Sorption behavior of Np(V) onto clays from Russian and Indian deposits

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Clays samples

Khakassia **Rajastan** **Kutch**

Characterization of clays

Characterization of clays

XRF: Elemental composition

Sample	Composition. %										
	LOI	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5
Rajastan clay	20.06	1.15	4.64	16.28	35.12	0.30	6.67	3.09	0.16	12.27	0.11
Kutch clay	21.43	0.72	2.02	12.33	42.52	0.11	2.77	1.42	0.19	15.58	0.27
Khakassia clay	12.74	2.98	2.48	15.19	58.36	0.97	3.05	0.63	0.09	3.42	0.11

Characterization of clays

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Characterization of clays

XRD: Phase composition

Khakassia clay

Smectite	66.0
Kaolinite	1.3
Quartz	16.9
Albite	6.6
Microcline	3.7
Orthoclase	1.6
Calcite	2.6
Dolomite	0.5
Gypsum	0.8

Rajastan clay

Smectite	46.8
Illite-smectite MLM	8
Kaolinite	14
Quartz	1.4
Goethite	1.3
Hematite	0.5
Calcite	2.8
Dolomite	8.0
Brushite	2.8
Gypsum	0.7
Anatase	1.7
Amorphous	

Kutch clay

Smectite	76
Goethite	2.5
Calcite	2.9
Quartz	3.0
Anatase	0.5
Amorphous	

Clay minerals:

67 %

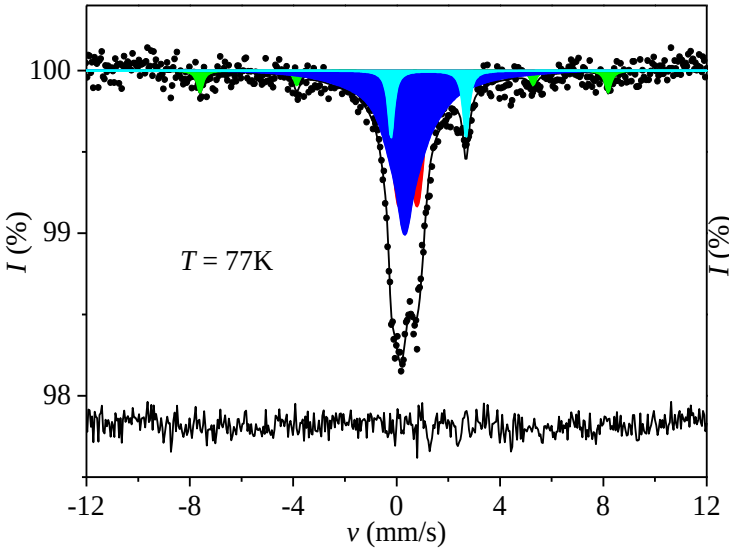
69%

76%

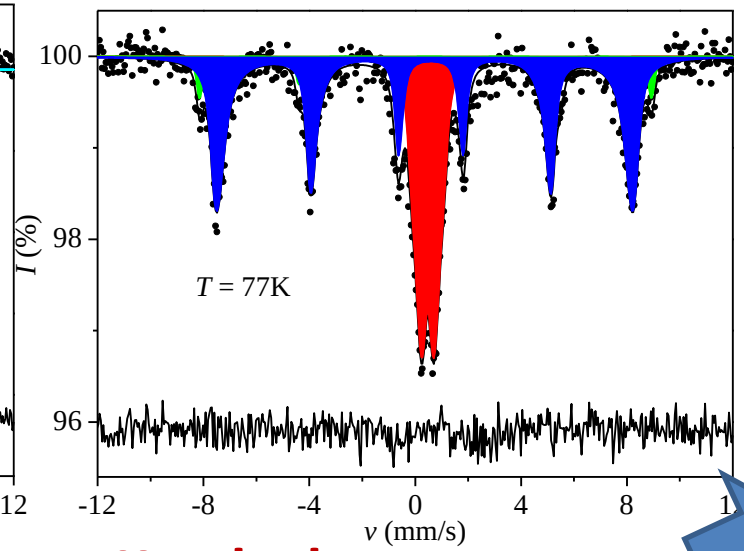
Characterization of clays

Mȍssbauer spectroscopy: Iron speciation

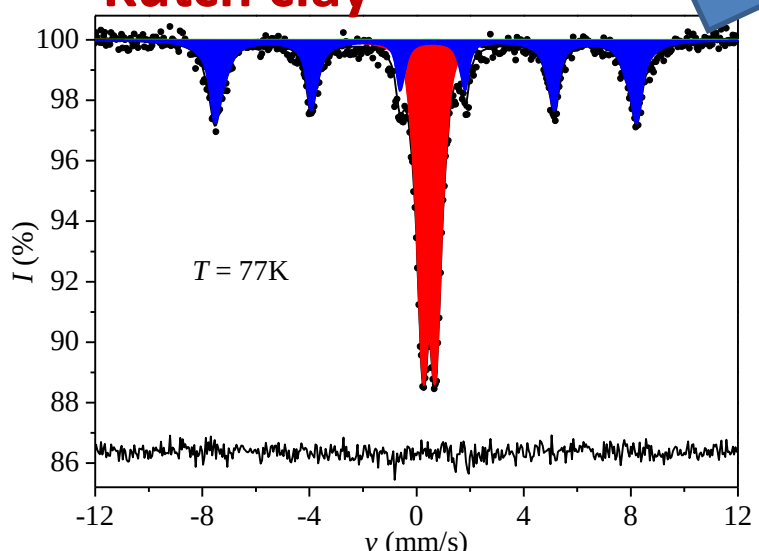
Khakassia clay



Rajastan clay



Kutch clay



Only Fe(III):
- structural iron,
- hematite (around 5%)
- Nanoparticles of goethite

Fe(II): structural iron
Fe(III): structural iron and nanoparticles of goethite

Summary of characterization

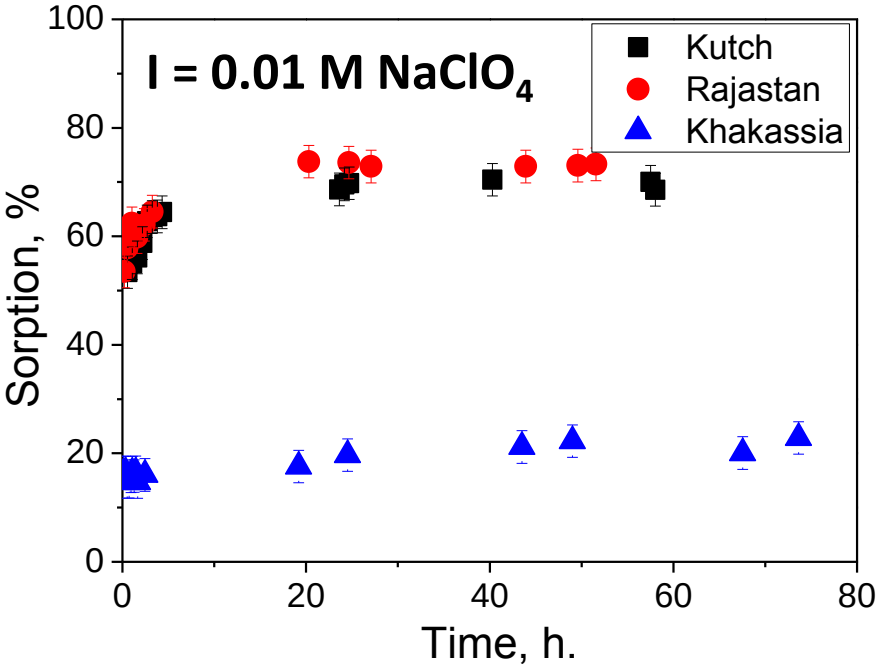
Na-Montmorillonite – 66%
Goethite – around 1.5%
No anatase
SA=15 m^2/g

Na-Montmorillonite – 47%
Illite-smectite MLM – 8%
Kaolinite – 14%
nanoparticles of Goethite – 12%
Hematite – 0.5%
Anatase – 1.7%
SA=50 m^2/g

Ca-Montmorillonite – 76%
nanoparticles of Goethite – 15%
Hematite – 0.5%
Anatase – 0.5%
SA=115 m^2/g

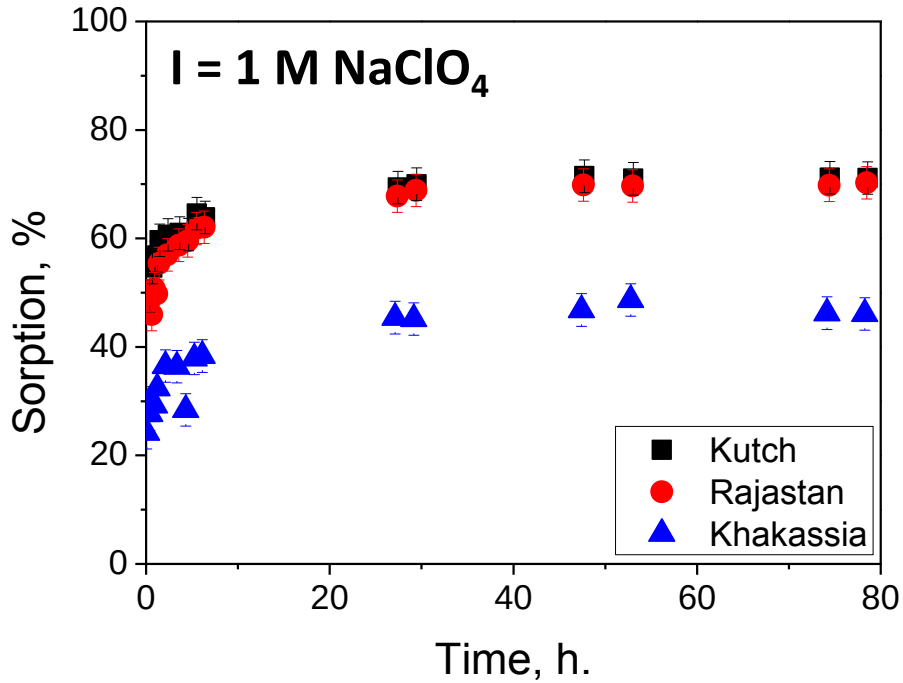
Sorption study

Kinetics of Np(V) sorption onto clay



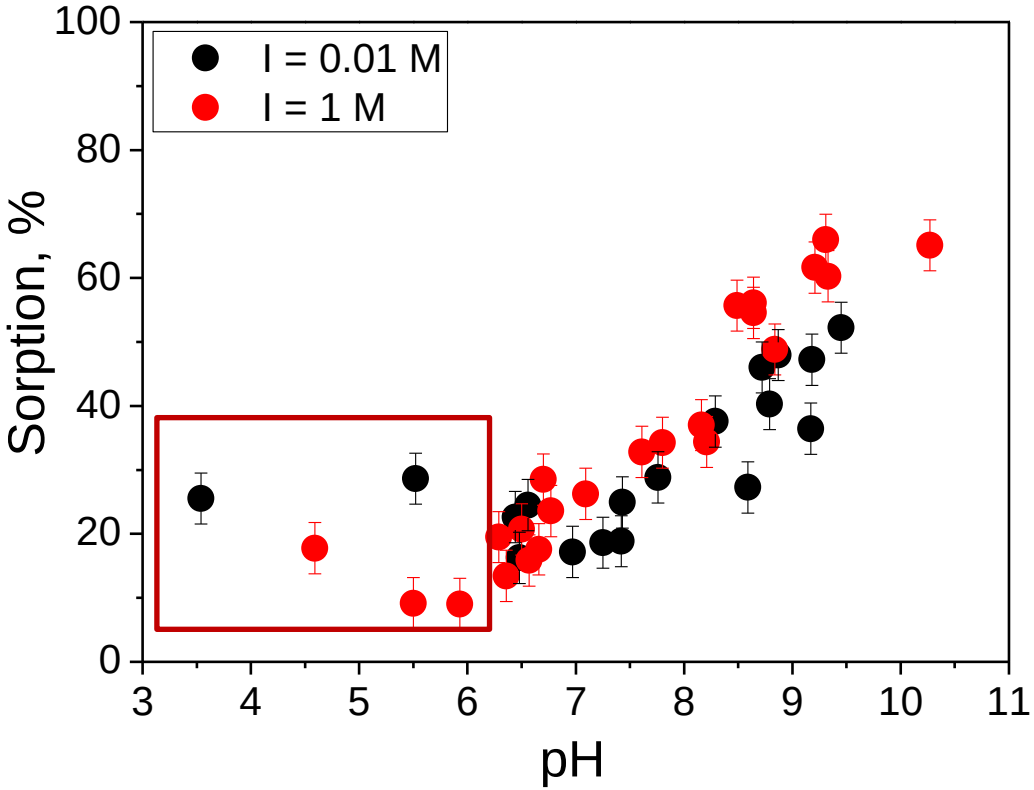
✓ Steady state for Np(V) sorption onto clay in ~24 hours

✓ Sorption of Np(V) onto Khakassia clay is lower but faster



Np(V) sorption pH-edge

Khakassia clay

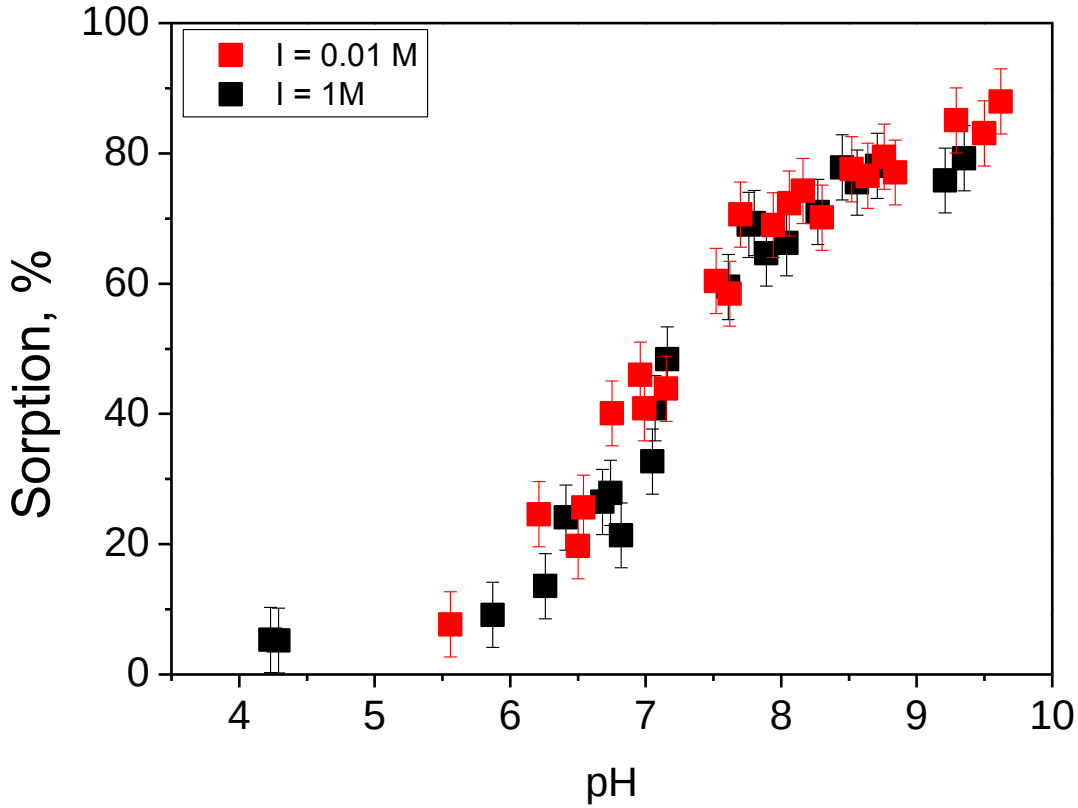


- ✓At pH > 6.5 sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption
- ✓At pH < 6.5 sorption increase with decreasing ionic strength – ion exchange is predominant mechanism

[solid phase] = 0.5 g/L
[Np] = $4 \cdot 10^{-14}$ M

Np(V) sorption pH-edge

Rajastan clay

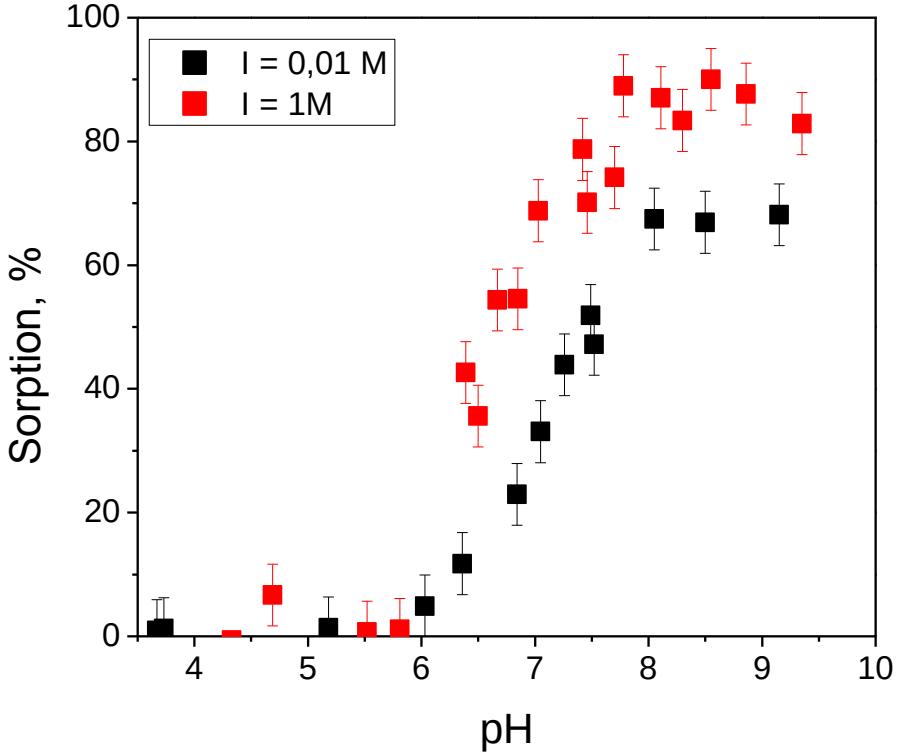


- ✓In all pH range sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption
- ✓Sorption is higher than on Khakassia clay

[solid phase] = 0.5 g/L
[Np] = $4 \cdot 10^{-14}$ M

Np(V) sorption pH-edge

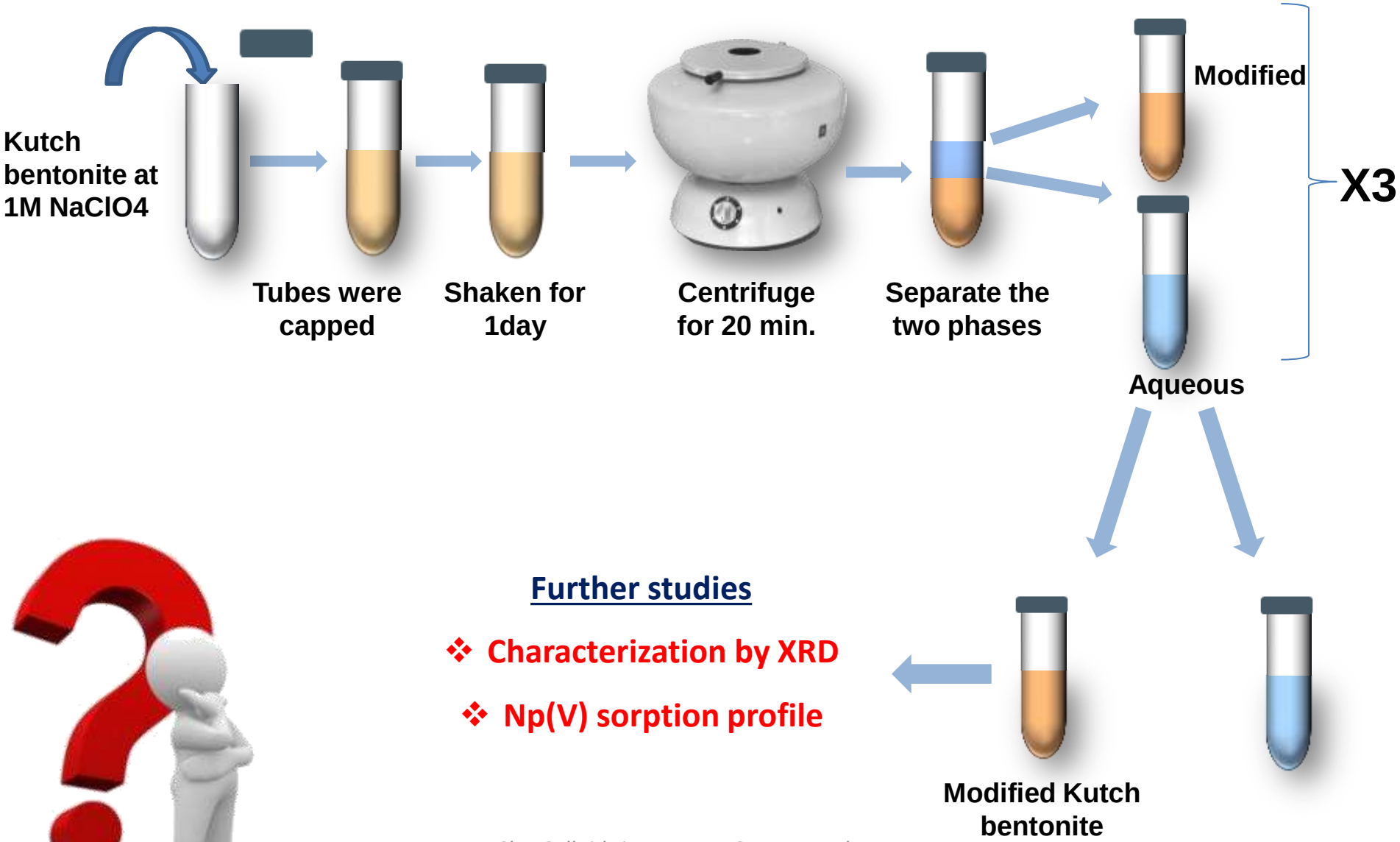
Kutch clay



✓Sorption is higher at I = 1MNaClO4

Ca-Montmorillonite influence???

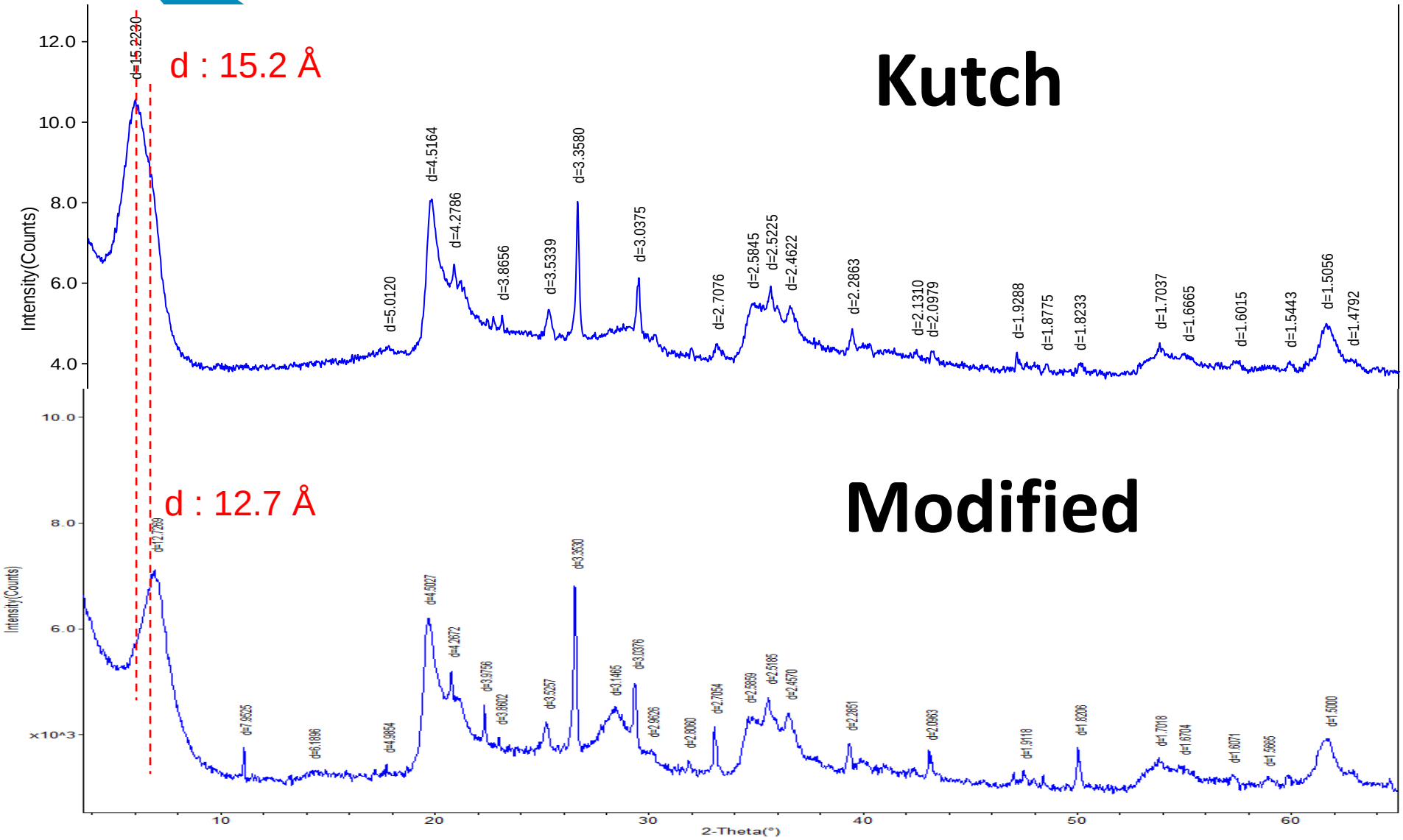
[solid phase] = 0.5 g/L
[Np] = $4 \cdot 10^{-14}$ M



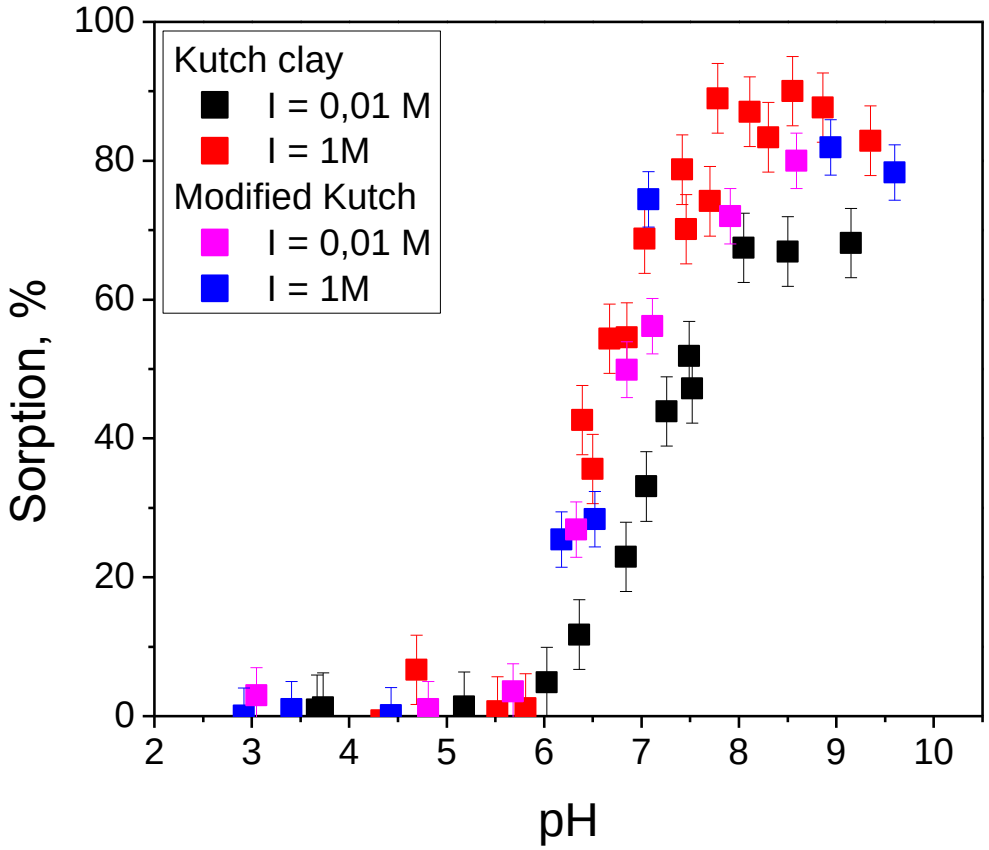
Further studies

- Characterization by XRD
- Np(V) sorption profile

XRD of Kutch and Modified bentonite

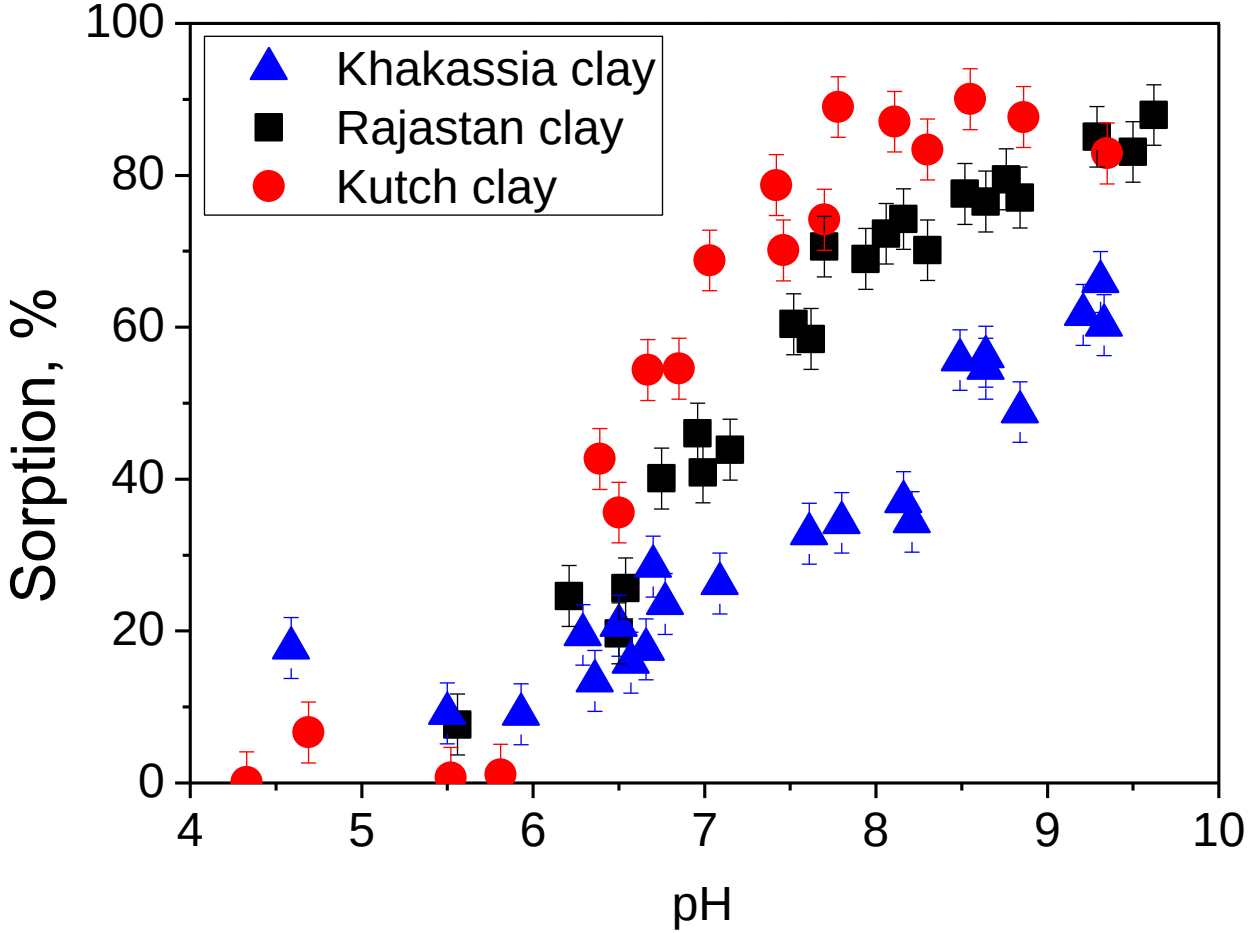


Kutch and Modified bentonite



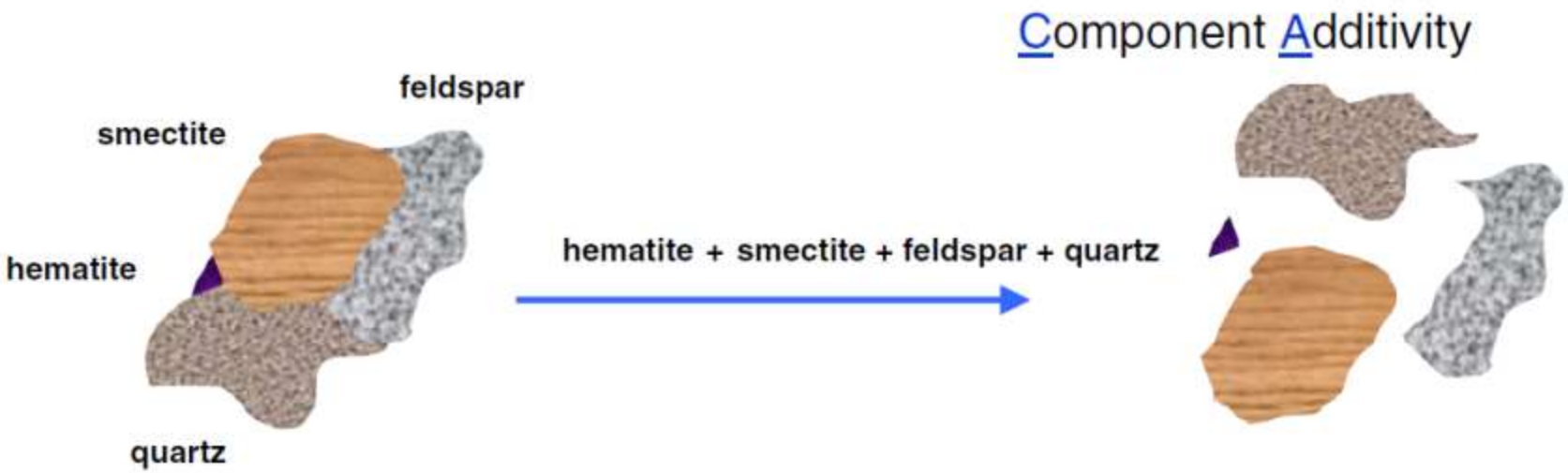
✓Ca-form demonstrate lower sorption

Summary of sorption data



Modeling

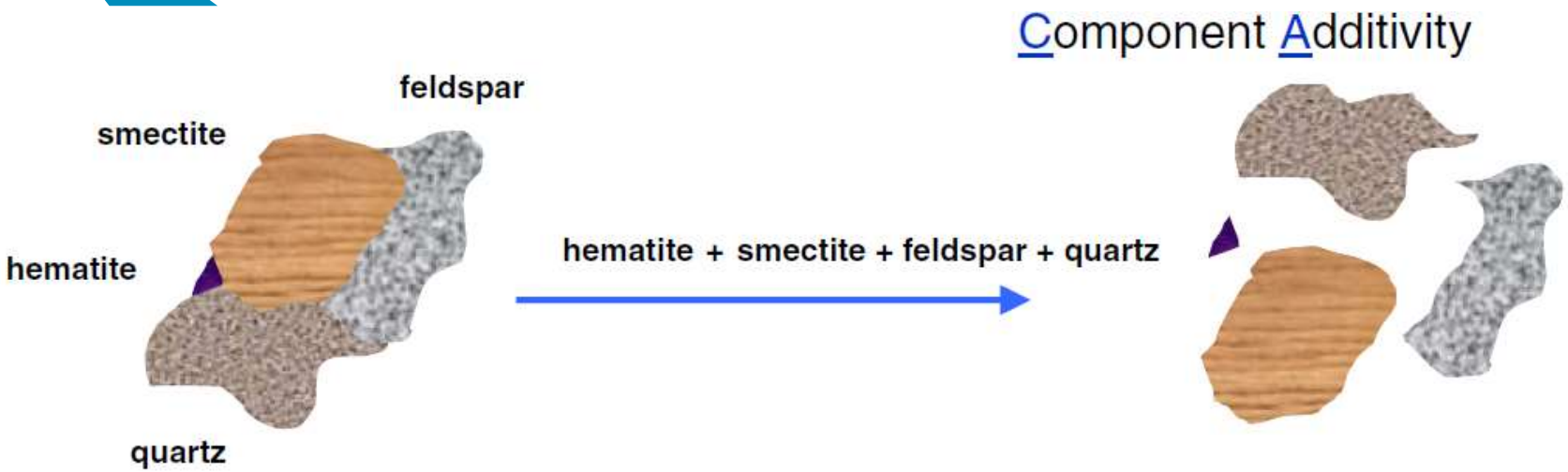
Thermodynamic modeling



- Mineral composition
- Surface properties for each component
- Equilibrium constant for sorption onto pure mineral

NEA Sorption Project Phase II, 2005

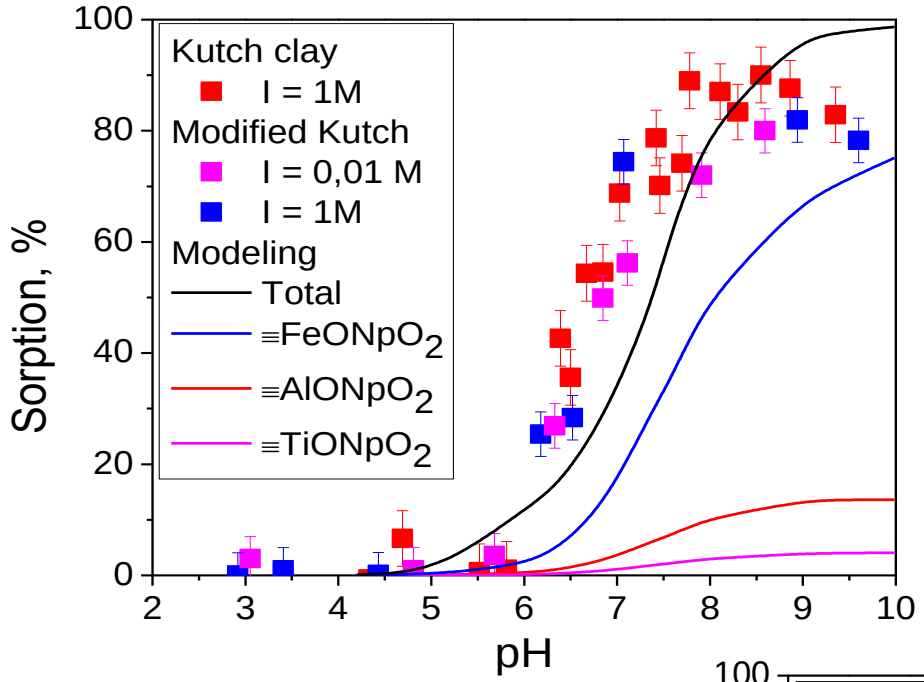
Thermodynamic modeling

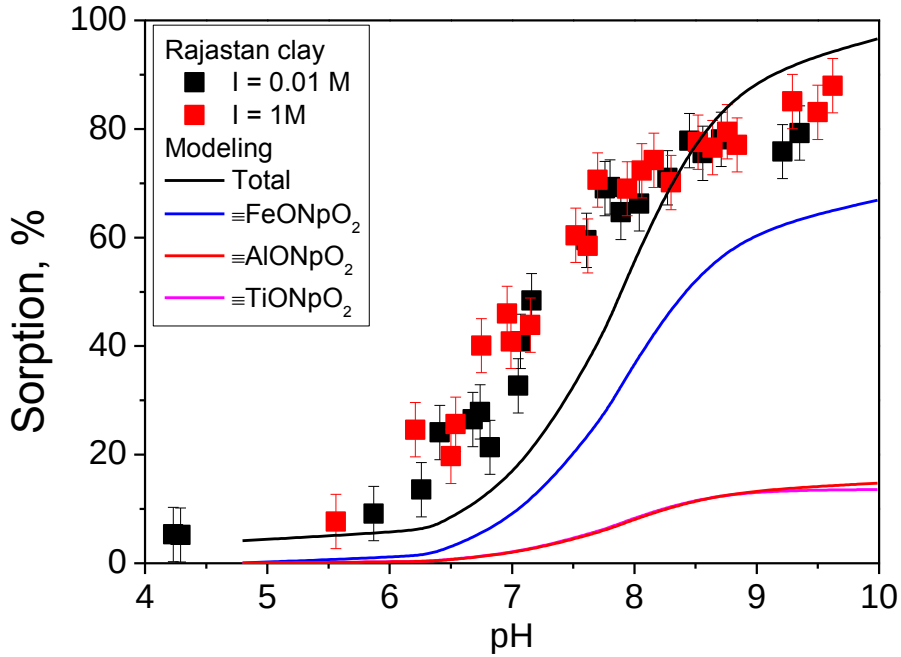


Literature data

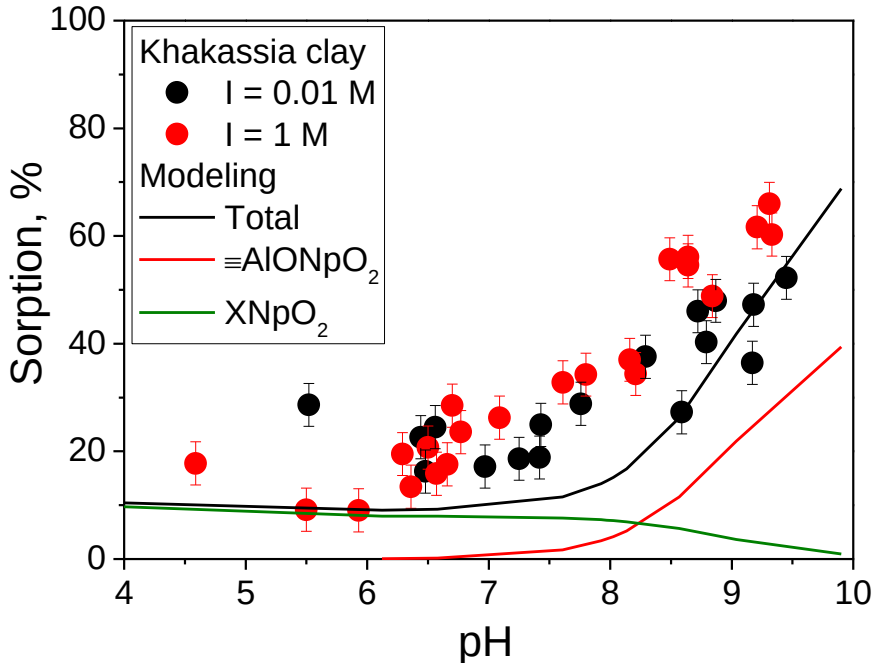
Reaction	log*K*
$\equiv AlOH + NpO_2^+ \rightarrow \equiv AlONpO_2 + H^+$	-4,55
$\equiv AlOH + NpO_2^+ + H_2O \rightarrow \equiv AlONpO_2OH^- + 2H^+$	-13,8
$\equiv FeOH + NpO_2^+ \rightarrow \equiv FeONpO_2 + H^+$	-3,32
$\equiv TiOH + NpO_2^+ \rightarrow \equiv TiONpO_2 + H^+$	-2,89
$NpO_2^+ + X- \rightarrow XNpO_2$	-0.26

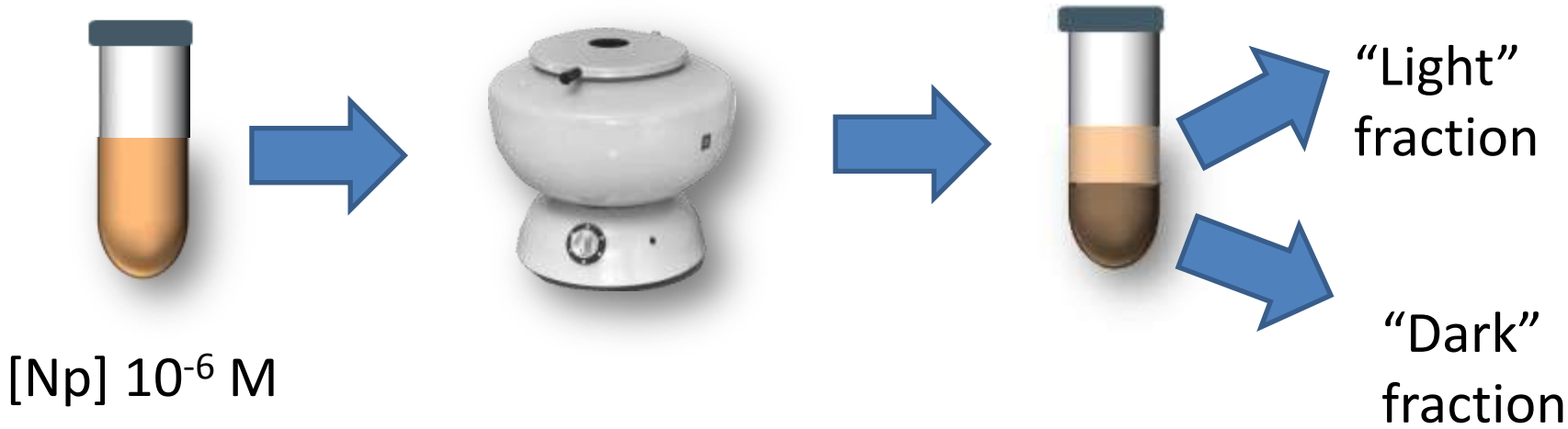
Thermodynamic modeling





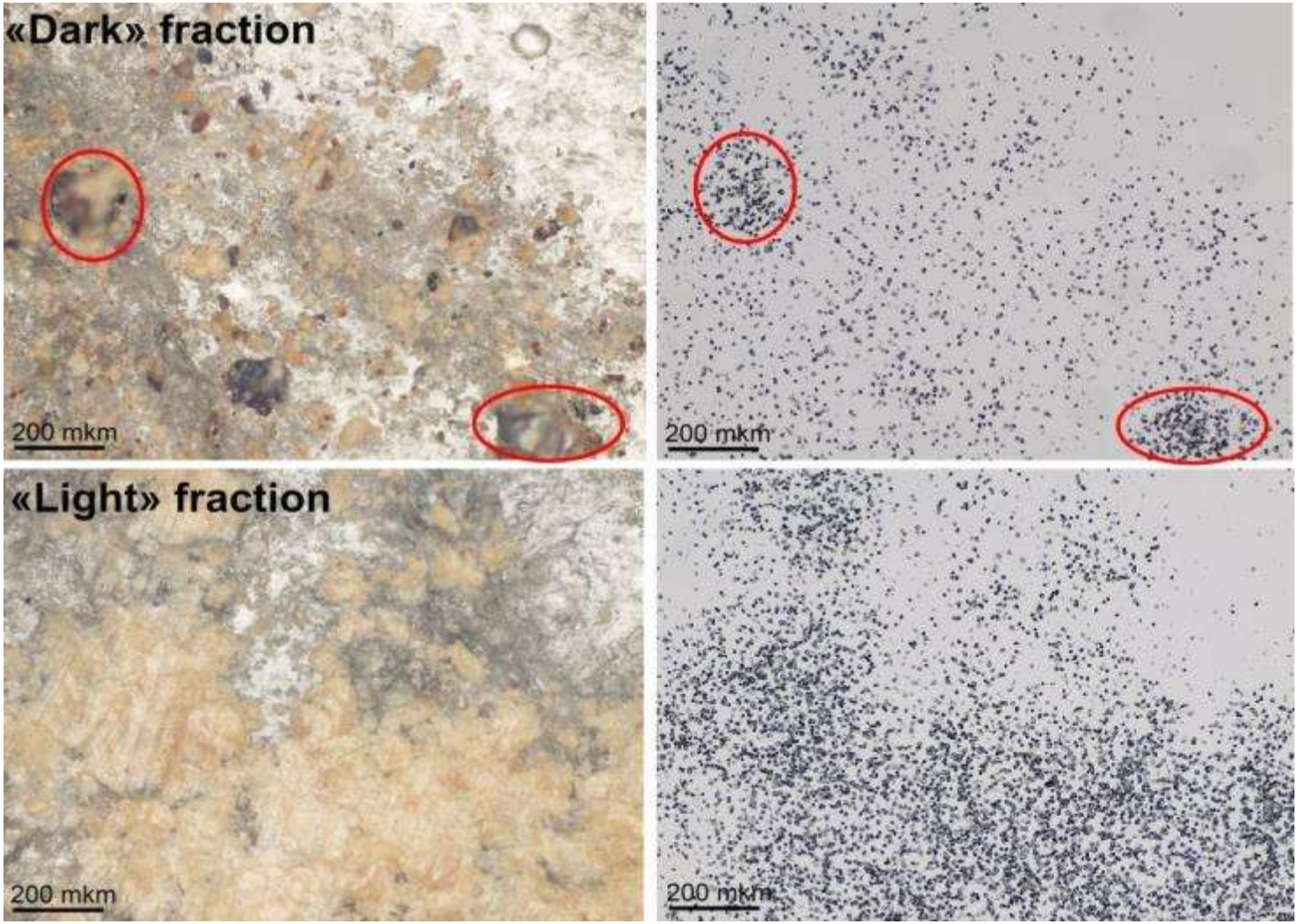
The same set of the equilibrium constants for different clays




[Np] 10^{-6} M
"Light" fraction
"Dark" fraction

α-track analysis images

Rajastan clay



Summary

- Non-clay minerals can dramatically affect on radionuclides sorption onto clay
- Thermodynamic modeling with CA-approach can be used for modeling sorption onto clays

Thank you for your attention!

Mòssbauer spectroscopy

Rajastan clay