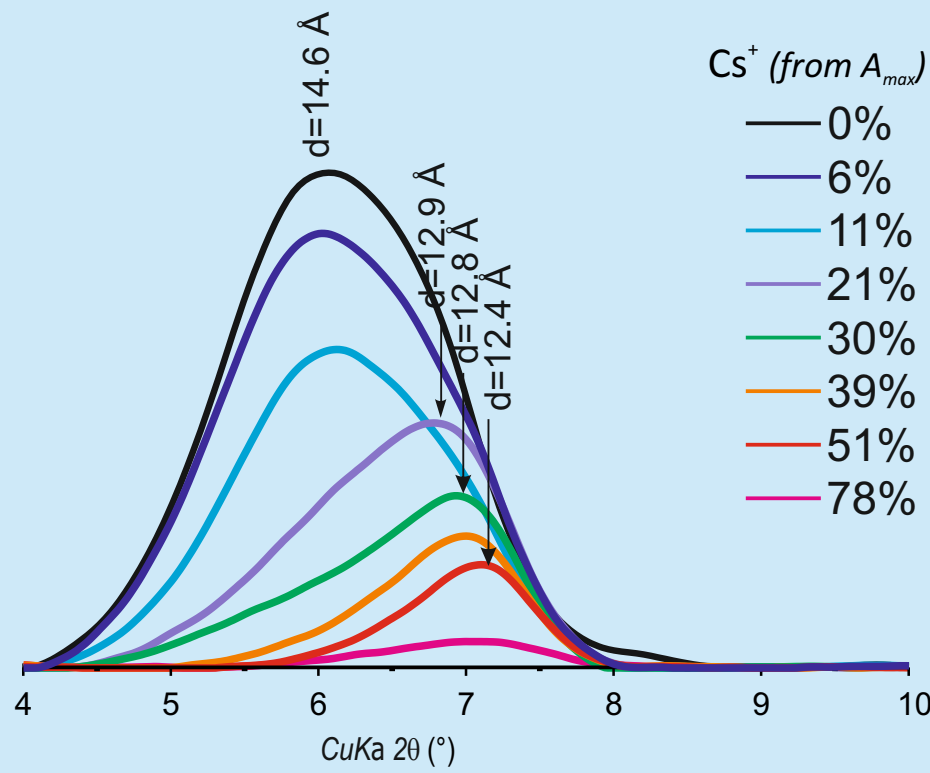


Cs adsorption on natural and acid-modified Taganskiy bentonite

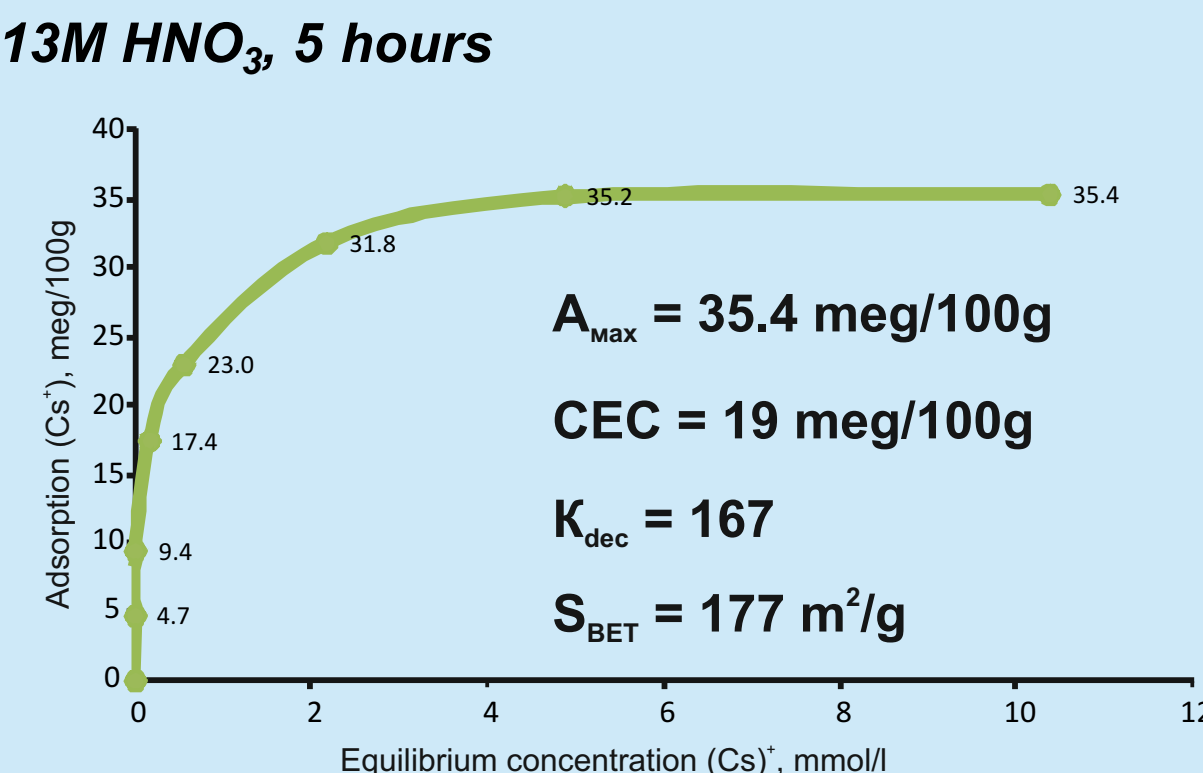
Isotherm of Cs⁺ adsorption



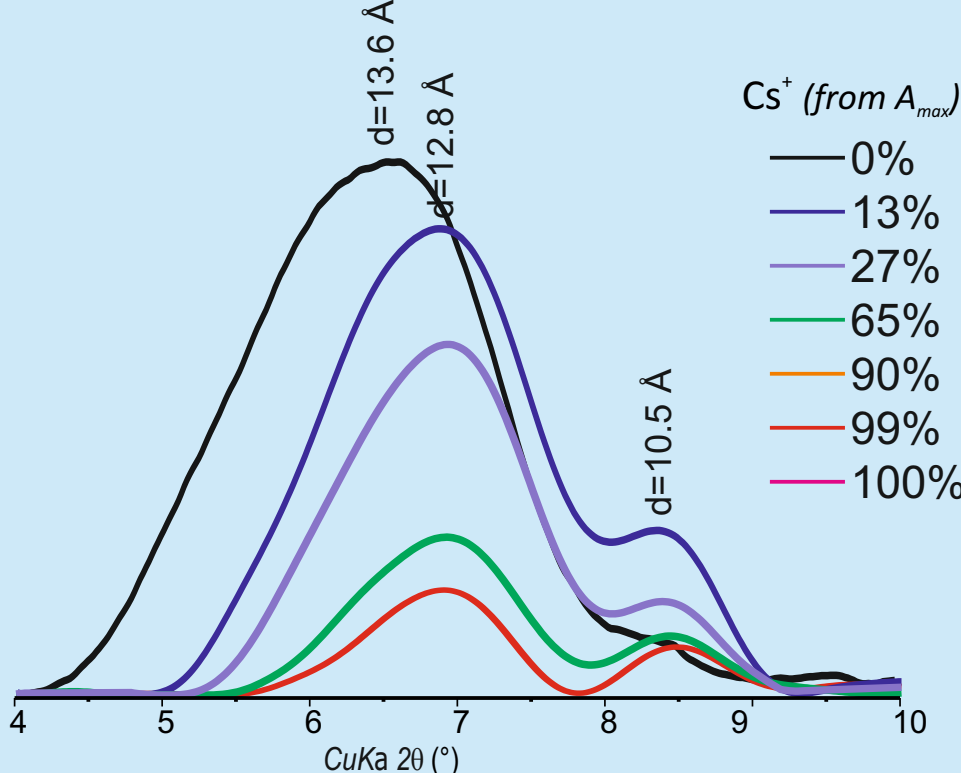
(001) XRD reflection



Isotherm of Cs⁺ adsorption



(001) XRD reflection



The mechanism of the cesium adsorption on montmorillonite after a thermochemical impact differs significantly from the natural montmorillonite. The main reason appears to be related to changes of the layer charge and a partial interlayer protonation. Cesium substitutes oxonium than Ca and Mg. The total amount of the adsorbed cesium is determined by capacitive abilities of montmorillonite and thus is reduced after a long-term treatment with nitric acid solutions.

The research results can be used in modeling the transformation of the montmorillonite structure and stability of bentonite barriers properties.

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Sellin P. and Leopin O.X. Clays and Clay Minerals (2013) 61, 477-498
Timofeeva MN, Volcho KP, Mikhailchenko OS, Panchenko VN, Krupskaya VV *et al.*, Journal of Molecular Catalysis A: Chemical 398 (2015) 26-34.
He H., Guo J.L., Xie X., Lin H. AND Li L. Clay Minerals (2002) 37, 337-344