Influence of groundwater residence time on radionuclides and bentonite colloids retention at the Grimsel Test Site

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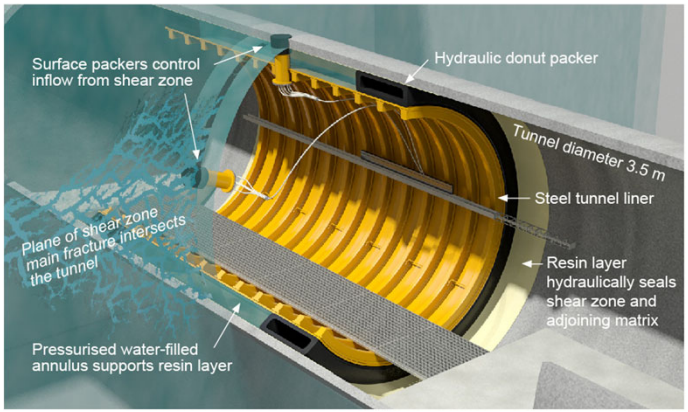
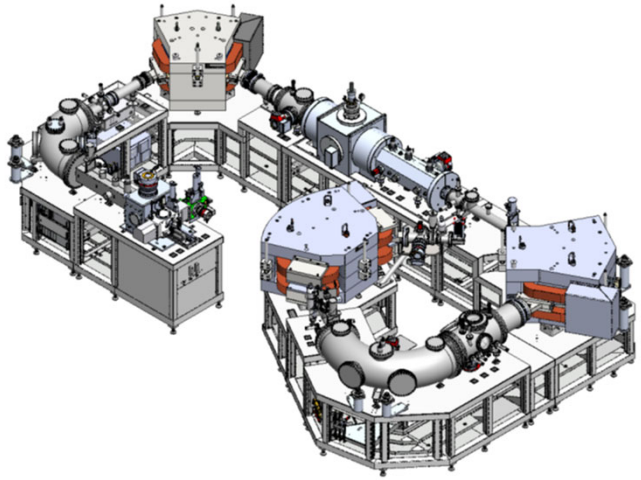


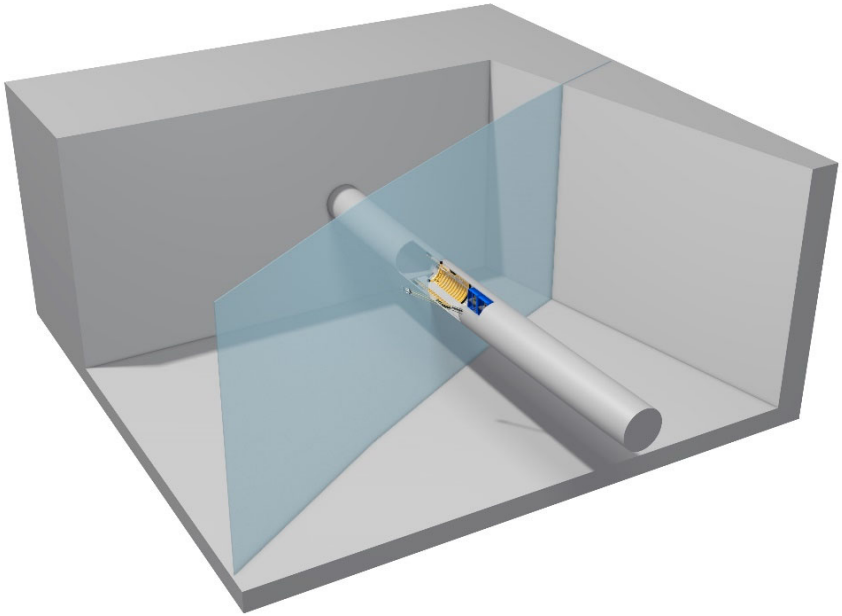


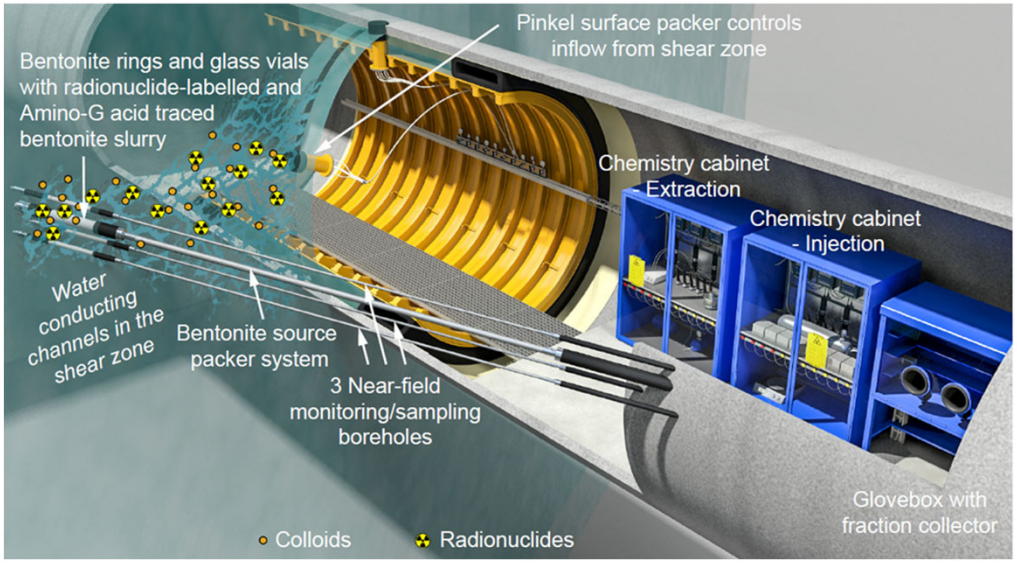
In-situ radionuclide tracer tests

NAGRA' s URL Grimsel Test Site

Radiation-controlled zone & Mega packer system

- Use of radioactive markers in the geosphere (in trace amounts of µg – 10 ng levels)
- Groundwater flow control





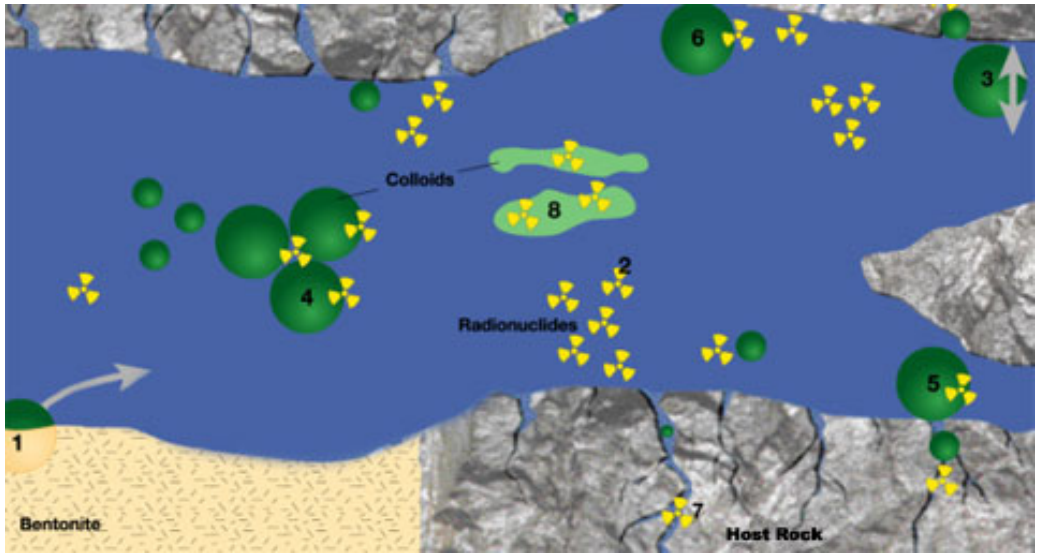
Scenarios: glacial melt water/low mineralized meteoric water intrusion in a DGR

Grimsel groundwater (GGW):

- EhSHE = -220 mV
- pH = 9.6; I = 10^{-3} M

=> high stability and mobility of bentonite colloids, possibly carriers for RNs

In-situ geochemical reactions of RNs in the ternary system:
fault gouge minerals/GGW/colloids

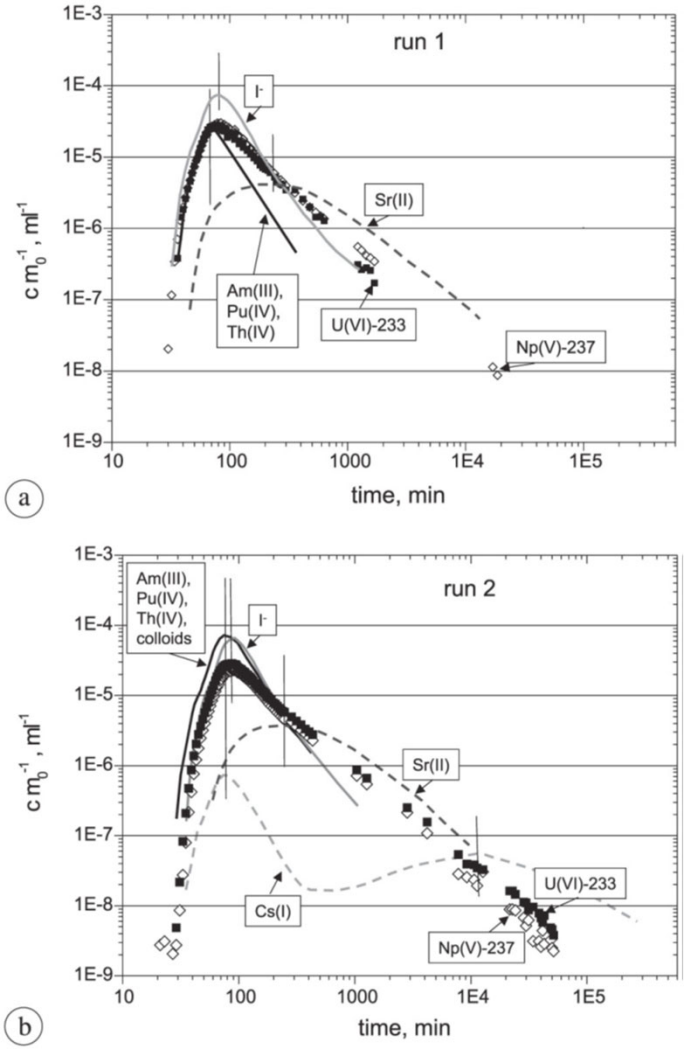


In-situ RN tracer tests in advective conditions

- Grimsel groundwater
- Na-Febex bentonite and Ni-Montmorillonite colloids
- Conservative tracer, e.g., fluorescence AminoG (AGA)
- U(VI), Np(V),
- Pu(IV), Am(III)

- On-line monitoring of pH, Eh, AGA at the injection and extraction pipes
- Groundwater samples are periodically collected

2002: Colloid and Radionuclide Retardation – CRR Experiment



- Am(III) and Th/Pu(IV): clay colloid-mediated "faster" transport
- U(VI) and Np(V) mainly dissolved species

Geckeis et al., Radiochim. Acta. 2004;92:675-674.

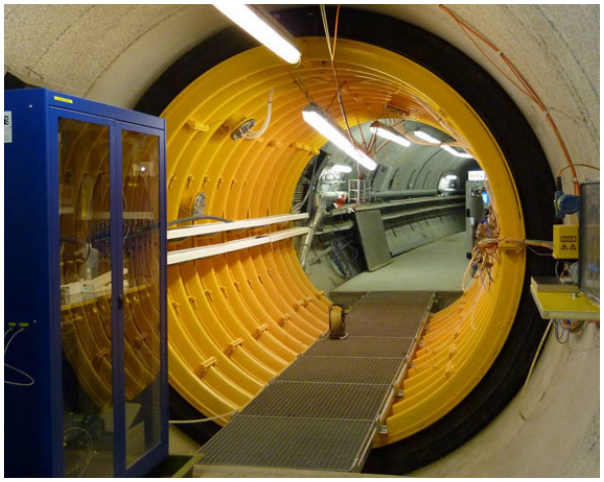
2002: Colloid and Radionuclide Retardation – CRR Experiment

	CRR run 32
Inj./Extr. rate	5/150 mL/min
Peak arrival	80 min
Cons. tracer	92%
^{233}U	103 ± 5%
^{237}Np	82 ± 4%
$^{241,243}Am$	70%
$^{242,244}Pu$	86 ± 9%
Colloids	85-100%

Almost quantitative recovery of the actinide tracers

increasing residence time => kinetic impact on recovery of colloid-bound actinides? And mobility of dissolved actinide U(VI)/Np(V) species?

2012: Colloid Formation and Migration – CFM Project



2009: Mega-packer and flow control system

Injection/Extraction (0.33/5 ml/min) 30 times slower than in CRR

Under advective flow close to repository-relevant conditions

Comparison CRR run 32 and CFM run 13-05

	CRR run 32		CFM run 13-05
Inj./Extr. rate	5/150 mL/min		0.33/5 mL/min
Peak arrival	80 min		2640 min
Cons. tracer	92%		93%
^{233}U	103 ± 5%		15%
^{237}Np	82 ± 4%		4%
$^{241,243}Am$	70%		25%
$^{242,244}Pu$	86 ± 9%		28%
Colloids	85-100%		35-37%

Longer arrival time of the breakthrough peaks

Decreased recovery of all the actinide nuclides

Comparison CRR run 32 and CFM run 13-05: Decreased recovery of Pu and Am

	CRR run 32		CFM run 13-05
Inj./Extr. rate	5/150 mL/min		0.33/5 mL/min
Peak arrival	80 min		2640 min
Cons. tracer	92%		93%
^{233}U	103 ± 5%		15%
^{237}Np	82 ± 4%		4%
$^{241,243}Am$	70%		25%
$^{242,244}Pu$	86 ± 9%		28%
Colloids	85-100%		35-37%

$Am(OH)_3$ and PuO_2 or $Pu(OH)_4$, and colloid retention mechanisms: adsorption and filtration at the fracture surface and in fracture-filling material pores

Comparison CRR run 32 and CFM run 13-05: Decreased recovery of U and Np

	CRR run 32		CFM run 13-05
Inj./Extr. rate	5/150 mL/min		0.33/5 mL/min
Peak arrival	80 min		2640 min
Cons. tracer	92%		93%
^{233}U	103 ± 5%		15%
^{237}Np	82 ± 4%		4%
$^{241,243}Am$	70%		25%
$^{242,244}Pu$	86 ± 9%		28%
Colloids	85-100%		35-37%

isotopic exchange with naturally occurring mineral phases or surface sorption of aquatic $^{233}UO_2^{2+}$ species

precipitation of $^{237}NpO_2$ or surface sorption of $^{237}Np(IV)$ species

2023: New experiment

	CRR run 32	new	CFM run 13-05
Inj./Extr. rate	5/150 mL/min	><	0.33/5 mL/min
Peak arrival	80 min	><	2640 min
Cons. tracer	92%	?	93%
^{233}U	103 ± 5%	?	15%
^{237}Np	82 ± 4%	?	4%
$^{241,243}Am$	70%	?	25%
$^{242,244}Pu$	86 ± 9%	?	28%
Colloids	85-100%	?	35-37%

CFM run 22-02 within the same borehole dipole

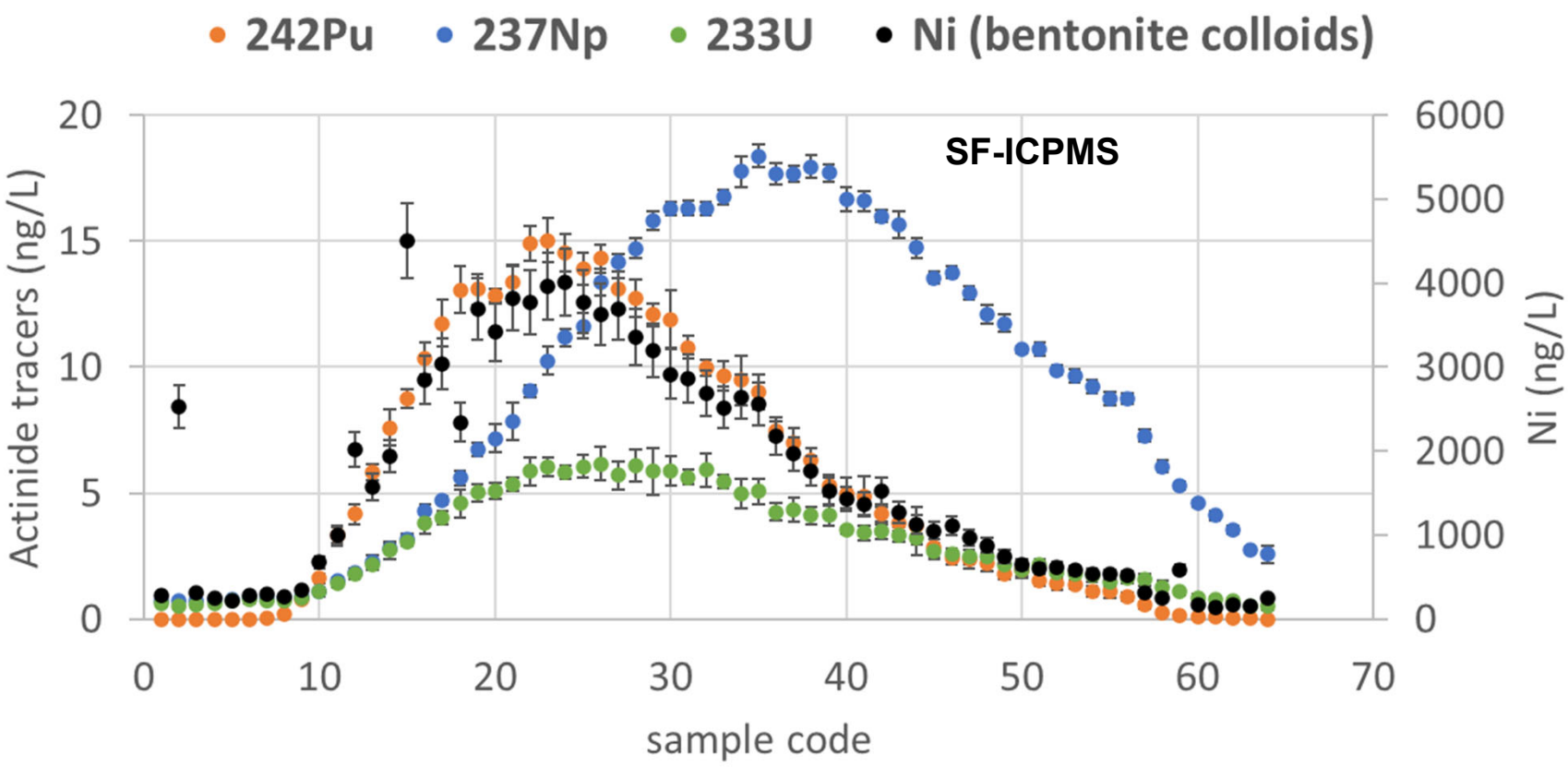
to better investigate the influence of residence time on in-situ retention mechanisms

Run 22-02

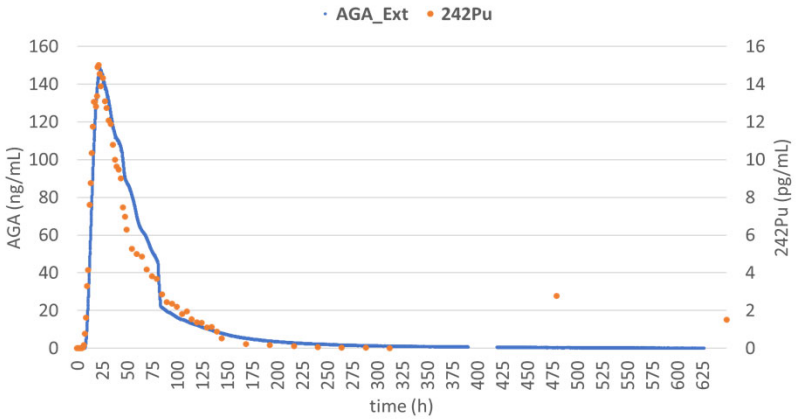
	CRR run 32	CFM run 22-02	CFM run 13-05
Inj./Extr. rate	5/150 mL/min	**0.66/10 mL/min**	0.33/5 mL/min
Peak arrival	80 min	**1406 min**	2640 min
Cons. tracer	92%	**94%**	93%
^{233}U	103 ± 5%	**36%**	15%
^{237}Np	82 ± 4%	**32%**	4%
$^{241,243}Am$	70%	**34%**	25%
$^{242,244}Pu$	86 ± 9%	**30%**	28%
Colloids	85-100%	**23%***	35-37%

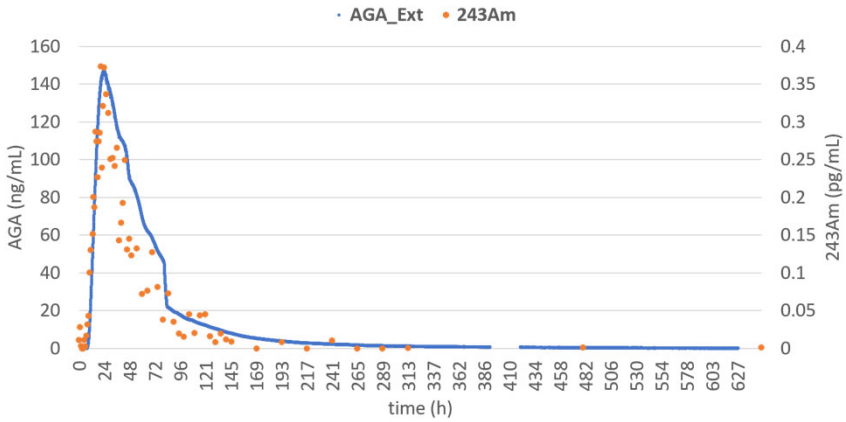
*Estimated from the analysis of Ni taken as the indicator for clay colloids (synthetic montmorillonite with structural Ni)

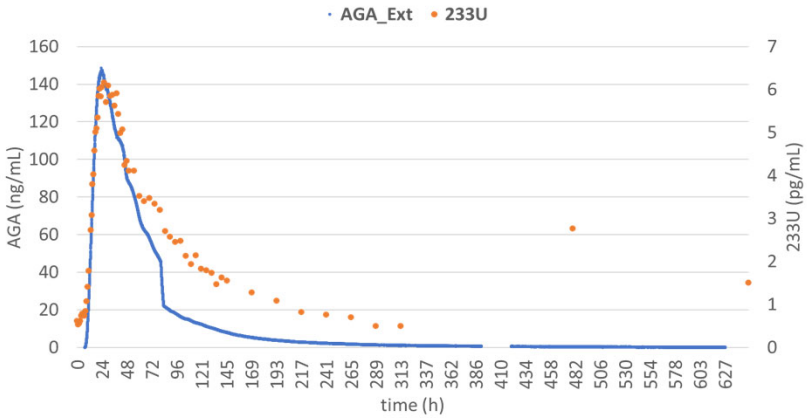
Breakthrough curves of ^{233}U, ^{237}Np, ^{242}Pu and Ni

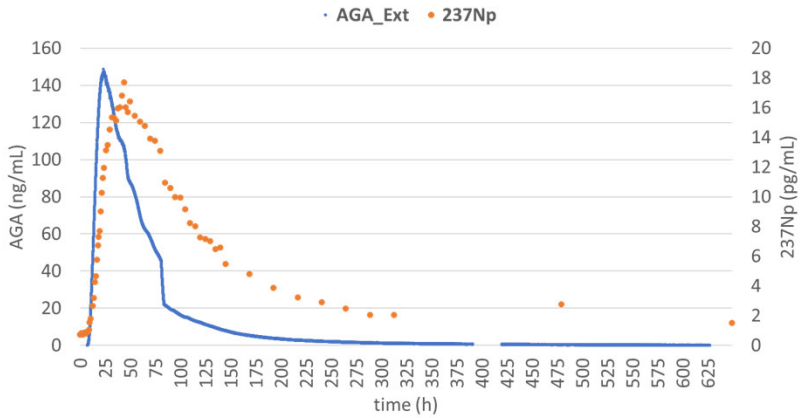


AGA and ^{242}Pu, ^{243}Am, ^{233}U and ^{237}Np breakthrough curves

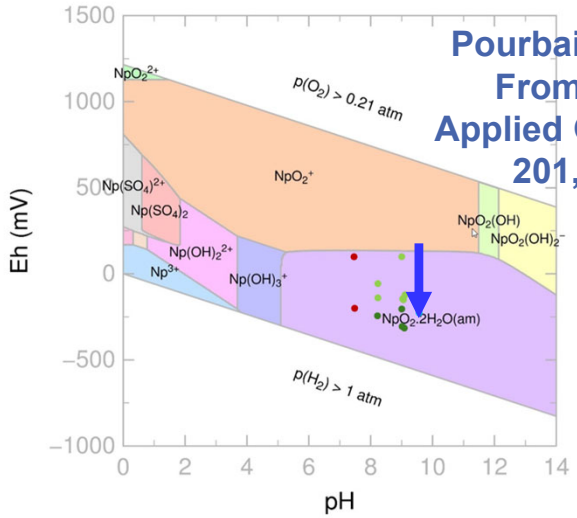




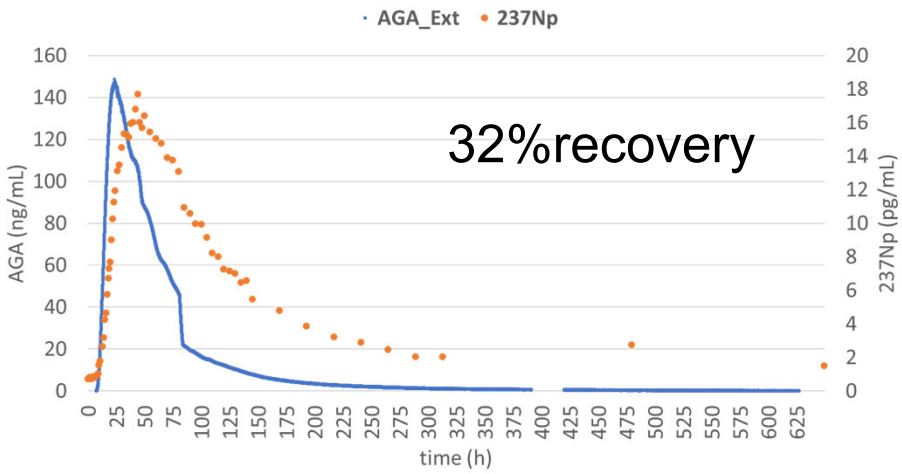




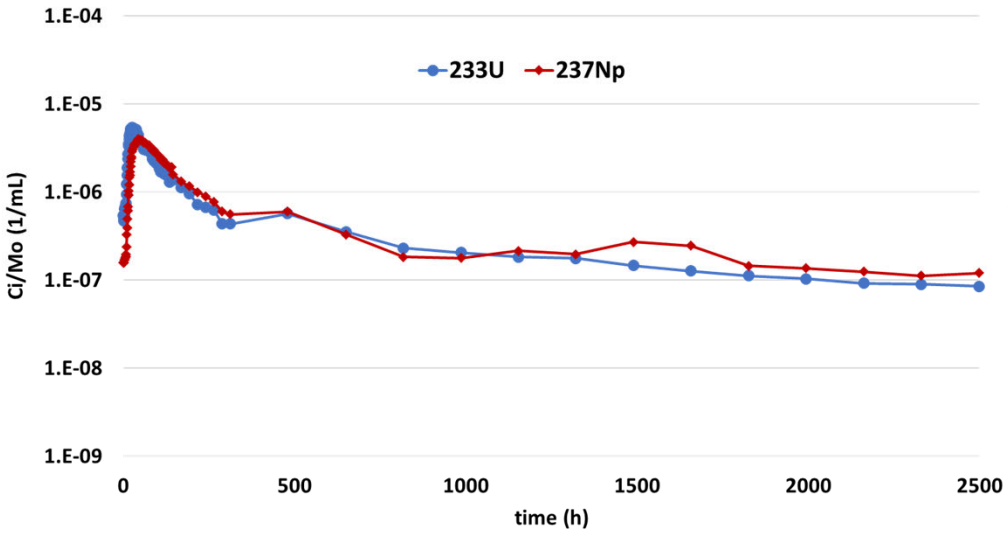
Results: in-situ reduction of Np(V) to Np(IV)

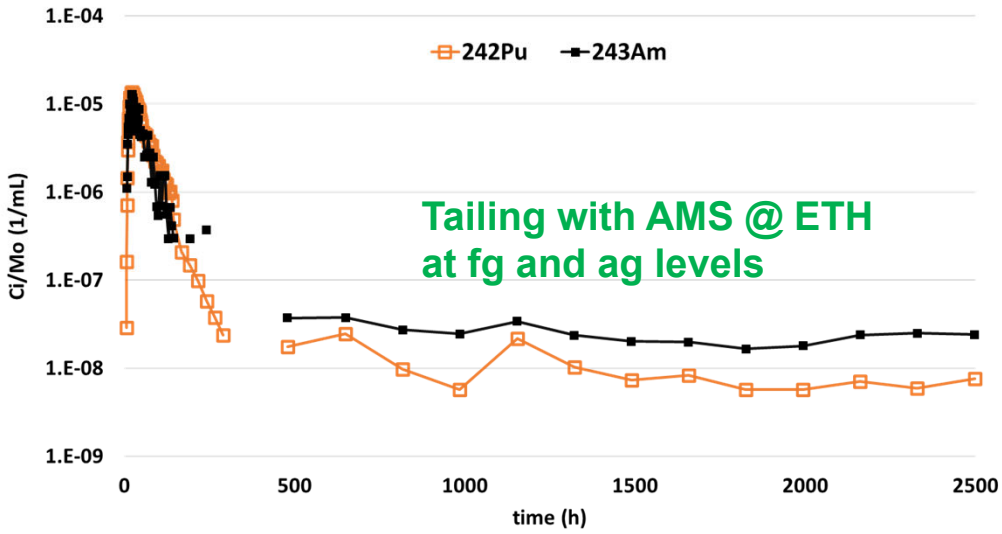


Pourbaix diagram for Np
From Noseck et al., Applied Geochemistry vol. 201, p. 106762-85



Breakthrough curves & tailings of ^{233}U, ^{237}Np, ^{242}Pu and ^{243}Am normalized to their injected inventories





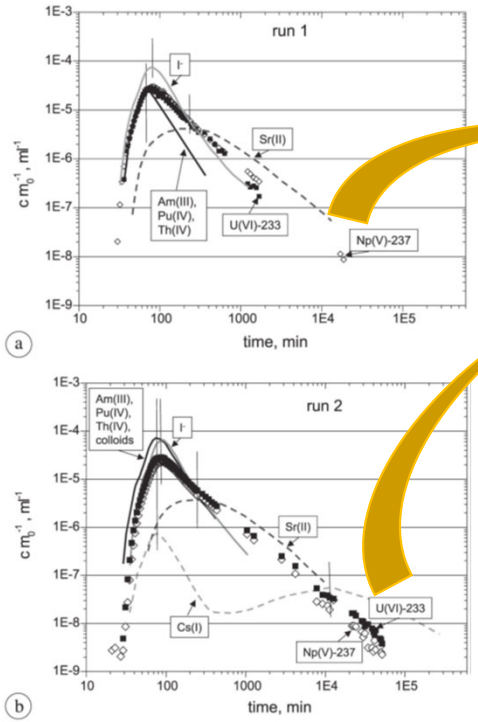
AMS Results: CFM run 13-05

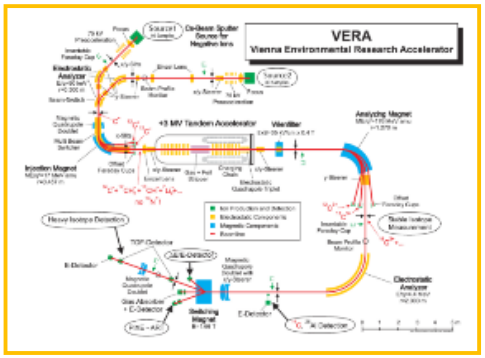
Long-term transport and retention of radionuclides in the ultra-trace range with AMS

Karlsruher Institut für Technologie

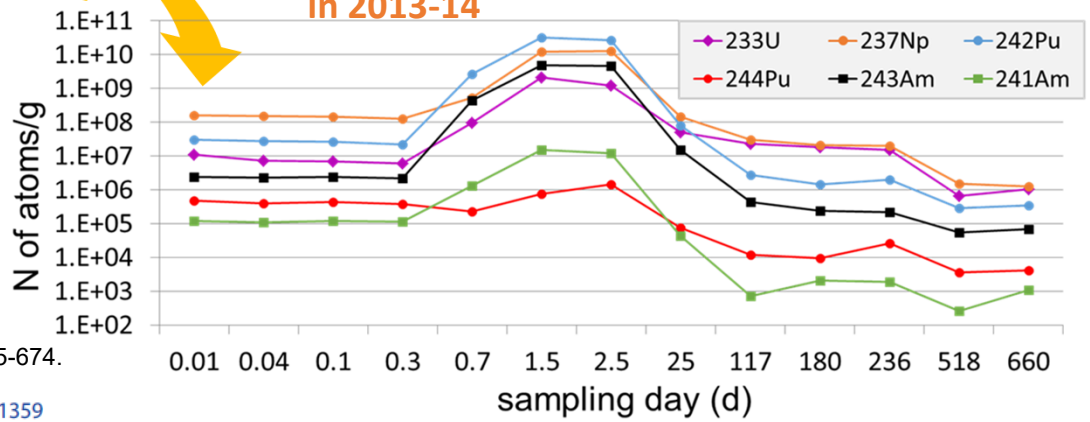
in 2002

Evidence of retention in the granodiorite fracture and **ultra-trace continuous release** through reversible reactions within the fracture and desorption (also colloid-mediated) from fracture surfaces of radionuclides **over a decade**





in 2013-14



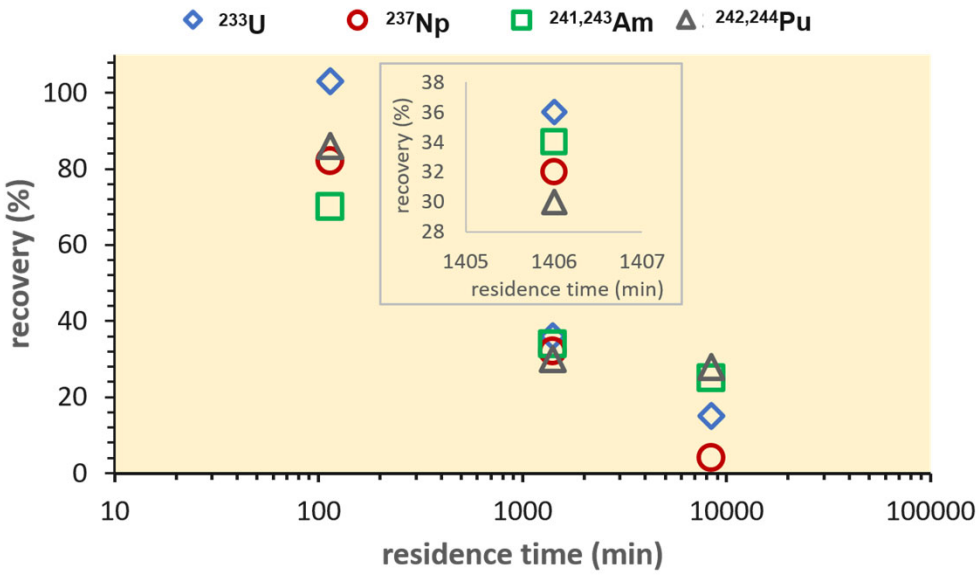
Radiochim. Acta. 2004;92:675-674.

DOI: 10.1021/acs.analchem.7b01359
Anal. Chem. 2017, 89, 7182−7189

Conclusions: URL experiments & ultra-trace analysis

- Insights on the **in-situ kinetics of retention mechanisms** for U(VI), Np(IV&V), Pu(IV) and Am(III) in field tests reproducing near-natural repository conditions

- Experimental determination of a **long-term ultra-trace release** of RNs as tailing after their breakthrough curves



KIT-INE new AMS facility – Research Topics:

cleanroom laboratory with **class ISO 4** => significant decrease of the ubiquitous global fallout background

further **increase in analytical sensitivity**

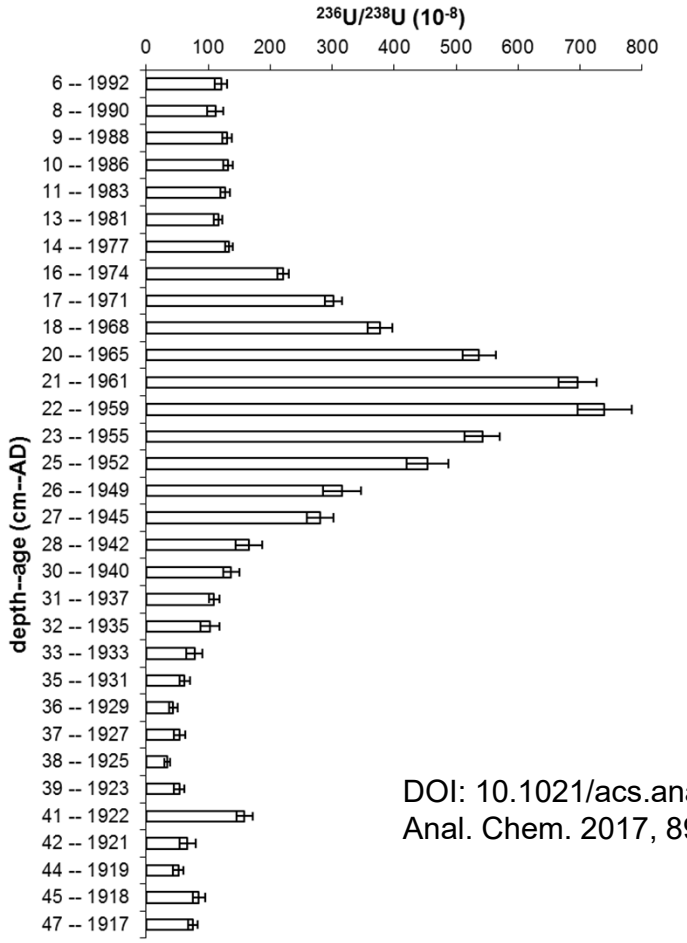
KIT-INE AMS facility will be dedicated to the themes of:

- Safety of nuclear waste disposal (URL experiments, Natural Analogues)
- Decommissioning & status quo-ante
- Environmental research & migration and partitioning of RNs among the geosphere´s and biosphere´s compartments
- Nuclear forensic – environmental samples

KIT-INE new AMS facility – Research Topics:

cleanroom laboratory with **class ISO 4** => significant decrease of the ubiquitous global fallout background

further **increase in analytical sensitivity**



DOI: 10.1021/acs.analchem.7b01359
Anal. Chem. 2017, 89, 7182−7189

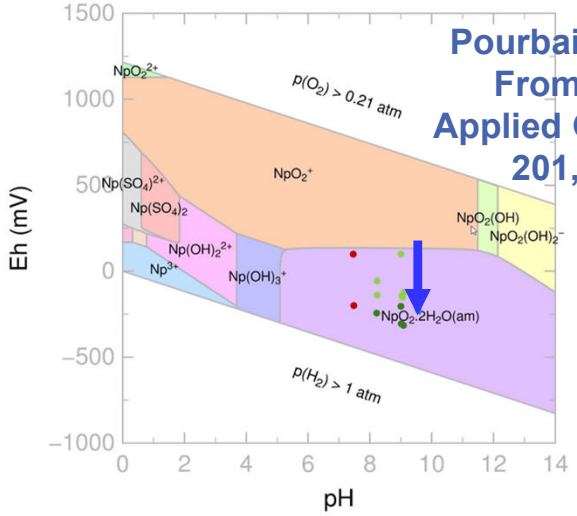
Thank you!

BMUKN funded EVIDENT Project - Förderkennzeichen: 02 E 12153B
Federal Ministry for Environment, Climate Action, Nature Conservation and Nuclear Safety

Results: in-situ redox conditions in the Injection and Extraction pipes

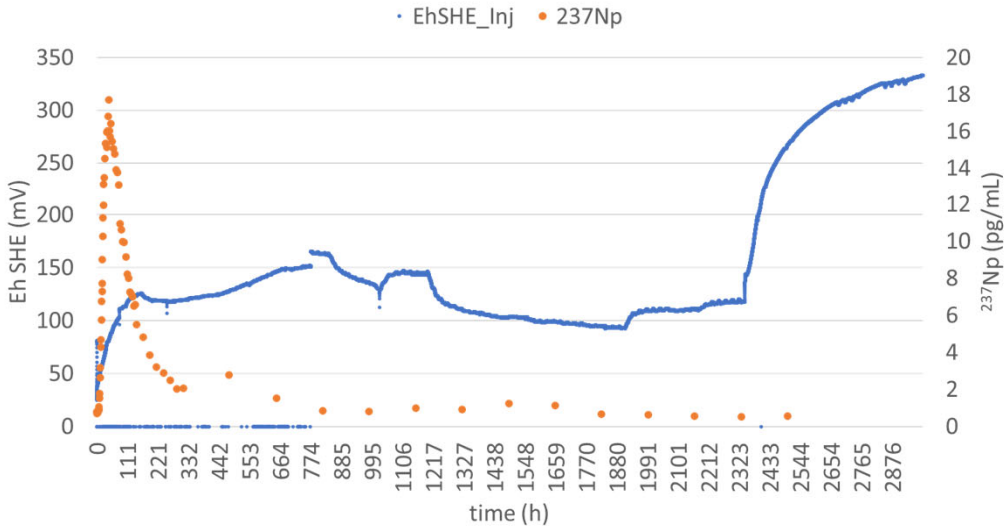
Eh of the cocktail + GGW in the injection pipe

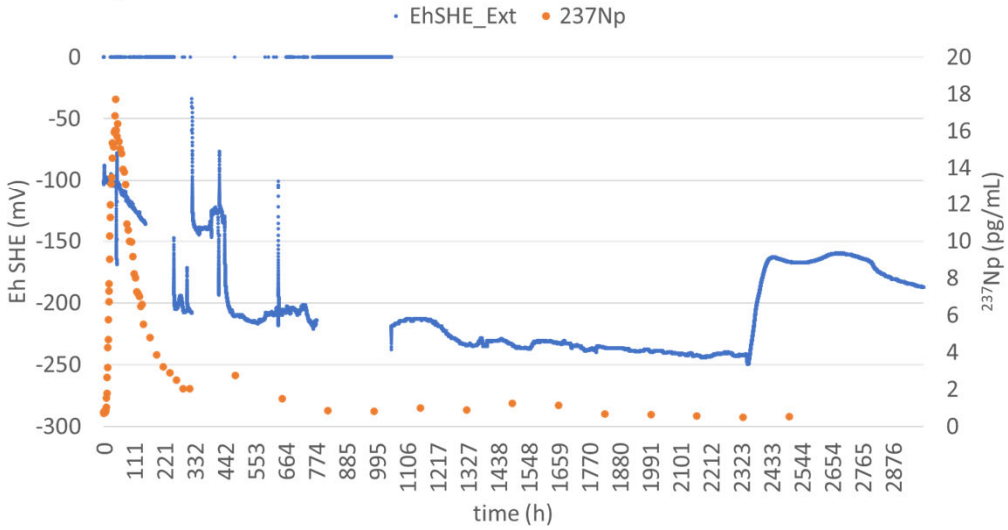
^{237}Np



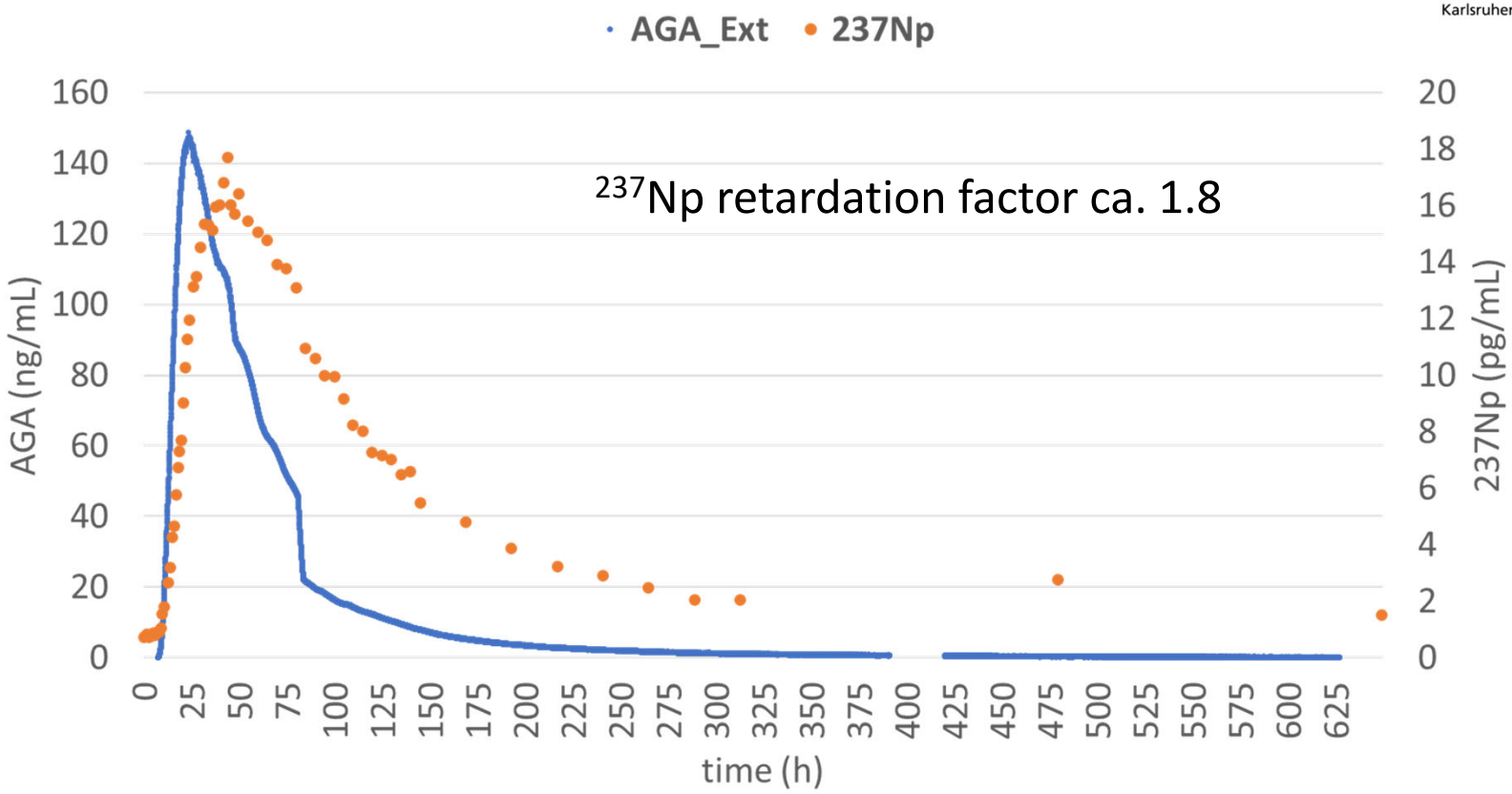
Pourbaix diagram for Np From Noseck et al., Applied Geochemistry vol. 201, p. 106762-85

Eh of the GGW samples in the extraction pipe

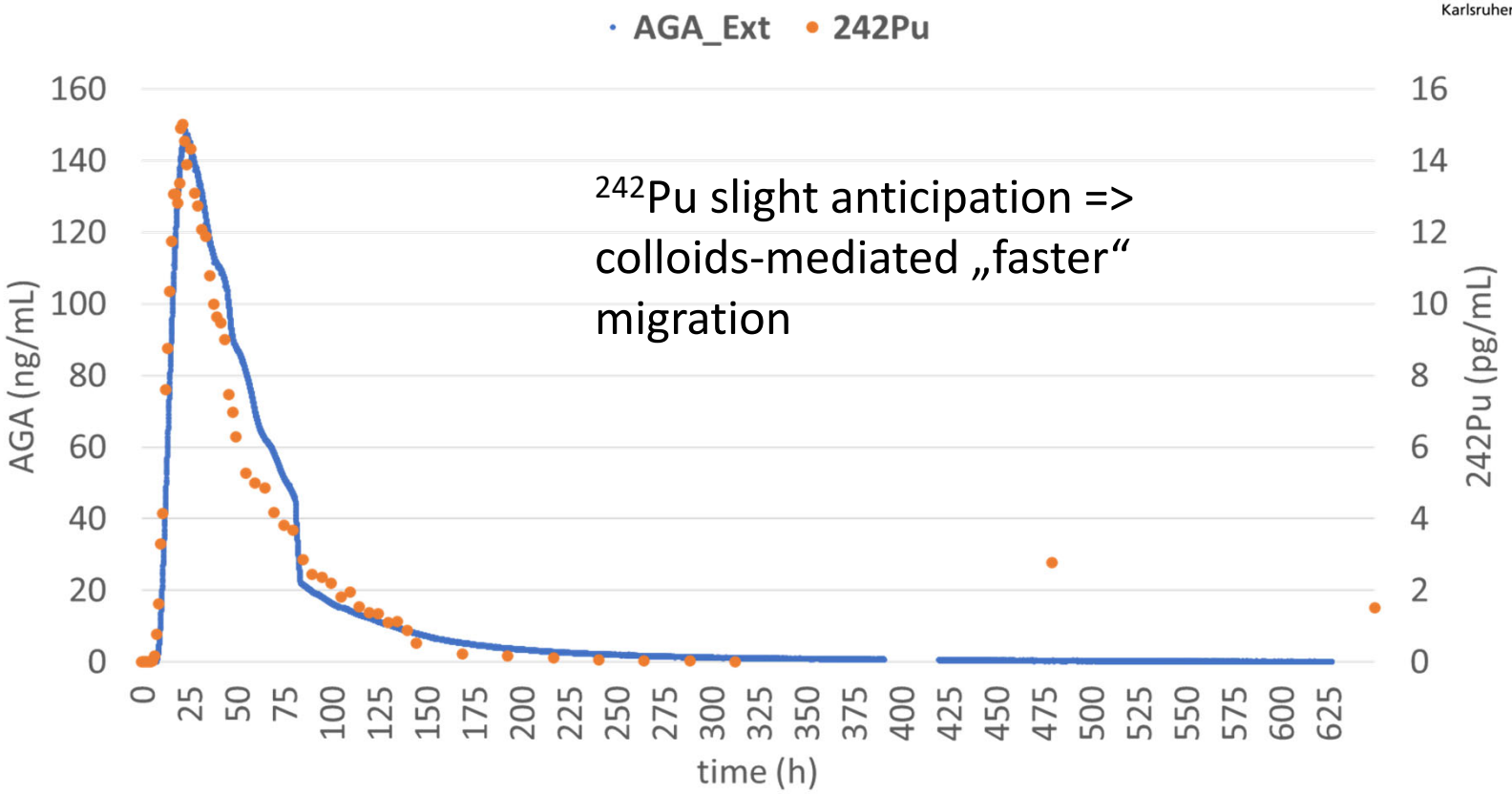




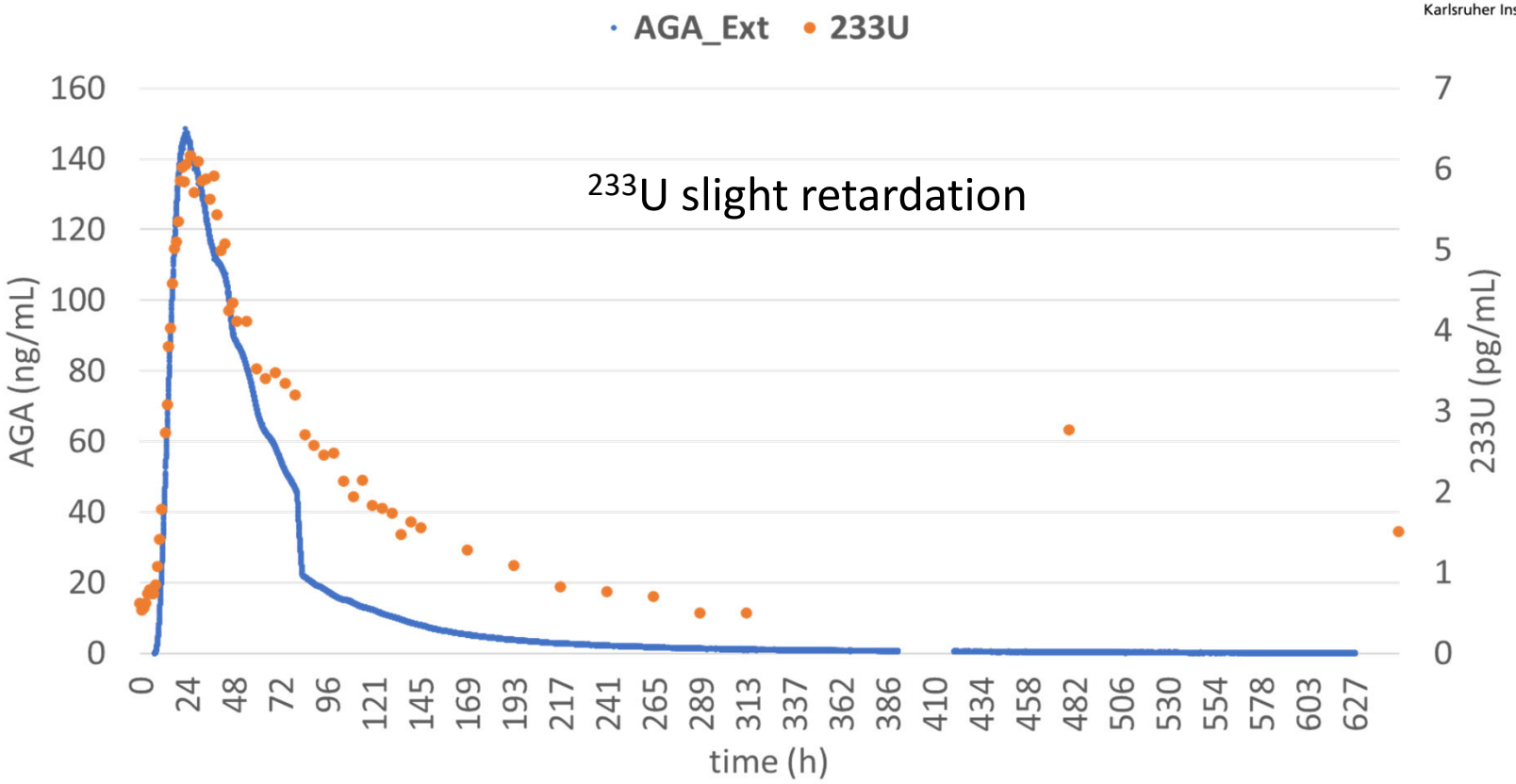
AGA and ^{237}Np breakthrough curves



AGA and ^{242}Pu breakthrough curves



AGA and ^{233}U breakthrough curves



Speciation U:

GGW	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
SLP	$UO_2 \cdot 2H_2O$(am)	UO_2(am)	Uranophane	Uranophane	$UO_2 \cdot 2H_2O$(am)	Uranophane
U_{tot}	2.6×10^{-05}	4.5×10^{-09}	3.4×10^{-08}	3.5×10^{-08}	3.1×10^{-05}	2.9×10^{-08}
$U(OH)_4$	<1	71	<1	<1	<1	<1
$UO_2(OH)_3^-$	2	2	<1	<1	2	<1
$UO_2(CO_3)_2^{2-}$	<1	1	<1	<1	<1	<1
$UO_2(CO_3)_3^{4-}$	9	25	5	5	6	8
$Ca_2UO_2(CO_3)_3$	12	n.i.d.	18	21	23	14
$CaUO_2(CO_3)_3^{2-}$	72	n.i.d.	75	72	58	75
$(UO_2)_2(CO_3)(OH)_3^-$	4	<1	<1	<1	10	<1

GGW	Group 2	Group 3	Group 4	Group 5	Group 6
SLP	Uranophane				
U_{tot}	2.3×10^{-09}	3.4×10^{-08}	3.5×10^{-08}	3.6×10^{-08}	2.9×10^{-08}
$UO_2(OH)_3^-$	8	<1	<1	<1	<1
$UO_2(CO_3)_3^{4-}$	87	5	5	5	8
$Ca_2UO_2(CO_3)_3$	n.i.d.	18	21	26	14
$CaUO_2(CO_3)_3^{2-}$	n.i.d.	75	72	68	75

Noseck et al, Applied Geochemistry, vol. 201, p. 106762-85

Solubility limiting phase (SLP), maximum concentrations [mol/kg water] and fraction of dominating species [%] calculated for uranium; n.c.: not used in calculations; n.i.d.: not in database

Speciation Np:

GGW						
SLP	$NpO_2 \cdot 2H_2O(am)$	$NpO_2(am)$	$NpO_2(am)$	$NpO_2 \cdot 2H_2O(am)$	$NpO_2 \cdot 2H_2O(am)$	$NpO_2 \cdot 2H_2O(am)$
Np_{tot}	1.0×10^{-09}	1.0×10^{-09}	1.0×10^{-09}	1.0×10^{-09}	1.0×10^{-09}	$1\text{-}0 \times 10^{-09}$
$Np(OH)_4$	98	97	100	98	93	98
$Np(CO_3)(OH)_3^-$	2	<1	<1	2	6	2
Np(OH)4(CO3)-2	<1	<1	n.i.d.	<1	1	<1
$Np(CO_3)_2(OH)_2^{2-}$	<1	3	n.i.d.	<1	<1	<1
$NpO_2SiO(OH)_3$	n.i.d.	?	<1	n.i.d.	n.i.d.	n.i.d.

Noseck et al, Applied Geochemistry, vol. 201, p. 106762-85

Solubility limiting phase (SLP), maximum concentrations [mol/kg water] and fraction of dominating species [%] calculated for uranium; n.c.: not used in calculations; n.i.d.: not in database

Speciation Pu:

GGW						
SLP	PuO_2(hyd,ag)	PuO_2(hyd,ag)	PuO_2(hyd.ag)	$Pu(OH)_4$(am)	PuO_2(hyd,ag)	PuO_2(hyd,ag)
Pu_{tot}	1.4×10^{-11}	3.8×10^{-11}	8.2×10^{-11}	5.5×10^{-10}	1.4×10^{-11}	1.5×10^{-11}
$Pu(OH)_4$	100	39	3	92	99	100
$Pu(OH)_3^+$	<1	<1	<1	8	<1	<1
$Pu(CO_3)_2(OH)_2^{2-}$	<1	61	n.i.d.	<1	<1	n.c
$Pu(CO_3)(OH)_3^-$	n.i.d.	n.i.d.	97	n.i.d.	n.i.d.	n.i.d.

Noseck et al, Applied Geochemistry, vol. 201, p. 106762-85

Solubility limiting phase (SLP), maximum concentrations [mol/kg water] and fraction of dominating species [%] calculated for uranium; n.c.: not used in calculations; n.i.d.: not in database

Speciation Am:

GGW						
SLP	$Am(CO_3)(OH)(am)$		$Am(OH)_3(am)$			
Am_{tot}	1.0×10^{-07}	1.7×10^{-07}	8.7×10^{-08}	5.0×10^{-08}	5.0×10^{-08}	7.7×10^{-08}
$Am(OH)^{2+}$	38	18	19	33	32	21
$Am(OH)_3$	1	<1	<1	1	1	<1
$Am(CO_3)^{+}$	13	10	10	13	14	11
$Am(CO_3)_2^{-}$	36	50	50	43	44	59
$AmOSi(OH)_3^{2+}$	11	21	20	9	9	7

Noseck et al, Applied Geochemistry, vol. 201, p. 106762-85

Solubility limiting phase (SLP), maximum concentrations [mol/kg water] and fraction of dominating species [%] calculated for uranium; n.c.: not used in calculations; n.i.d.: not in database