

Comparative U(VI) sorption on Fe-rich smectites with and without accessory Fe-oxides

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INTRODUCTION

- Bentonites with high smectite content are selected as barriers in radioactive waste repositories for their suitable confinement properties and for their high radionuclide retention capabilities.
- To guarantee safety, all processes that may affect radionuclide retention need to be assessed. In particular, the presence of Fe may play a role in the immobilization of redox-sensitive contaminants like uranium [1].
- Uranium retention in the clay barrier can be affected differently depending on the oxidation state and nature of the Fe present in the system: (1) Structural Fe²⁺/Fe³⁺ in the clays; (2) Fe(II/III)-oxides as accessory minerals; (3) Dissolved Fe²⁺/Fe³⁺.

MATERIALS

- Smectite clays: Fe-rich nontronites (NAu1 and NAu2 from Uley Mine, Australia) [2]. A low iron Ca-Mg bentonite (FEBEX from Cortijo de Archidona, Spain) [3].
- Purified fractions without accessory Fe-oxides were obtained following the methodology described in [4].

EXPERIMENTAL: SORPTION EXPERIMENTS

Batch sorption experiments

- Uranium (VI) sorption was analyzed by adding ²³³U on raw and on Fe-oxide-free clay suspensions (2 g/L) prepared in NaClO₄ at 10⁻¹ M, under anoxic conditions. After one week, samples were centrifuged and ²³³U concentration was determined in solution by liquid scintillation counting.
- Distribution coefficients (K_d) were obtained as a function of pH, ionic strength and by varying uranium concentration.
- The competition of dissolved Fe²⁺ and Fe³⁺ with U for cation exchange sites in the clay was analyzed.
- Sorption experiments were carried out on Fe-oxide-free FEBEX clay, adding a fixed uranium concentration and varying Fe²⁺ or Fe³⁺ content.

SORPTION RESULTS

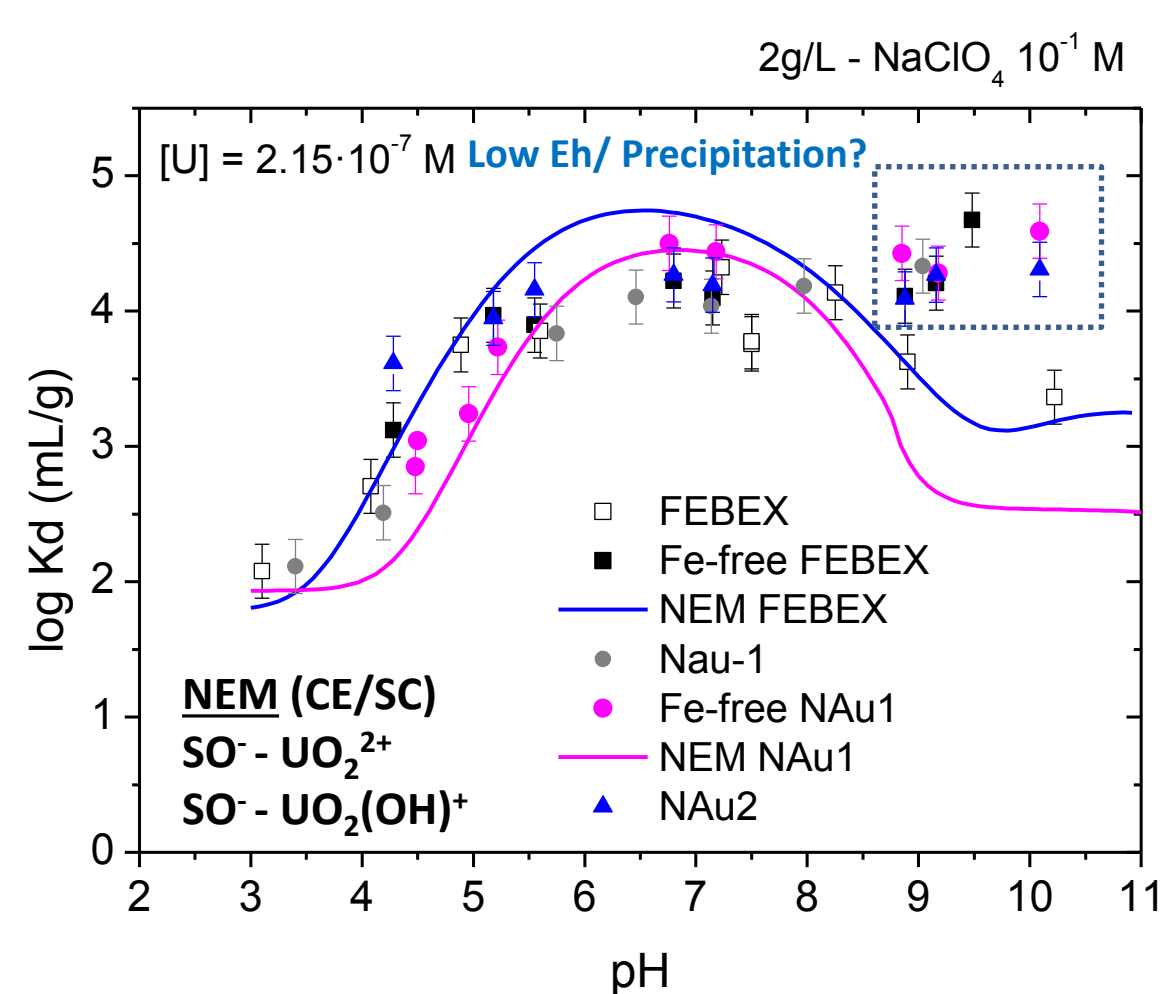


Fig. 4. U(VI) distribution coefficient on raw and Fe-free NAu1, NAu2 and FEBEX measured under anoxic conditions as a function of pH. Contact time 7 days.

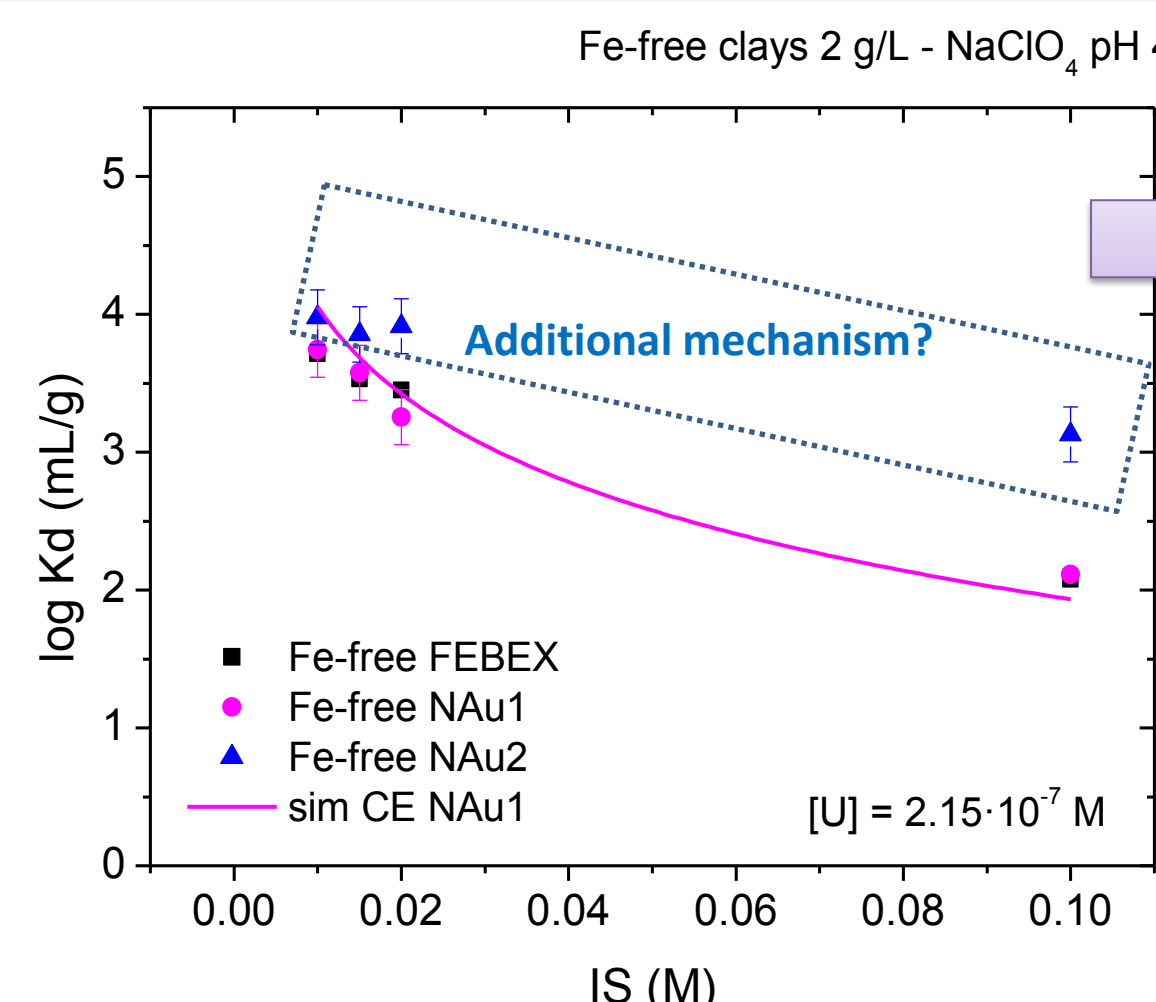


Fig. 5. U(VI) distribution coefficient on Fe-free NAu1, NAu2 and FEBEX measured under anoxic conditions as a function of ionic strength (IS). Contact time 7 days.

At short equilibration times, no large differences on U(VI) retention on raw and Fe-oxide free smectite fractions were observed. This suggests that, in this case, the influence of Fe-accessory minerals is limited.

Increased U sorption measured at alkaline conditions may be due to precipitation or U reduction (in Nau-1 and NAu2, Eh after 1 week = 40 mV).

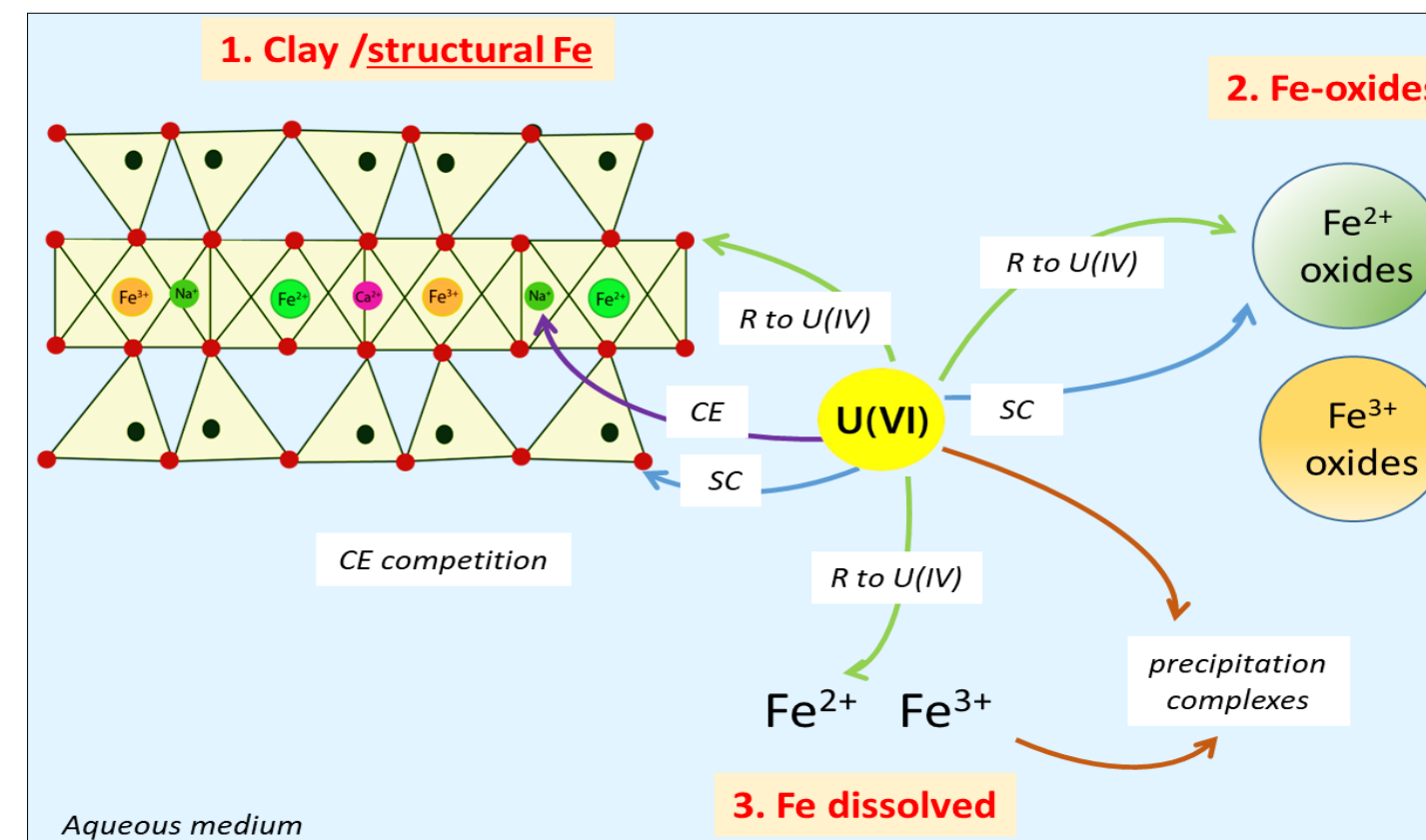


Fig. 1. Main source of Fe and relevant processes expected in the system: (1) Structural Fe²⁺/Fe³⁺ in the clays; (2) Fe(II/III)-oxides as accessory minerals; (3) Dissolved Fe²⁺/Fe³⁺. SC = surface complexation; CE = cation exchange; R = reduction

URANIUM AND IRON SPECIATION

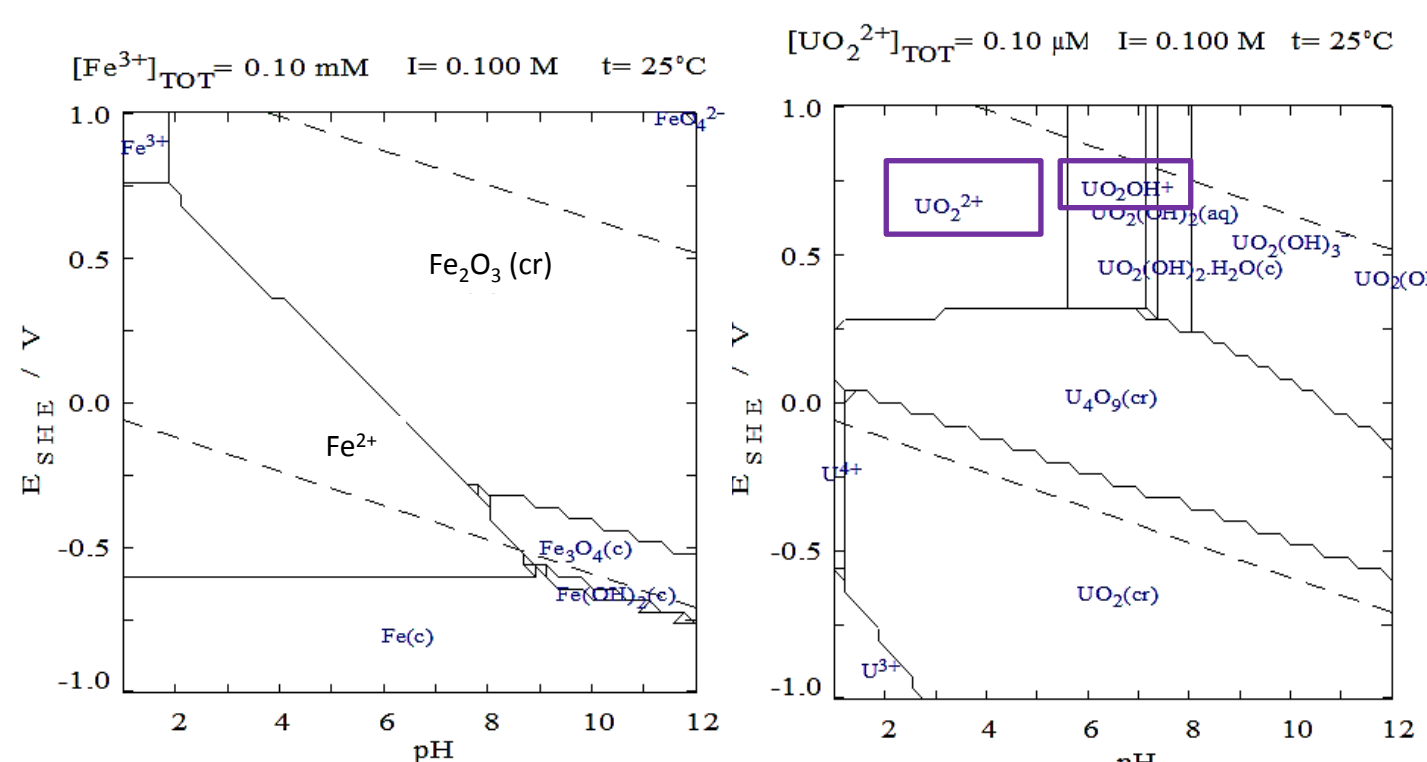


Fig. 2. Fe (left) and uranium (right) speciation diagrams at I = 10⁻¹ M and t=25°C. [Fe³⁺]_{TOT}=0.10 mM and [UO₂²⁺]_{TOT}=0.10 mM

DISSOLVED FE. CE COMPETITION

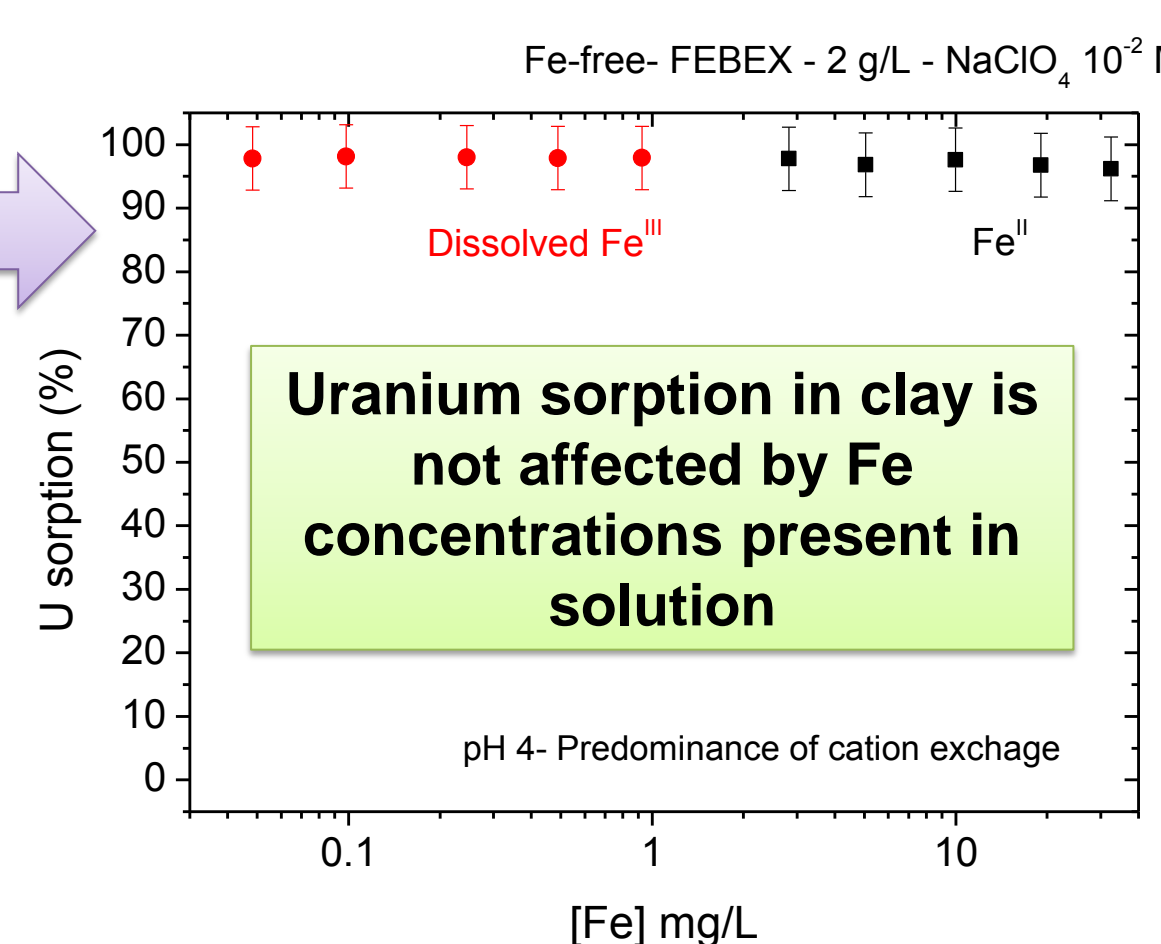


Fig. 6. U(VI) sorption on Fe-free-FEBEX measured under anoxic conditions, adding different Fe(II) or Fe(III) concentrations in solution. Contact time 7 days.

Equilibrium solutions (2 g/L)	Minimum Fe (mg/l)	Maximum Fe (mg/l)
Fe-free NAu1	14 (pH 7.6)	130 (pH 9.6)
Fe-free Nau2	5.1 (pH 4.4)	17 (pH 9.9)
Fe-free FEBEX	0.09 (pH 4.5)	1.7 (pH 9.4)

Table 3. Total Fe dissolved after 1 week from Fe-oxides-free NAu1, NAu2 and FEBEX clays as a function of pH.

CHARACTERISATION

Physico-chemical characterization of raw and Fe-oxides-free clay fractions allowed to identify the location of structural Fe and the Fe-oxides and to evaluate relevant surface parameters, by different techniques (XRD, FT-IR, CEC,...)

Samples	Mineralogy (in weight %) (XRD analyses)							
	Total Phyllosilicates	Quartz	K-Feldspar	Plagioclase	Calcite	Goethite	Biotite	Cristobalite
NAu-1	97	1	Tz	--	1	Tz	Tz	--
NAu-2	95	1	--	1	1	2	Tz	Tz
FEBEX	94	--	1.3	0.4	2.5	--	--	2

Table 1. Main mineralogical composition (in weight %) obtained by XRD analyses on selected smectites. Tz = trace. Accessory minerals with Fe content are highlighted.

POTENTIOMETRIC TITRATIONS / Non-electrostatic model (NEM)

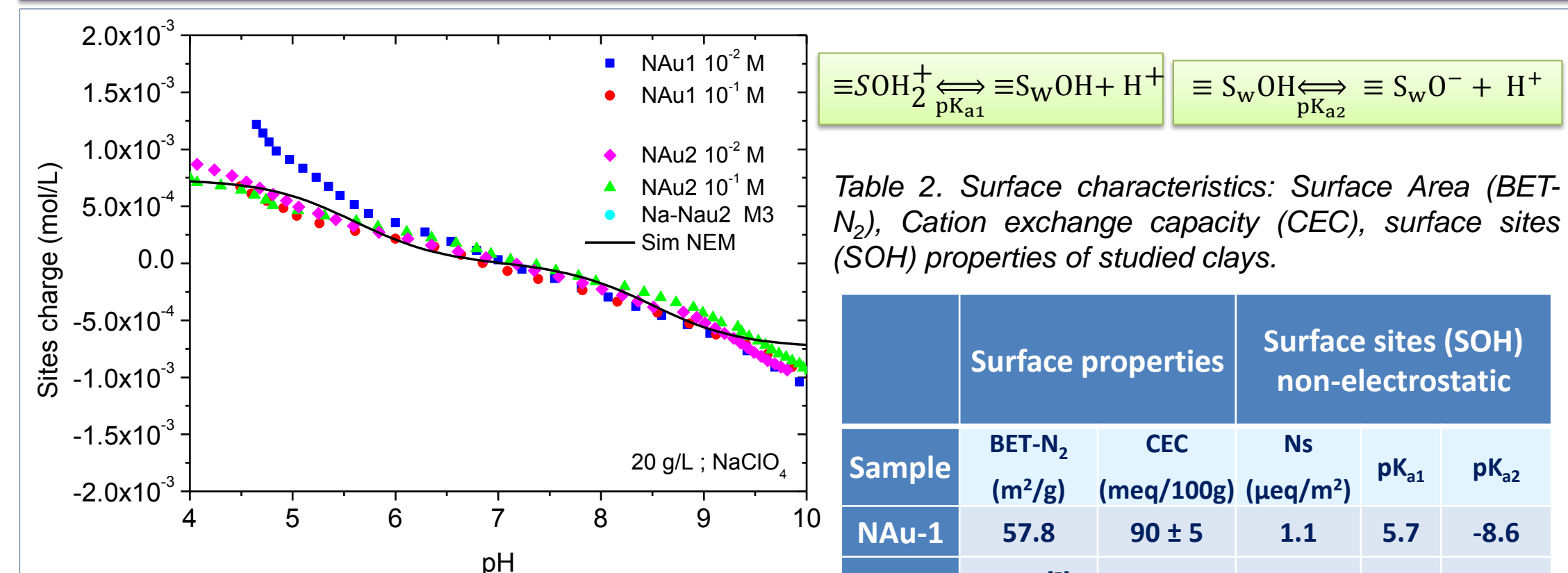


Fig. 3. Potentiometric titrations of NAu1 and NAu2 (20 g/L) in NaClO₄ at 10⁻¹ M and 10⁻² M. Simulation carried out considering a non-electrostatic model (NEM).

Table 2. Surface characteristics: Surface Area (BET-N₂), Cation exchange capacity (CEC), surface sites (SOH) properties of studied clays.

Sample	Surface properties		Surface sites (SOH) non-electrostatic		
	BET-N ₂ (m ² /g)	CEC (meq/100g)	Ns (μeq/m ²)	pK _{a1}	pK _{a2}
NAu-1	57.8	90 ± 5	1.1	5.7	-8.6
NAu-2	33.5 [5]	78 ± 5	1.1	5.6	-8.5
FEBEX	59.2 [6]	100 ± 4 [6]	1.02 [6]	5.3	-8.4

EFFECT OF FE-OXIDES

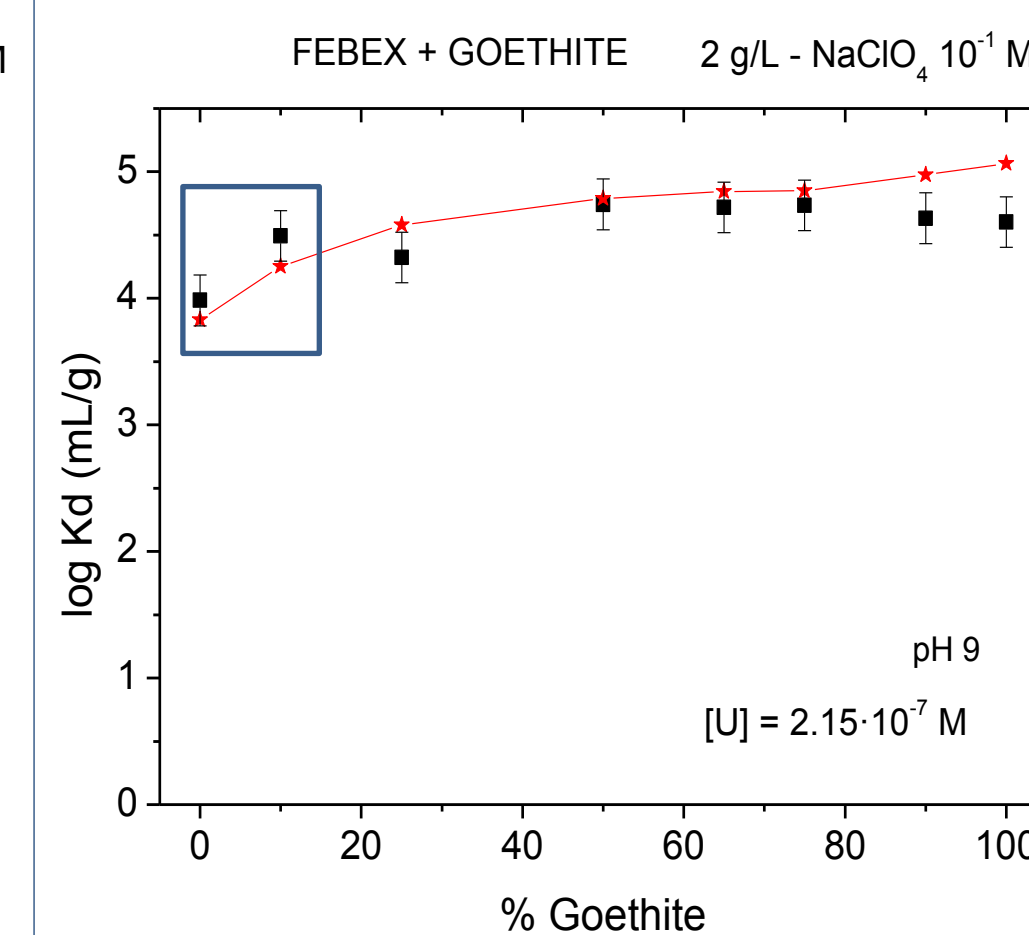


Fig. 7. U(VI) sorption on mixtures of FEBEX smectite with different goethite concentration (%) measured under anoxic conditions. Contact time 7 days.

A 10% of goethite increases U retention in smectite a 4%

CONCLUSIONS

- The retention of U(VI) by cation exchange mechanisms was limited and the competition of dissolved Fe²⁺ and Fe³⁺ was found to be minimal.
- In contrast, the reduction capability of Fe²⁺ played a relevant role of U and may favour U retention at longer times.
- The results contribute to weigh the different role played by Fe as a structural cation or as an accessory oxide in the immobilization of U(VI) in clays.

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