Wednesday 10 September, Room2

PREDICTIVE MODELLING OF RADIONUCLIDE (RN) BEHAVIOR AND THERMODYNAMIC DATABASES (RAMPEC AND DITUSC) – TOPICAL SESSION 2

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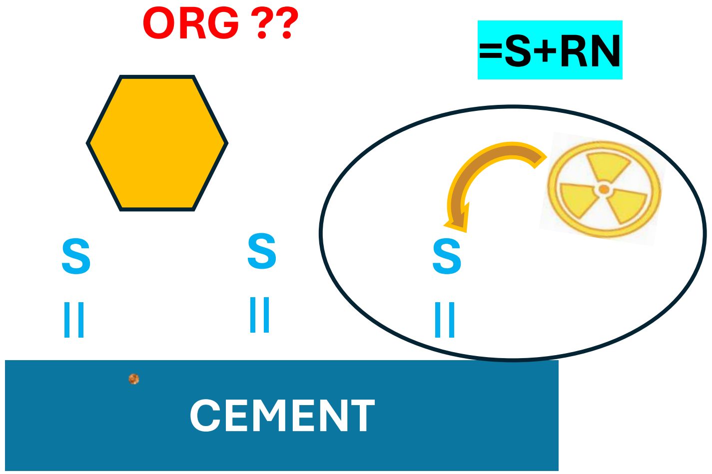
CONTENTS

- “NEW” SORPTION DATABASE
  - ➔ RAMPEC Task 2.3 [Knowledge Management]

- MODELLING OF RN+CEM+ORG SORPTION DATA in WP - CORI
  - ➔ TDB : Related to DITUSC work



Predictive modelling of radionuclide (RN) behavior

Sorption models are a very powerful tools to understand RN behaviour:

1. *RELIABLE AND COMPLETE SORPTION DATA* → **SORPTION DATABASES (SD)**

2. *RN AQUEOUS SPECIATION* → **THERMODYNAMIC DATABASES (TD)**

3. *COMPREHENSIVE INFORMATION ON THE CHEMICAL SYSTEM (WATER + SOLID)* → **Systematically incorporate this information in the SD may help data interpretation and sorption modelling. (?)**

“NEW” SD: PROOF-OF-CONCEPT

SD compiles sorption data, but it is designed to correlate K_d values with: 1) key physicochemical properties of solid phases and 2) their equilibrium water chemistry and 3) experimental conditions, enabling the identification of possible controlling factors and trends. It will contain also transport parameters.

K_d

D_e D_a ε R_f

- **Not site-specific → Generalized “knowledge”**
- **A “simple” RN was selected for its well-known and documented sorption behaviour (Cs). But crystalline rocks are complex enough to provide a good example of natural variability.**

SD structure "now"

SD contains ~1000 K_d values → materials from different countries and sites. According to the objectives each line contains additional information structured in four main blocks.

Block 1

General Information
SITE, COUNTRY
BOREHOLE
SAMPLE NAME
PROJECT

Block 2

Experimental Information
ATHMOSPHERE (OXIC, ANOXIC)
CONTACT TIME (t)
SOLID TO LIQUID RATIO (g/L; V/m)
INITIAL RADIONUCLIDE CONCENTRATION (mol/L)
GRAIN SIZE (mm)

Block 3

Contact Water Chemistry
pH
[K+] (mg/L)
[Na+] (mg/L)
[Ca^{2+} + Mg^{2+}] (mg/L)
[HCO3-] (mg/L)
[sorbate] (μg/L)
Electrical conductivity (μS/cm)

Block 4

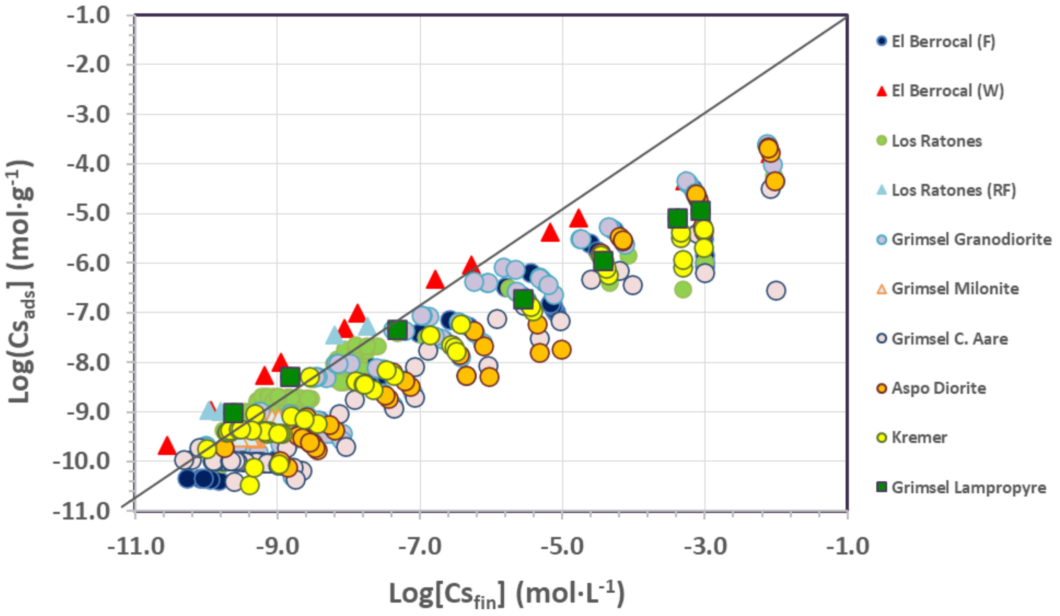
Solid Properties
N_2-BET (m^2/g)
CEC (meq/100g)
Quartz, Q (%)
Potassic Feldpar, FdK (%)
Feldspar, Fd (%)
Micas, Mi (%)
[sorbate] (μg/L)
Others - Comments

Granite (Quartz, Potassic Feldpar, Feldspar, Micas)

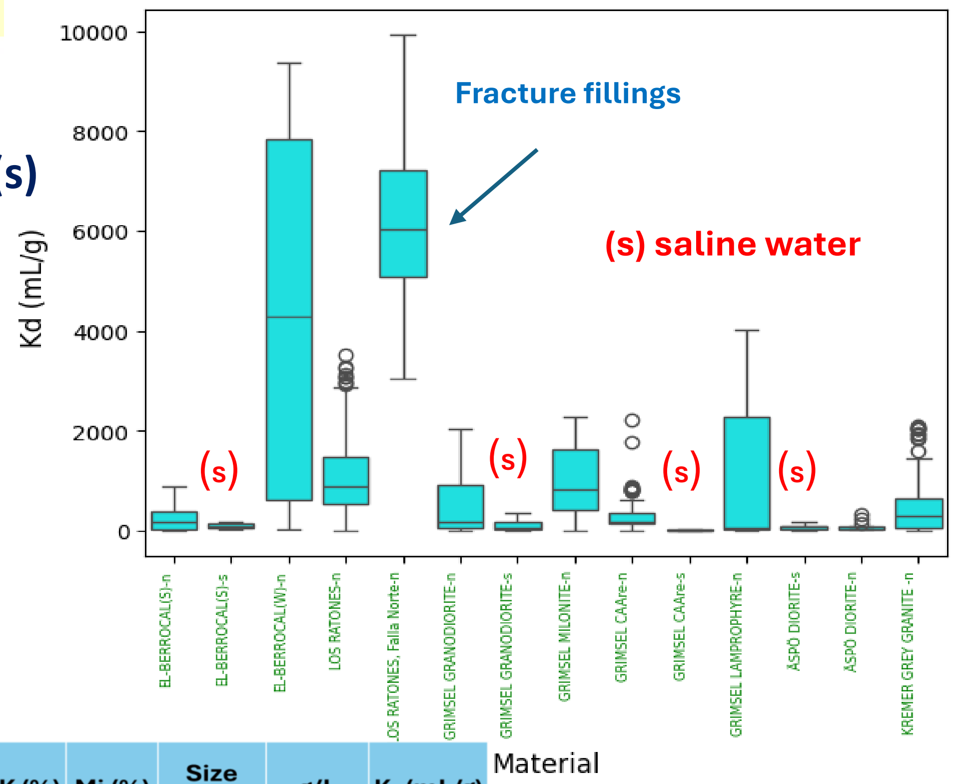
- Flexible and open structure.

EXAMPLE OF DATA WITHIN ➔ DESCRIPTIVE STATISTICS

Log-log plot of experimental data



Boxplot(s)



index	time (days)	[Cs]	pH	[K] (mg/L)	[Na] (mg/L)	[Ca+Mg] (mg/L)	BET (m2/g)	CEC (meq/100 g)	Q (%)	FdK (%)	Mi (%)	Size (mm)	g/L	K_d (mL/g)
mean	19.68	3.73E-04	7.21	98.43	315.20	160.45	2.18	1.78	31.70	21.53	17.08	0.93	26.78	736.60
std	25.65	1.72E-03	0.81	574.88	694.75	362.83	5.85	3.26	11.67	8.56	8.89	1.10	42.93	1186.38
min	0.00	1.00E-09	3.52	0.00	1.50	0.00	0.01	0.10	14.00	0.80	6.30	0.06	1.05	0.03
0.25	10.00	5.47E-09	6.74	0.00	8.30	6.78	0.09	0.66	27.00	15.00	12.00	0.10	10.00	69.89
0.5	14.00	5.37E-08	7.10	1.10	13.00	7.00	0.89	0.92	31.00	18.50	14.10	0.50	10.06	313.53
0.75	14.00	9.91E-07	7.72	2.10	15.00	57.00	2.78	1.20	40.80	28.00	18.00	1.00	20.00	939.86
max	240.00	9.85E-03	9.90	3900.00	2299.00	1162.00	40.20	19.42	67.50	41.30	46.50	4.00	250.00	9931.54

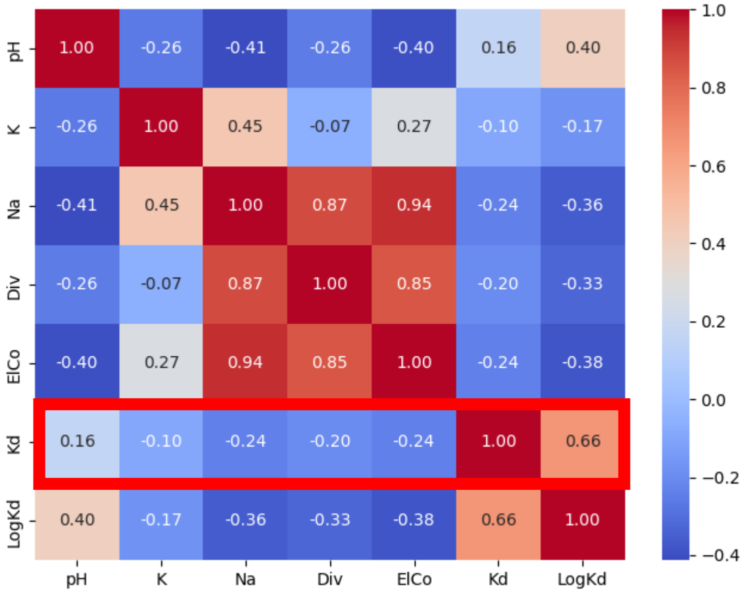
LARGE VARIABILITY

eurad 2

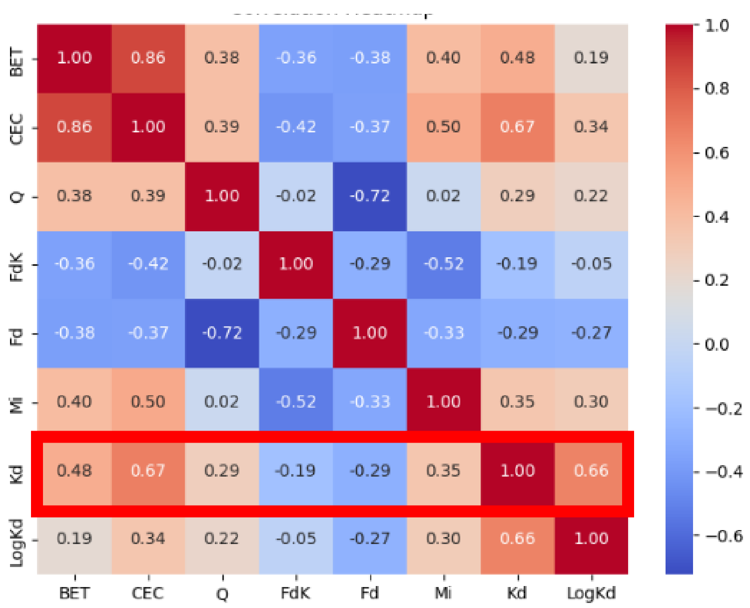
EXAMPLE OF CORRELATIONS ➔ “blocks” can change

EXPERIMENTAL BLOCK

WATER P. BLOCK

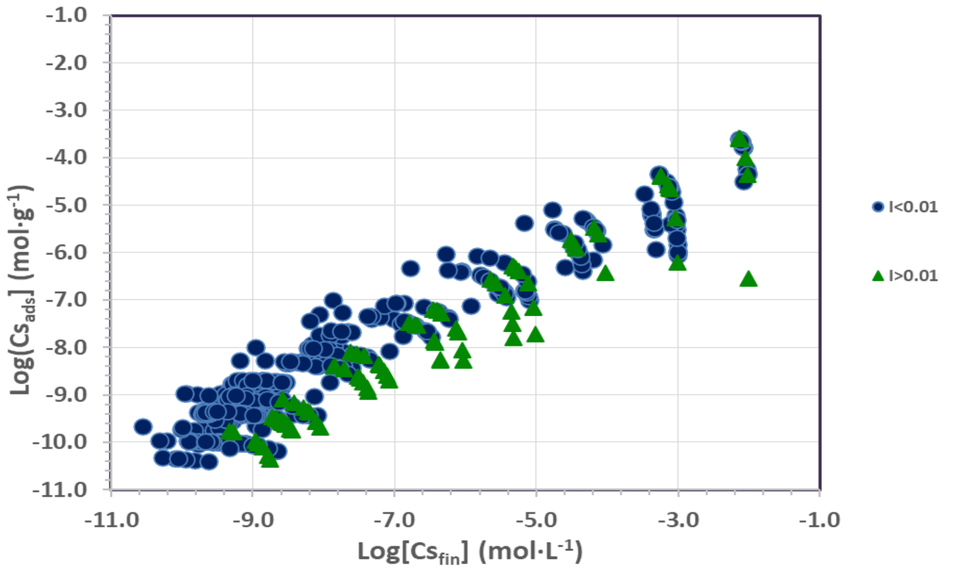


SOLID P. BLOCK



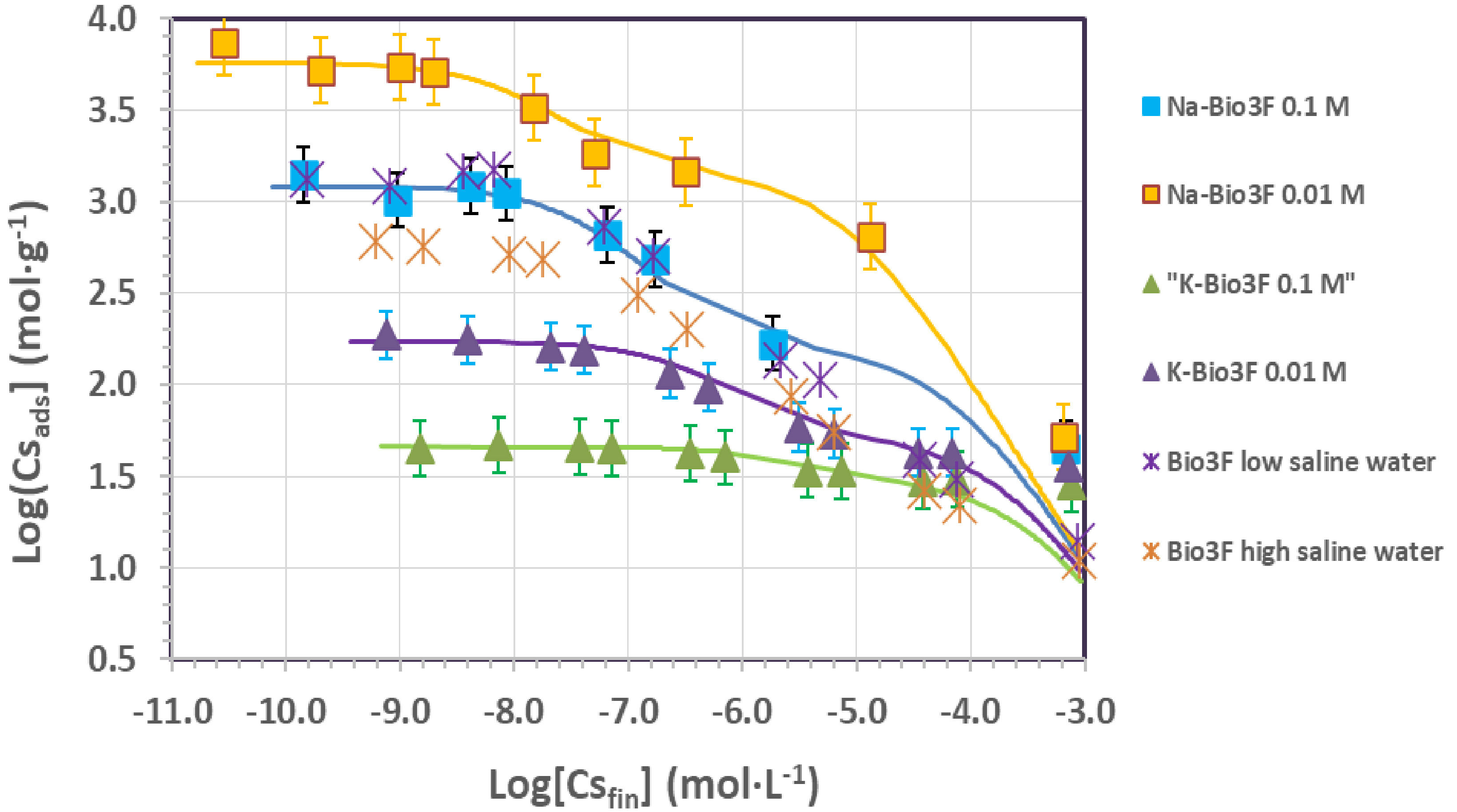
- Positive correlation: CEC, BET, Mi.
- Negative correlation: El.Cond, Fd.
- Clearly negative for Cs concentration

Clustering can improve correlations
(Ex: eliminating fracture fillings, salinity)



NOT ONLY STATISTICS: VISUALIZATION→COMPARISON →MODELLING

Statistical analysis used to define key trends or anomalies; identify data subsets suitable for modelling → evaluate the predictive capacity of existing sorption models against empirical trends. New models.



- ❑ Selectivity coefficients
- ❑ Complexation constants

New inputs

CONCLUSIONS (SD)

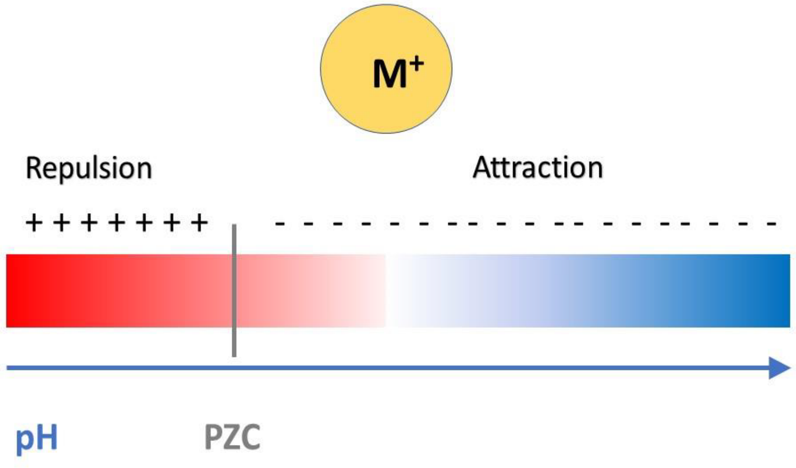
- SD structure: systematic data organization; easy data extraction, visualization and transferability to other programmes.
- Advanced analysis (AI tools) possible ➔ combine statistical analysis with geochemical modelling is better.
- SD will remain open, accessible, continuously updated, and flexible enough to incorporate new parameters, as required by future research needs.
- Although cesium is used here as a case study, the concept is applicable to other systems.

  → Two other cases will be proposed in the frame of EURAD 2 – RAMPEC WP: one for clays (anions) and one for cements (RN+organics).

2nd part: CORI - Role of organics on RN mobility in cementitious materials (very different systems)

DIFFICULTIES IN SORPTION MODELLING➔Cement are quite complicate systems. Very high pH; high salinity; complex chemistry (multimineral); Evolving with time. Not always all the information on chemistry is (or can be) precise.

SORPTION



➔Scarce /null information on "surface" properties.

➔What about TDB ??

THERMODYNAMIC DATA

- We selected ThermoChimie (TC) being the most complete TDB for RN+ORG.

- During CORI: From V10a to V12a…New version….new calculations….

- SOME ISSUES ENCOUNTERED on RN+ORG sorption in portlandite or CSH phases (simple systems).

RN + CITRATE

- ❑ Eu(III) + CIT ➔ No data in TDB ➔ Analogy with Am ✓
- ❑ Pu(IV) + CIT ➔ No data in TDB ➔ Analogy with Th(IV) ??? ☒

pH<5

- No other complexes selected (more in the paper)
- Not valid for cementitious environment

Table 8-21. Th-citrate complexes and corresponding Log K° values selected in TC vs.12a, in comparison with those in TC vs.11a.

Species	Log K° TC vs.12a	Reference	Log K° TC vs 11a	Reference
$ThCit^{+}$	14.13	Raymond *et al.* (1987)	16.80 ± 0.30	Akram and Bourbon (1995)
$Th(Cit)_2^{2-}$	24.29	Raymond *et al.* (1987)	25.80 ± 0.30	Akram and Bourbon (1995)

Older

- ❑ U(VI) + CIT ➔ Data added in V12 (2023)

Table 8-22. U(VI)-citrate complexes and corresponding Log K° values selected in TC vs.12a, in comparison with those in TC vs.11a.

Species	Log K° TC vs.12a	Reference	Log K° TC vs 11a	Reference
$(UO_2)_2(Cit)_2^{2-}$	21.3 ± 0.5	Hummel *et al.* (2005)	21.3 ± 0.5	Hummel *et al.* (2005)
$UO_2(Cit)^{-}$	8.96 ± 0.17	Hummel *et al.* (2005)	8.96 ± 0.17	Hummel *et al.* (2005)
$UO_2(HCit)$	11.36 ± 1	Hummel *et al.* (2005)	11.36 ± 1	Hummel *et al.* (2005)
$(UO_2)_2(Cit)_2(OH)_2^{4-}$	9.29±0.03	Berto *et al.* (2012)	-	-
$(UO_2)_2(Cit)_2(OH)^{3-}$	16.04±0.04	Berto *et al.* (2012)	-	-
$(UO_2)_2(Cit)(OH)_2^{-}$	5.30±0.01	Berto *et al.* (2012)	-	-
$(UO_2)_2(Cit)(OH)$	9.65±0.07	Berto *et al.* (2012)	-	-

2012

➢ NO "NEW" EXPERIMENTAL DATA

ISA + Ni

Not enough thermodynamic data. Is it correct to use data not included in "official databases"?

We were guilty....

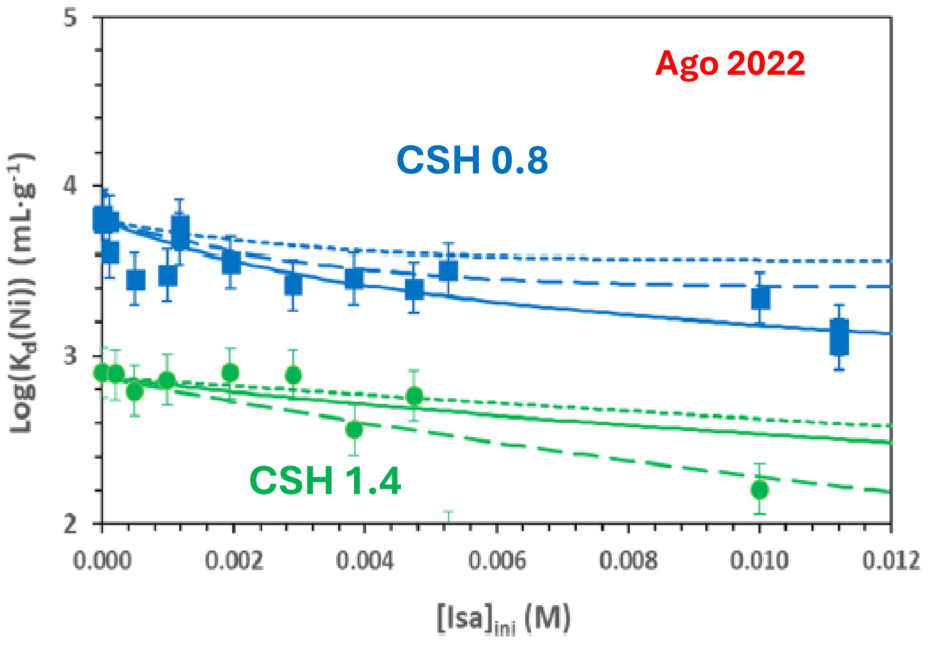


Fig. 4. Logarithm of Ni distribution coefficient *vs.* initial Isa concentration Squares correspond to CSH(0.8), and circles correspond to CSH(1.4) (10 g·L^{-1}) The lines correspond to the modelling of the distribution coefficients. Contin uous line: no adsorption of Isa on the CSH; dotted line: Isa adsorption only ir the weak site; dashed line: Isa adsorption on strong and weak sites.

Table 1
Thermodynamic data for Isa complexes with Ni and other cations of interest. Basis species: Isa[-]. TC= [13]; GS= González-Siso (2018).

Species	Composition (CHESS code)	TC LogK	GS LogK
$Ca(Isa)_2(cr)$	1 Ca[2 +], 2 Isa[-]	6.4	6.4
Ca(Isa) [+]	1 Ca[2 +], 1 Isa[-]	1.7	1.7
Ca(Isa)(aq)	1 Ca[2 +], − 1 H[+], 1 Isa[-]	-10.4	-10.4
HIsa(aq)	1 H[+],1 Isa[-]	4	4
Ni(Isa) [+]	1 Ni[2 +], 1 Isa[-]	2.8	2.8
$Ni(OH)_3$(Isa) [2-]	1 Ni[2 +], 1 Isa[-], 3 H_2O, − 3 H[+]	-26.5	-31
$Ni(OH)_2$(Isa) [-]	1 Ni[2 +], 1 Isa[-], 2 H_2O, − 2 H[+]	–	-17.6
Ni(OH)(Isa)	1 Ni[2 +], 1 Isa[-], 1 H_2O, − 1 H[+]	–	-6.5

Comparison between the two cases

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Table 8-3. *Complexes and corresponding Log K° values selected in TC vs.12a, in comparison with those in TC vs.11a.*

Species	Log K° TC vs.12a	Reference	Log K° TC vs 11a	Reference
$Ni(HIsa)^+$	-	-	2.80 ± 0.40	Grive *et al.* (2012)
Ni(OH)(HIsa)(aq)	-6.50 ± 0.30	González-Siso *et al.* (2018) and Bruno (2018)	-	-
$Ni(OH)_2(HIsa)^-$	-17.60 ± 0.50	González-Siso *et al.* (2018) and Bruno (2018)	-	-
$Ni(OH)_3(HIsa)^{2-}$	-31.00 ± 0.70	González-Siso *et al.* (2018) and Bruno (2018)	-26.50 ± 1.00	Grive *et al.* (2012)

RN+PHTH; ternary/quaternary complexes

- Pu(IV) + PHTH → No data in TDB
- In general, not very much data for PHTH. No solid phases.
- Almost no data for ternary / quaternary complexes: Ca-RN-(OH)-ORG

Ca quite important element in cement

CONCLUSIONS (TD)

- Difficult and / or slow incorporation of "new" studies (when they exist)

- Lack of experimental data → most important drawback.

Thanks for your attention !