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Process understanding of radionuclide-colloid interaction with special emphasis on sorption reversibility

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Aim and Objectives

Aim:

- To establish if radionuclides are irreversibly bound by clay colloids (since slow dissociation will promote transport)

Objectives:

- Determining radionuclide distribution between different sized bentonite colloids by sequential ultrafiltration

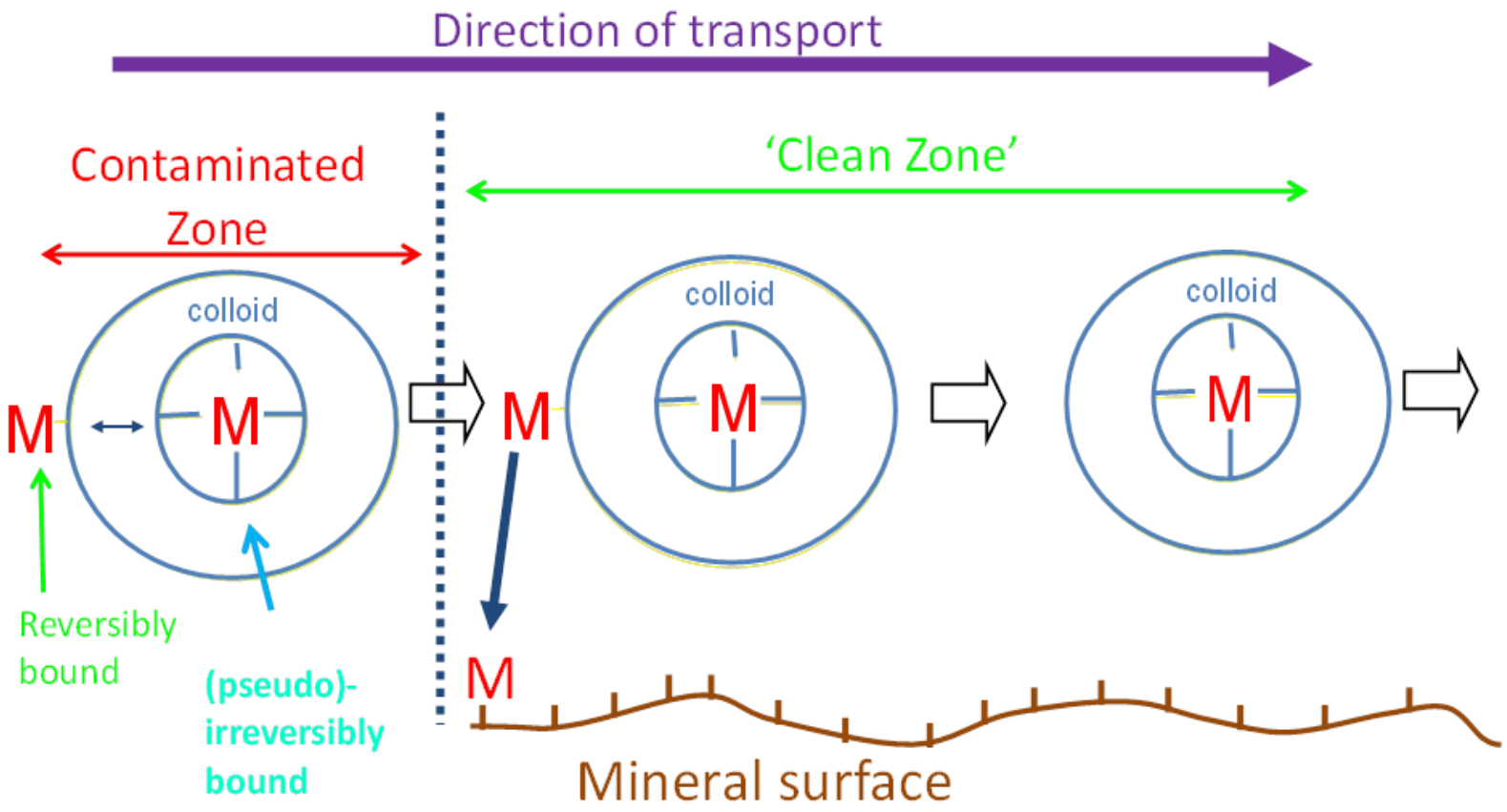
- Measuring dissociation kinetics for bulk and colloidal bentonite

Outline

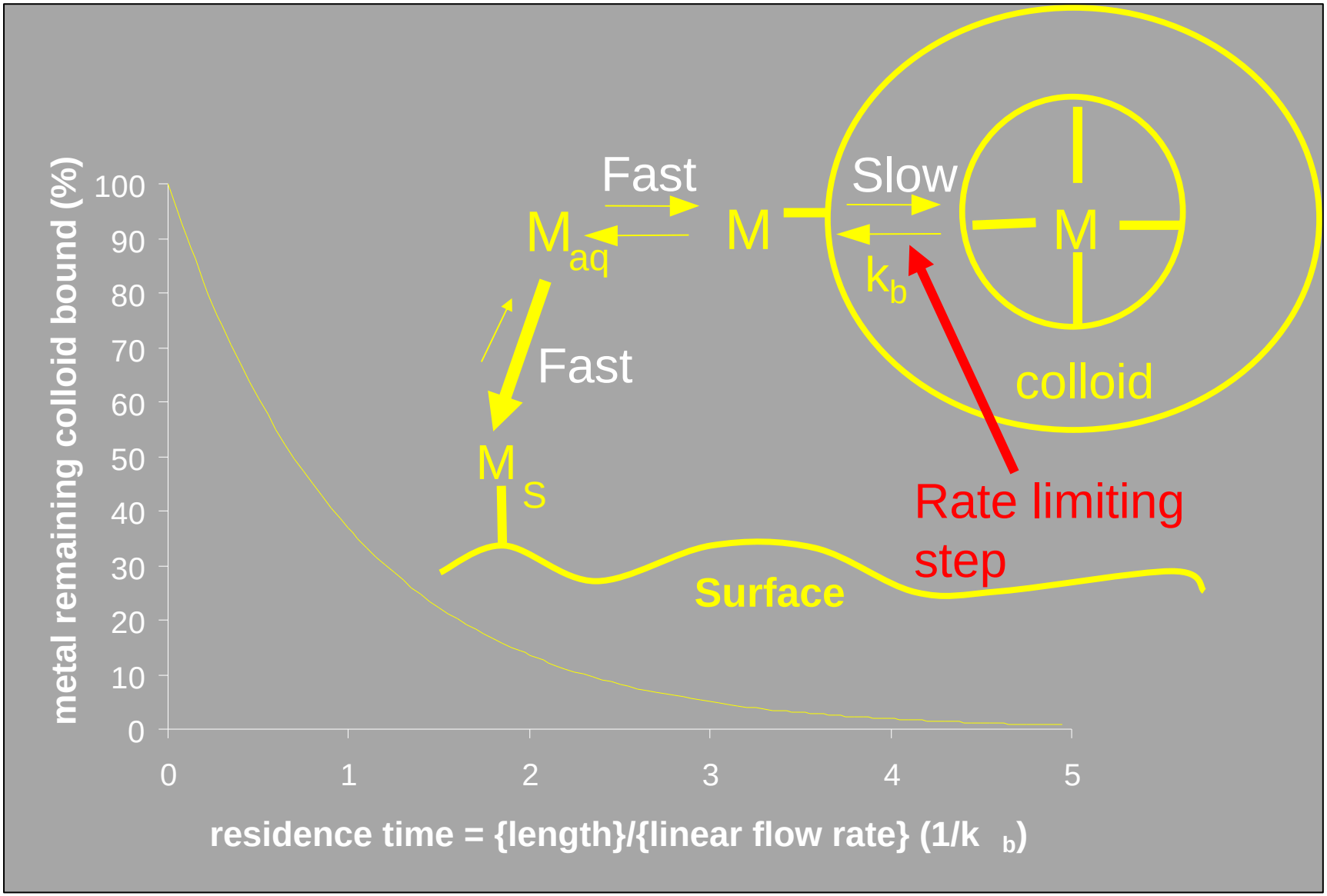
- Introduction to radionuclide dissociation from bulk and colloidal bentonite
- Materials and Methods
- Radionuclide interactions with bulk bentonite: U(VI) and Pu(III) bulk bentonite dissociation; Eu(III) uptake on bulk bentonite
- Colloid size distributions (Eu, U, Th, Am)
- Irreversibility in bentonite-RN interactions:
  - Eu/bentonite bulk and colloid systems
  - U/bentonite colloid systems
  - Th and Am/bentonite colloid system
- Conclusions

Radionuclide dissociation from bulk and colloidal bentonite

- Bentonite is a proposed backfill for a Geological Disposal Facility
- If bentonite colloids form, then they have the potential to act as a transport vector
- If radionuclide binding is reversible, then transport is not expected due to competition with surface binding sites, but (pseudo)-irreversibly bound (slowly dissociating) radionuclides could transport



Effect of dissociation rate constant (k_b) on transport



- Residence time of colloidal material in solution needs to be less than the half time of dissociation reaction; migration increases with reaction half-time

Materials and Methods

- Na-Wyoming bentonite used in this work
- All water was deionized (18 MΩ) and all reagents were analytical grade
- All experiments repeated in triplicate
- Bulk dissociation/uptake with humic acid: ^{237}U(IV), ^{237}Pu(III), ^{152}Eu(III)
- RN distribution between different sized bentonite colloids determined by sequential filtration with syringe filters and ultrafiltration membranes
- Bentonite/RN experiments performed with:
  - Bulk and colloid Eu dissociation: ^{152}Eu(III), 1 kBq
  - Colloid U dissociation: ^{232}U(IV), 15 kBq
  - Colloid Th dissociation: ^{228}Th(IV), 920 Bq
  - Colloid Am dissociation: ^{241}Am(III), 1 kBq
- Radionuclide was added to the bentonite and allowed to pre-equilibrate, before EDTA (bulk) or Dowex cation exchange resin (colloids) were used to remove the radionuclide and determine the dissociation rate constants

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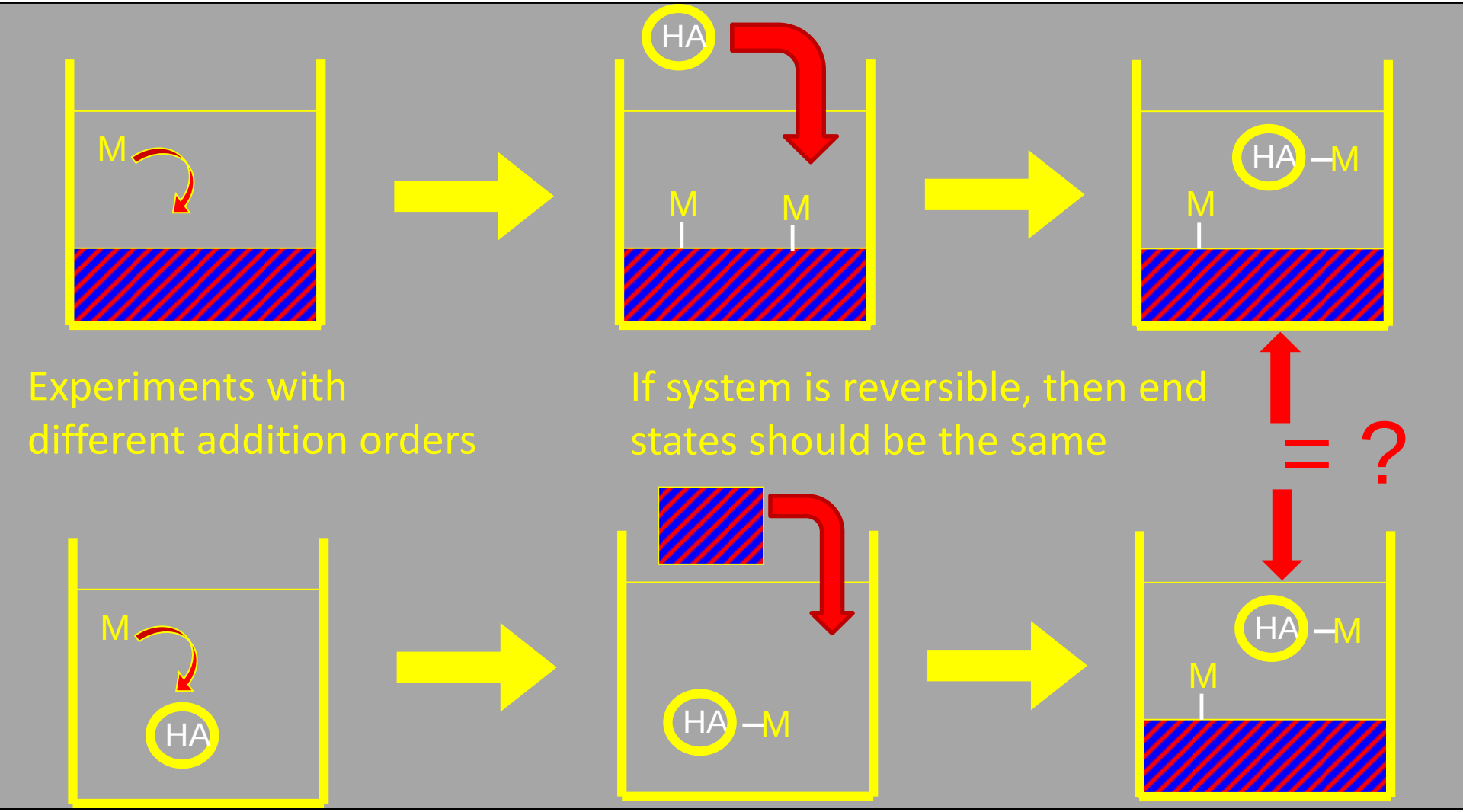
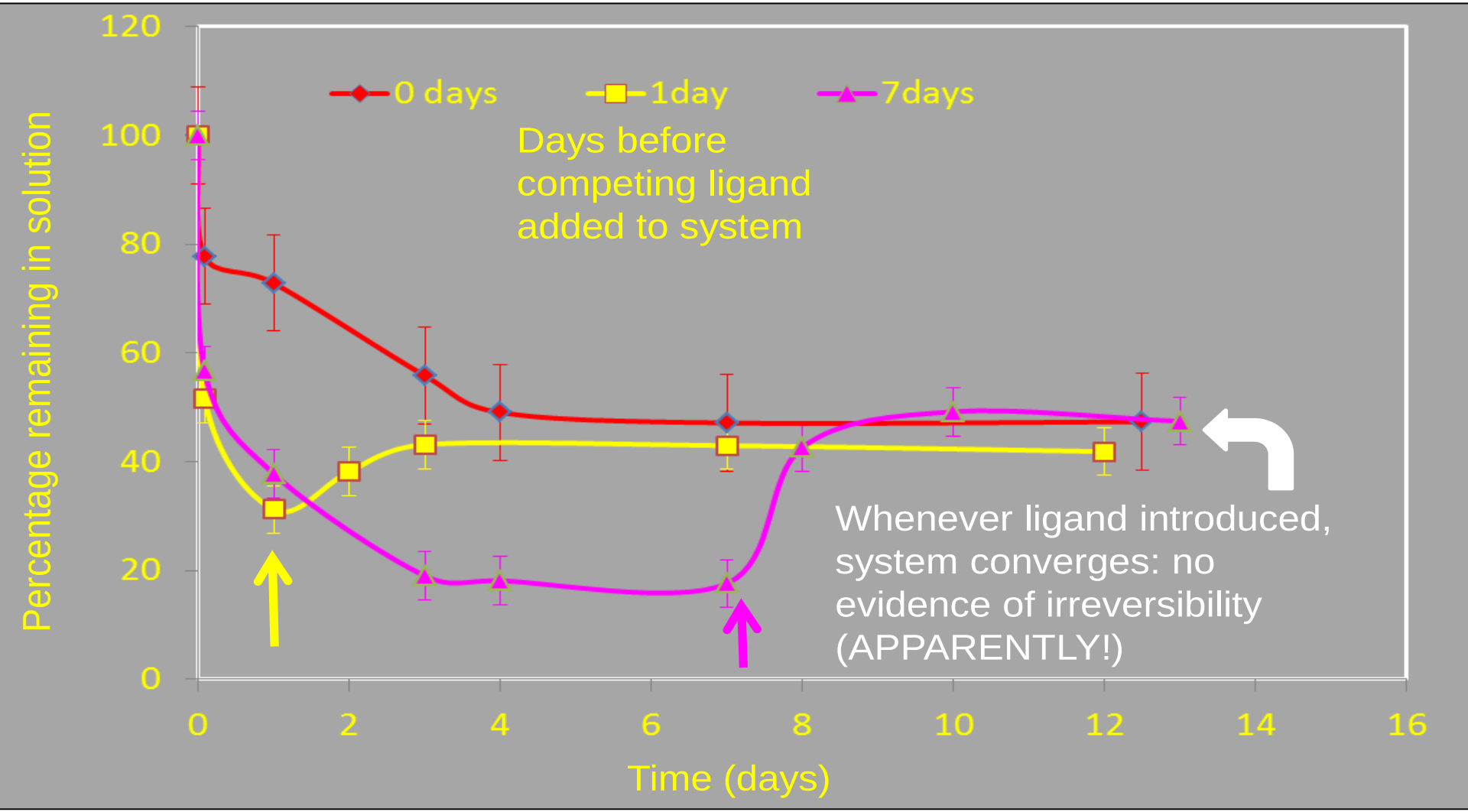
Radionuclide interactions with bulk bentonite: Reversibility in Ternary Systems



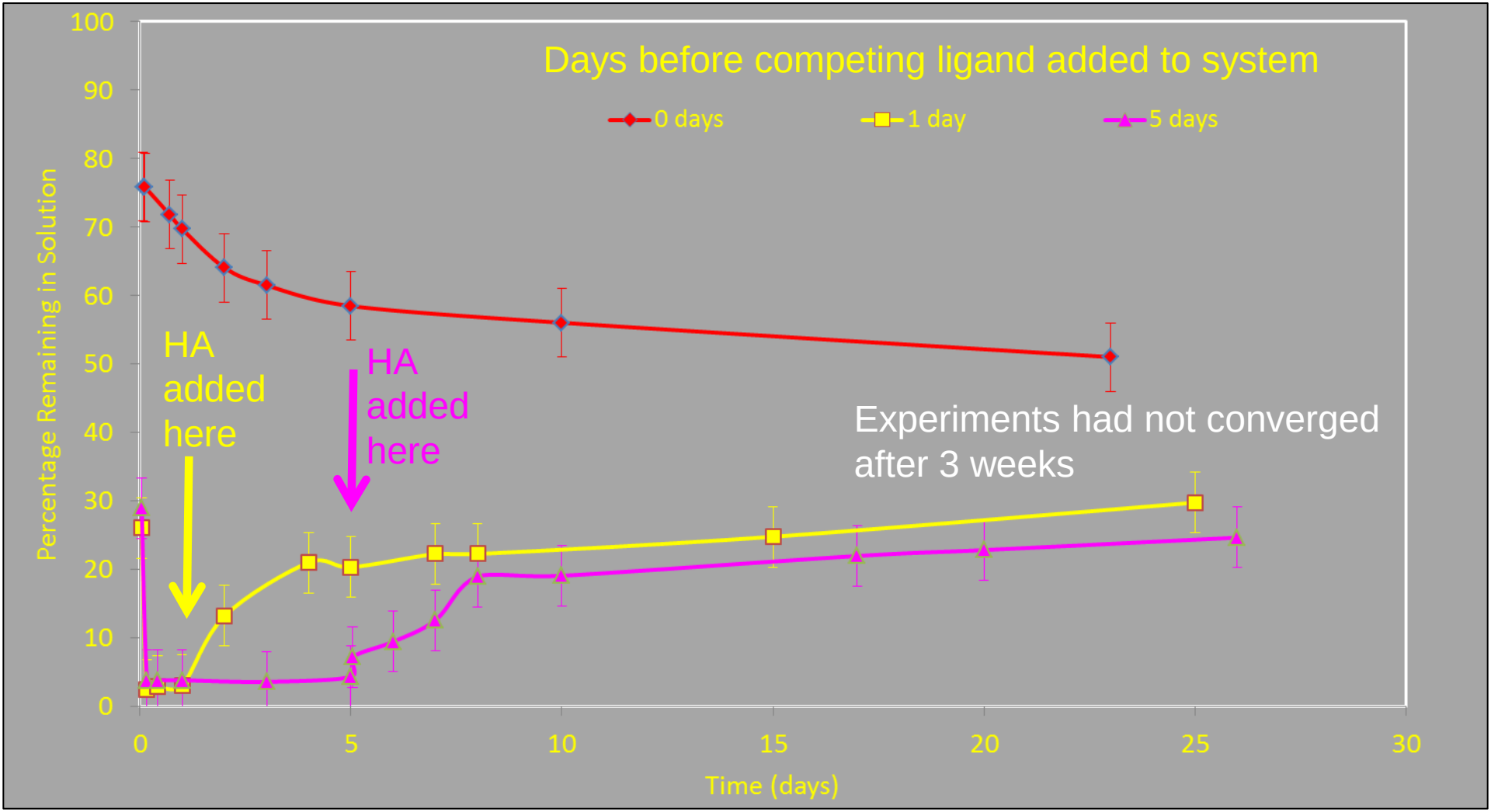
- 'Reversible' systems should be insensitive to order of addition; time taken for systems to recover is an indication of importance of kinetics.

^{237}U(VI) bulk bentonite dissociation



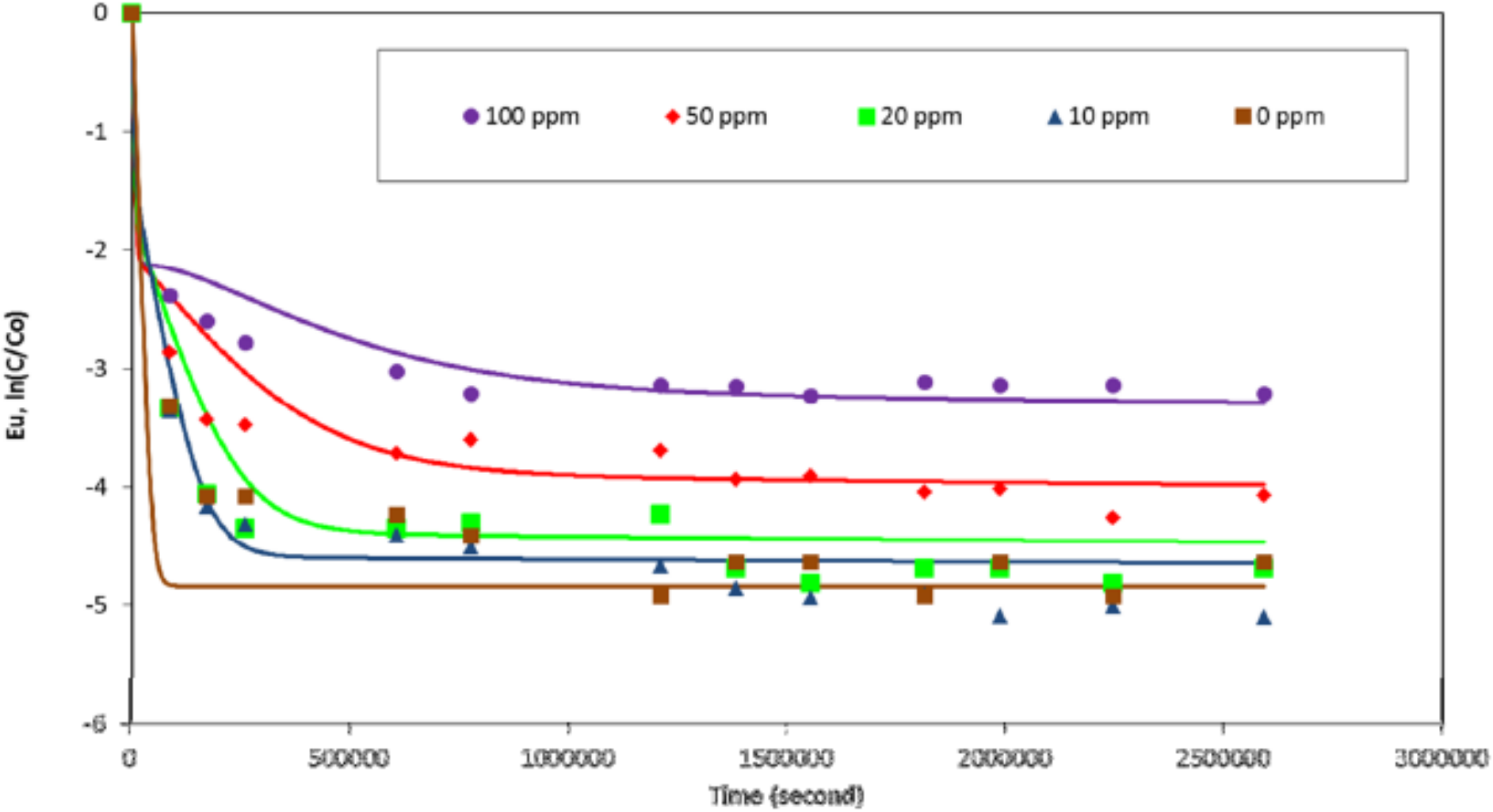
- Slow kinetics of U (10^{-10} M) distribution between supernatant and solid phase in the presence of HA (equilibrium reached after ~4 days)
- No evidence for irreversibility, or even slow dissociation for U(VI)

^{237}Pu(III) bulk bentonite dissociation



- Dissociation of Pu (10^{-11} M) from bentonite much slower (equilibrium not reached after 25 days)
- Evidence of slow dissociation but no direct evidence for irreversibility

^{152}Eu(III) bulk bentonite uptake



- Slow uptake kinetics of Eu (10^{-10} M) even in absence of a competing ligand; slow component ~2.5 % of total bound
- Reversible → irreversible

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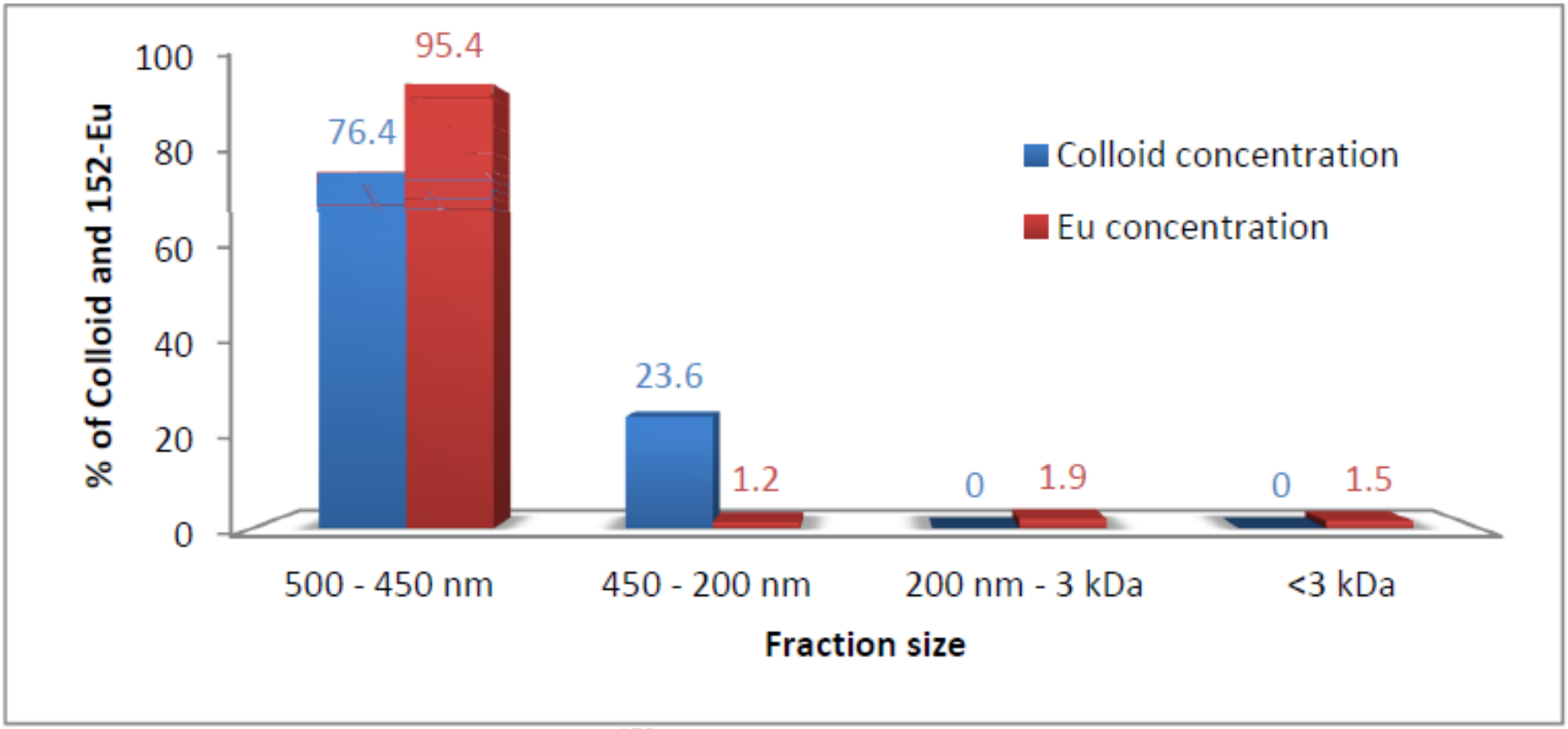
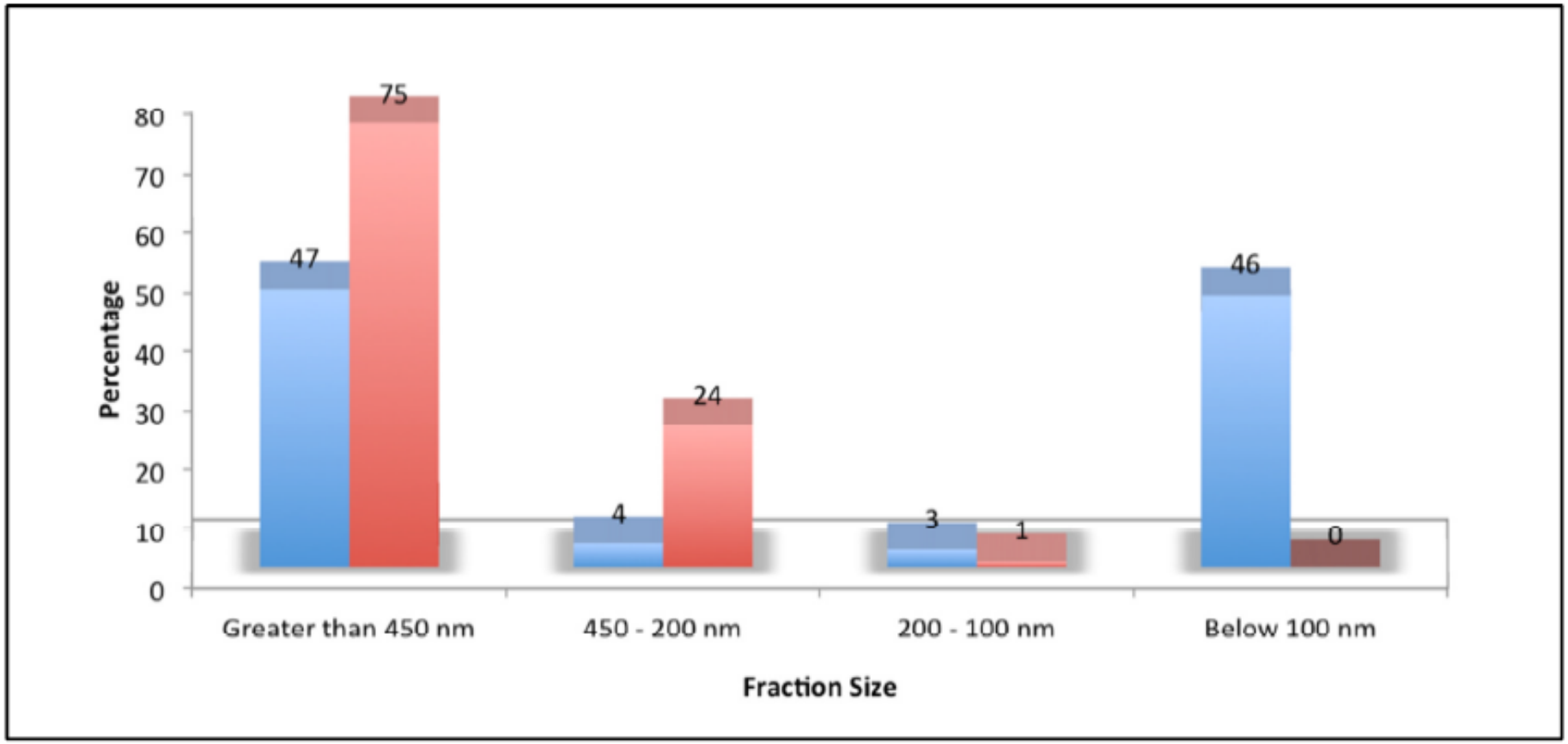
Colloid size distribution: Colloid/Eu(III) concentrations in each size fraction



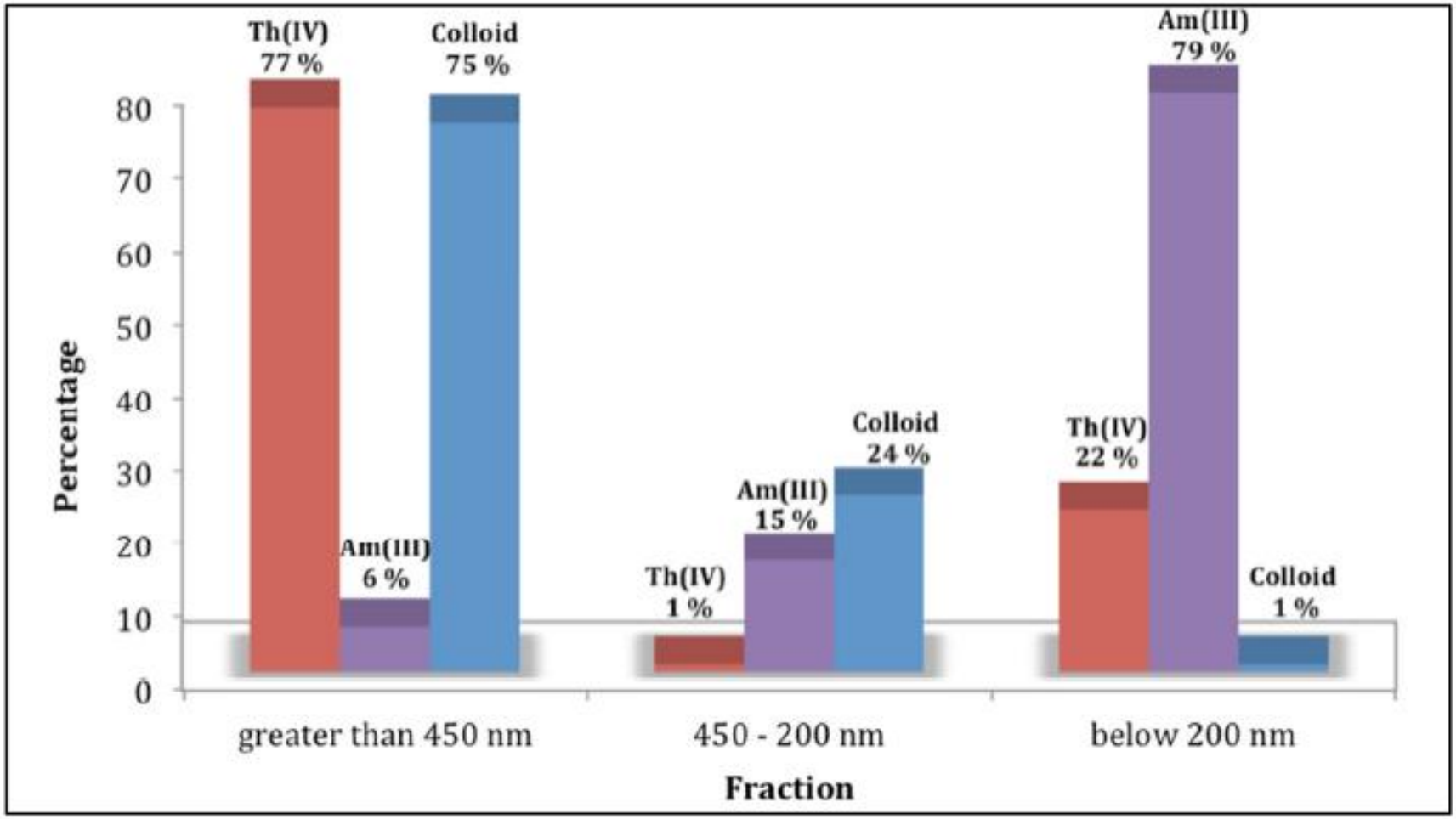
- Vast majority of bentonite colloids were in nominal size fractions > 200 nm
- > 98.5 % of the Eu is colloid associated with only 1.5 % remaining in true solution fraction (<3 kDa)

Colloid size distribution: Colloid/U(VI) concentrations in each size fraction



- 75% of bentonite colloids were in nominal size fractions > 450 nm
- In absence of bentonite colloids, no U(VI) is found in >100 nm fraction, therefore ~54 % of U(VI) is bentonite colloid associated.
- 46 % in <100 nm fraction is not bentonite colloid associated

Colloid size distribution: Colloid/Th(IV) and Am(III) concentrations in each size fraction



- 75% of bentonite colloids were in nominal size fractions > 450 nm
- 78% of Th(IV) in > 200 nm fraction, 22% Th(IV) not bentonite colloid associated
- Only 21% of Am(III) is bentonite colloid associated with 79% in <200 nm fraction

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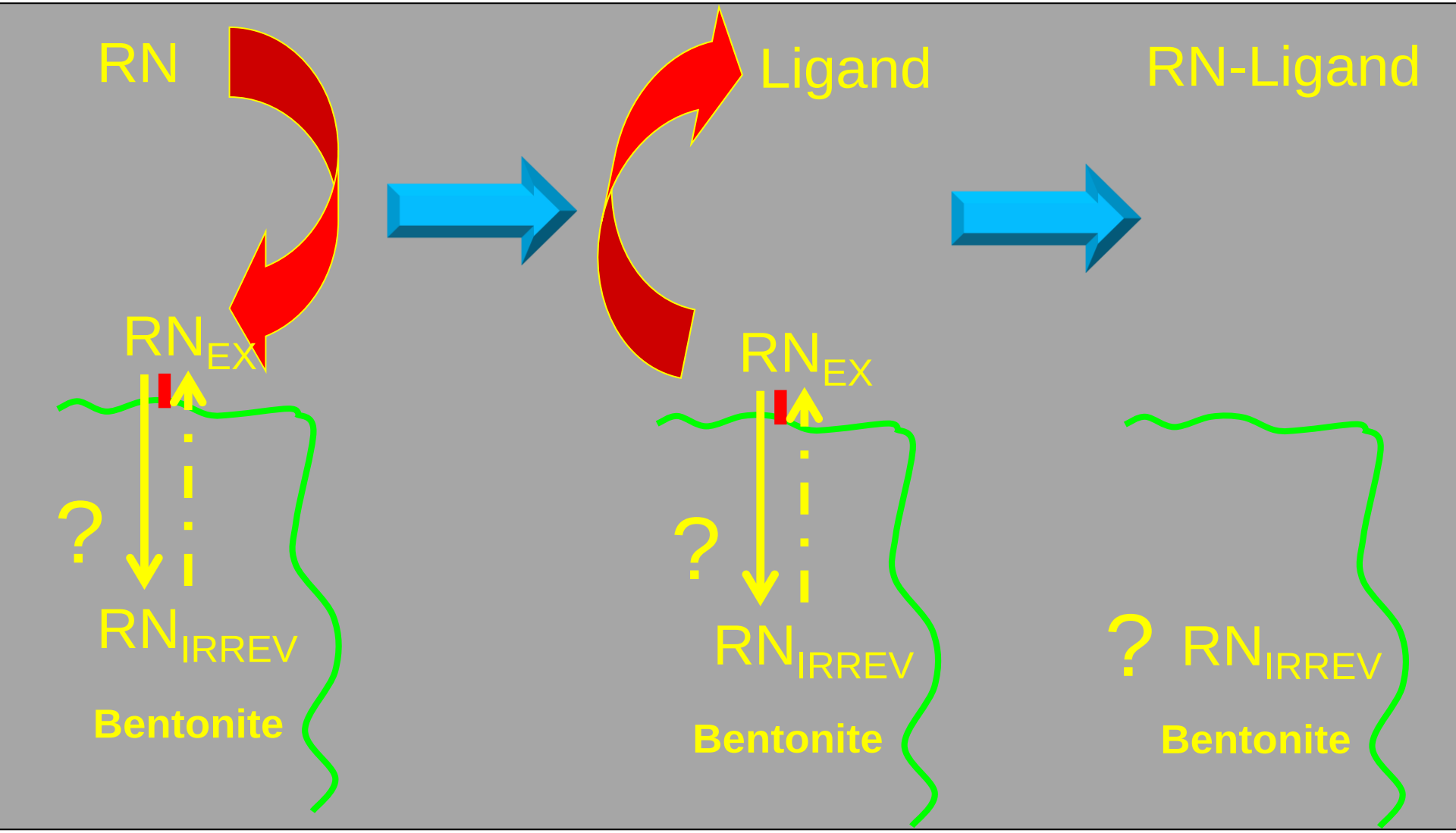
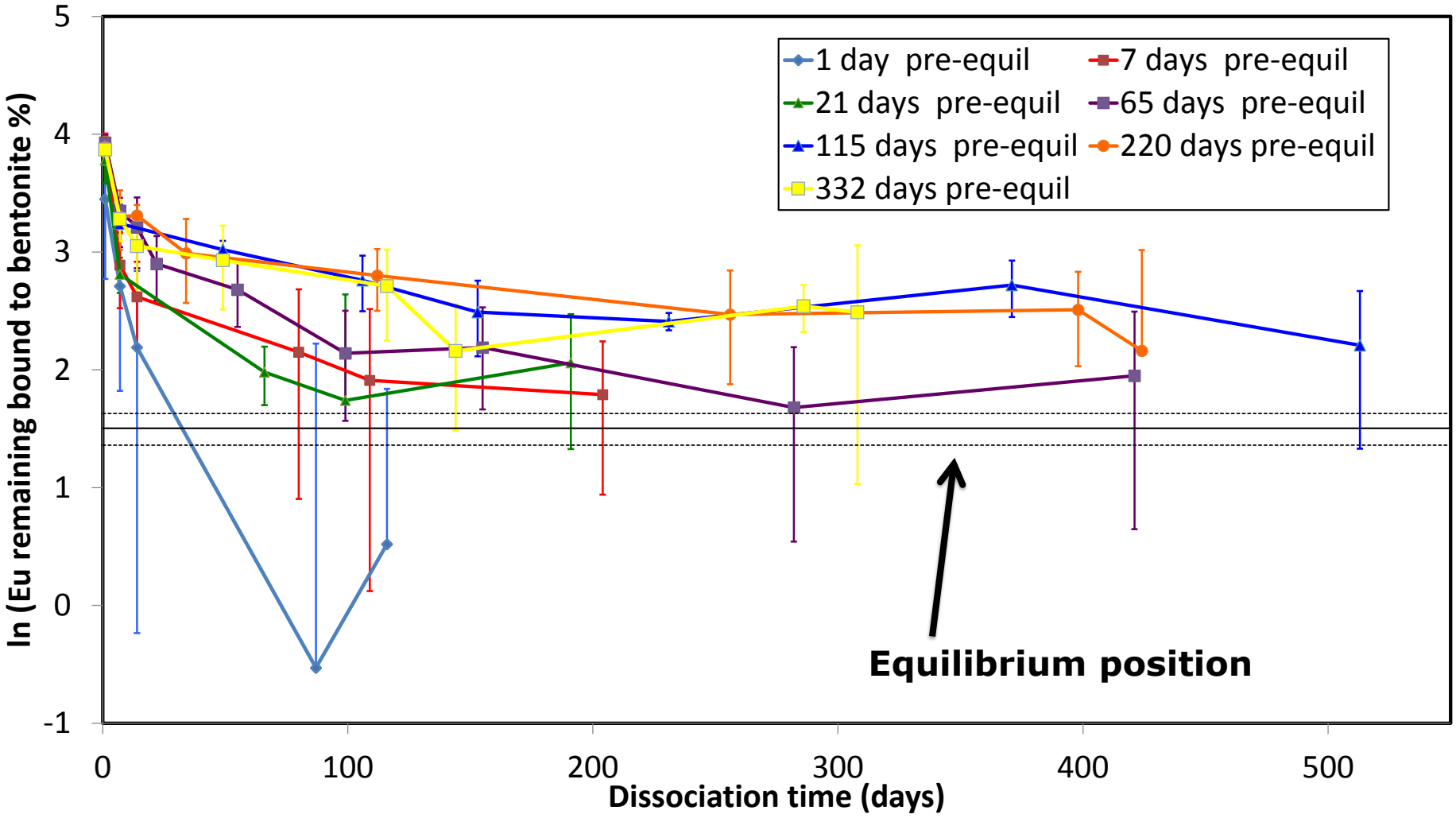
Irreversibility: Ligand Competition



- Using ligand competition to test for irreversibility in bentonite-RN interactions

^{152}Eu(III) bulk bentonite dissociation



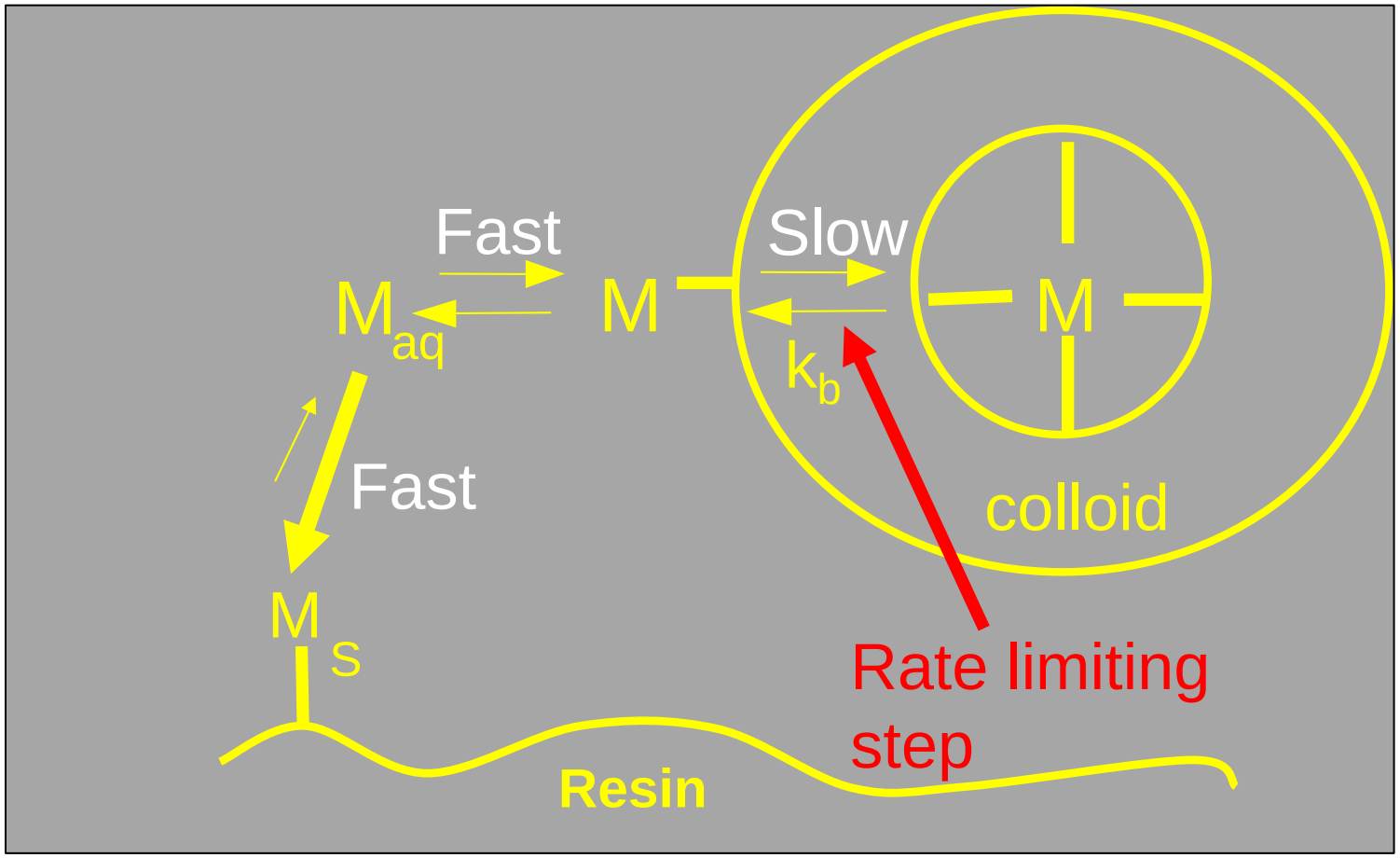
- Dissociation rate constant does not depend upon pre-equilibration time (beyond 1 week)
- Small increase in amount slowly dissociating with pre-equilibration time

^{152}Eu(III) bulk bentonite dissociation

Pre-equilibration time (days)	Dissociation rate constant (s^{-1})	Amount of Eu in fraction (%)	τ (days)
7	1.01×10^{-7} ($\pm 6.23 \times 10^{-8}$)	17.3 (+3.1; -2.9)	79
21	4.19×10^{-8} ($\pm 8.51 \times 10^{-8}$)	11.9 (+25.2; -4.8)	192
65	3.93×10^{-8} ($\pm 1.35 \times 10^{-8}$)	19.3 (+5.4; -3.5)	204
115	2.17×10^{-8} ($\pm 1.70 \times 10^{-8}$)	20.5 (+8.6; -6.0)	370
220	2.61×10^{-8} ($\pm 1.14 \times 10^{-8}$)	24.3 (+6.7; -5.2)	308
332	2.56×10^{-8} ($\pm 2.87 \times 10^{-8}$)	20.7 (+11.2; -7.3)	314

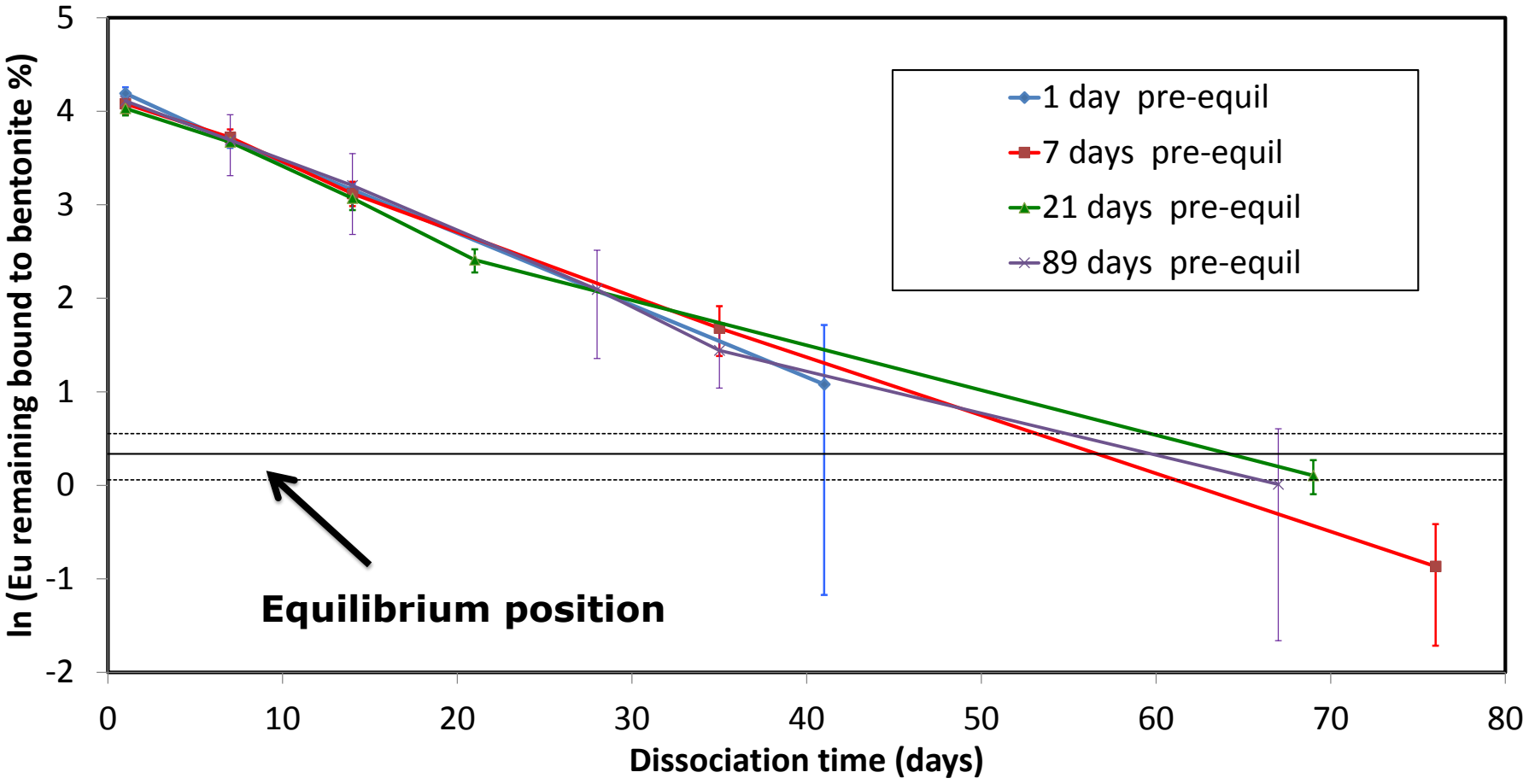
- A fraction of the Eu was released instantaneously (30 - 50 %), but a significant amount remained bound. With time, the amount of Eu(III) retained by the bentonite reduced
- Eventually, the amount of Eu(III) remaining bound to the bentonite was within error of that when EDTA was present prior to contact (equilibrium position)

Measuring Colloid Dissociation Rates



- For colloids, no phase separation therefore can't use competing ligands; cation exchange resin used to remove radionuclides from bentonite colloids

^{152}Eu(III) colloid bentonite dissociation



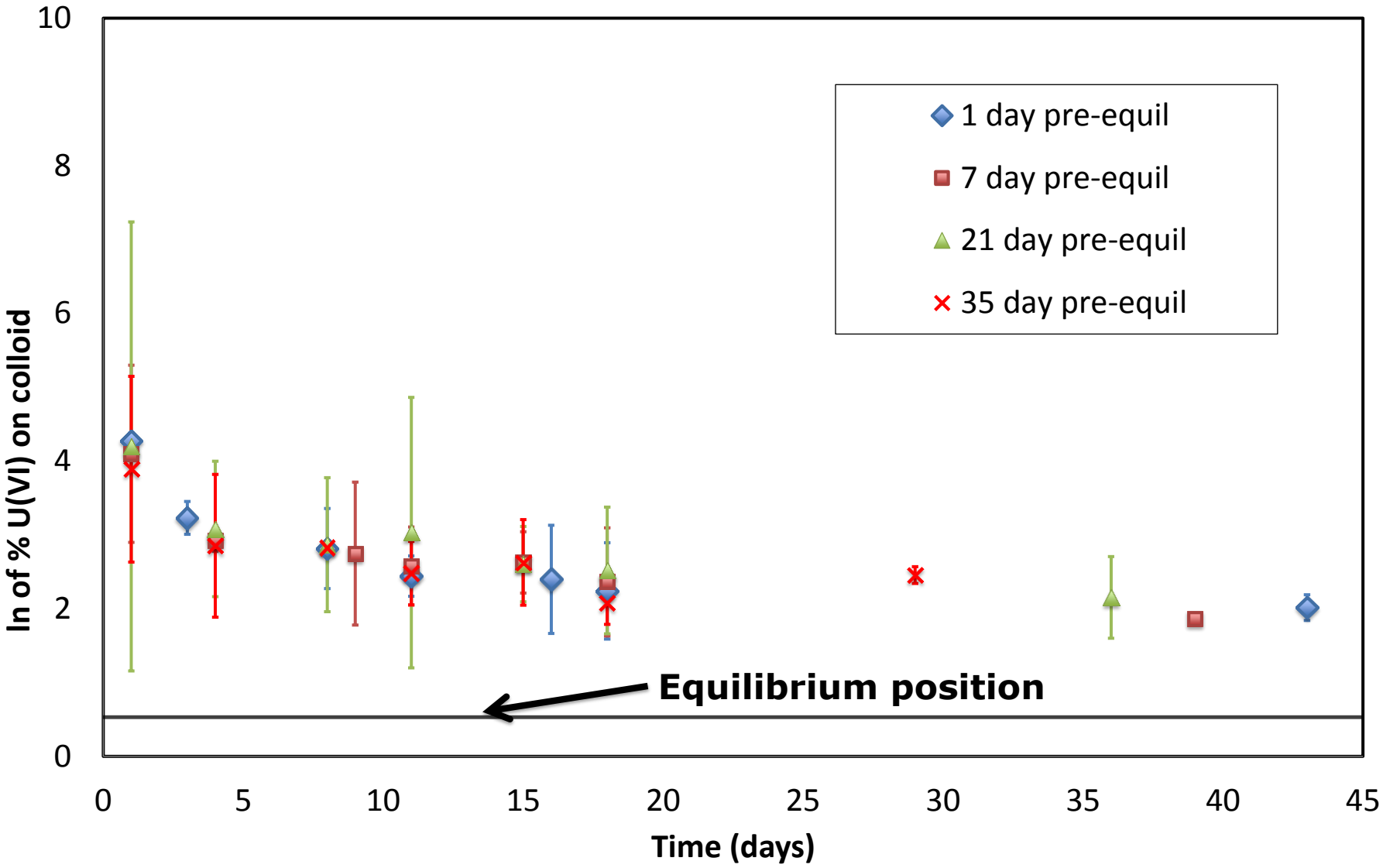
- Evidence for slow release of Eu(III) from the bentonite with all systems heading towards equilibrium.

^{152}Eu(III) colloid bentonite dissociation

Pre-equilibration time (days)	Dissociation rate constant (s^{-1})	Amount of Eu in fraction (%)	τ (days)
1	8.97×10^{-7} ($\pm 2.27 \times 10^{-8}$)	69.8 (+3.1; -2.9)	8.94
7	7.66×10^{-7} ($\pm 5.63 \times 10^{-8}$)	60.8 (+12.4; -10.3)	10.5
21	9.47×10^{-7} ($\pm 2.63 \times 10^{-7}$)	64.9 (+22; -17)	8.47
89	9.04×10^{-7} ($\pm 2.55 \times 10^{-8}$)	69.2 (+11; -9.5)	8.87

- For the colloids, more Eu was found in the slowly dissociating fraction (60 – 70 %), but the first order dissociation rate constant was faster (approximately an order of magnitude), with an average rate constant of 8.8×10^{-7} s^{-1} and a range of 7.7×10^{-7} – 9.5×10^{-7} s^{-1}
- Unlike the bulk system, dissociation was characterised by a single rate constant

^{232}U(VI) colloid bentonite dissociation

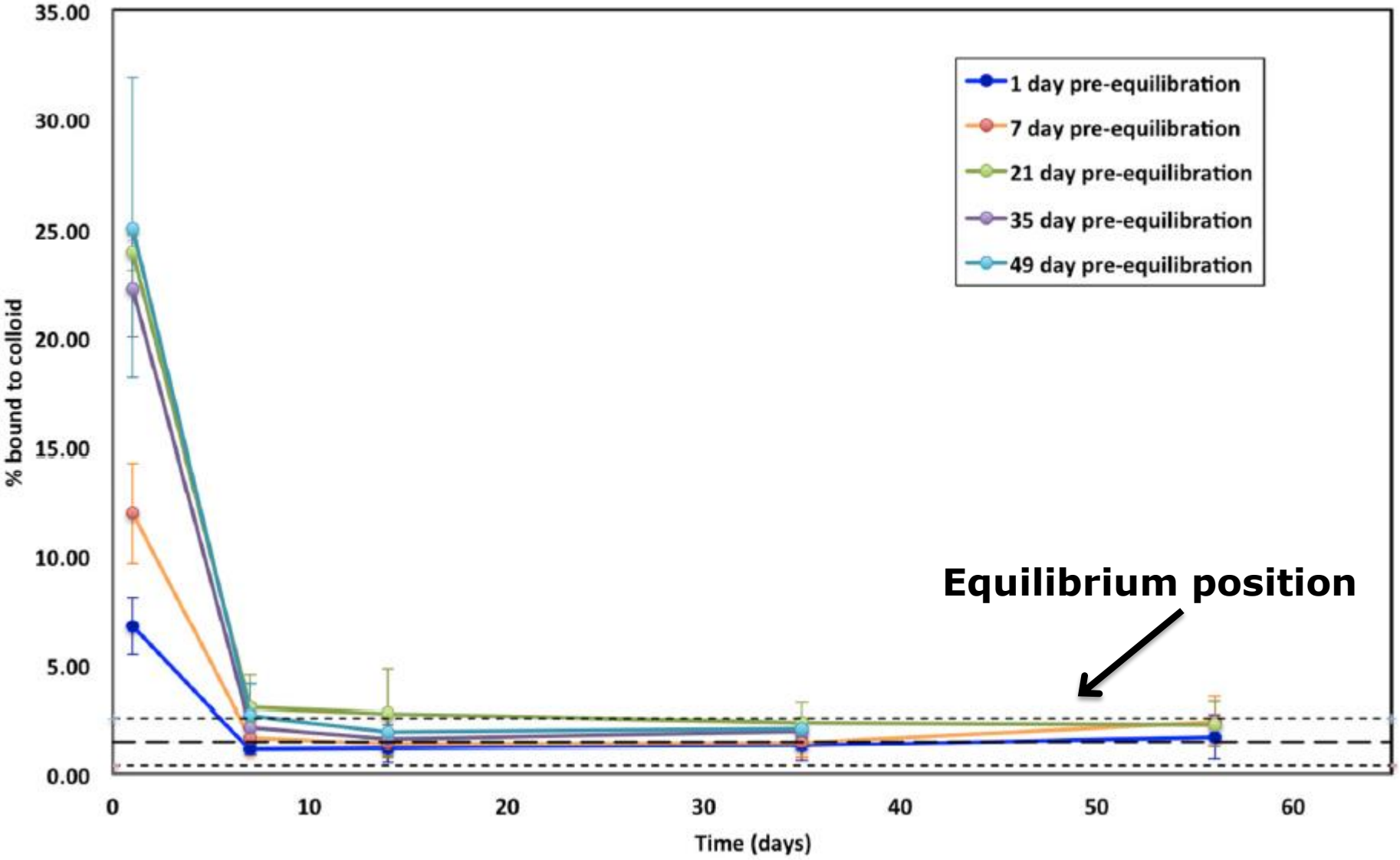


^{232}U(VI) colloid bentonite dissociation

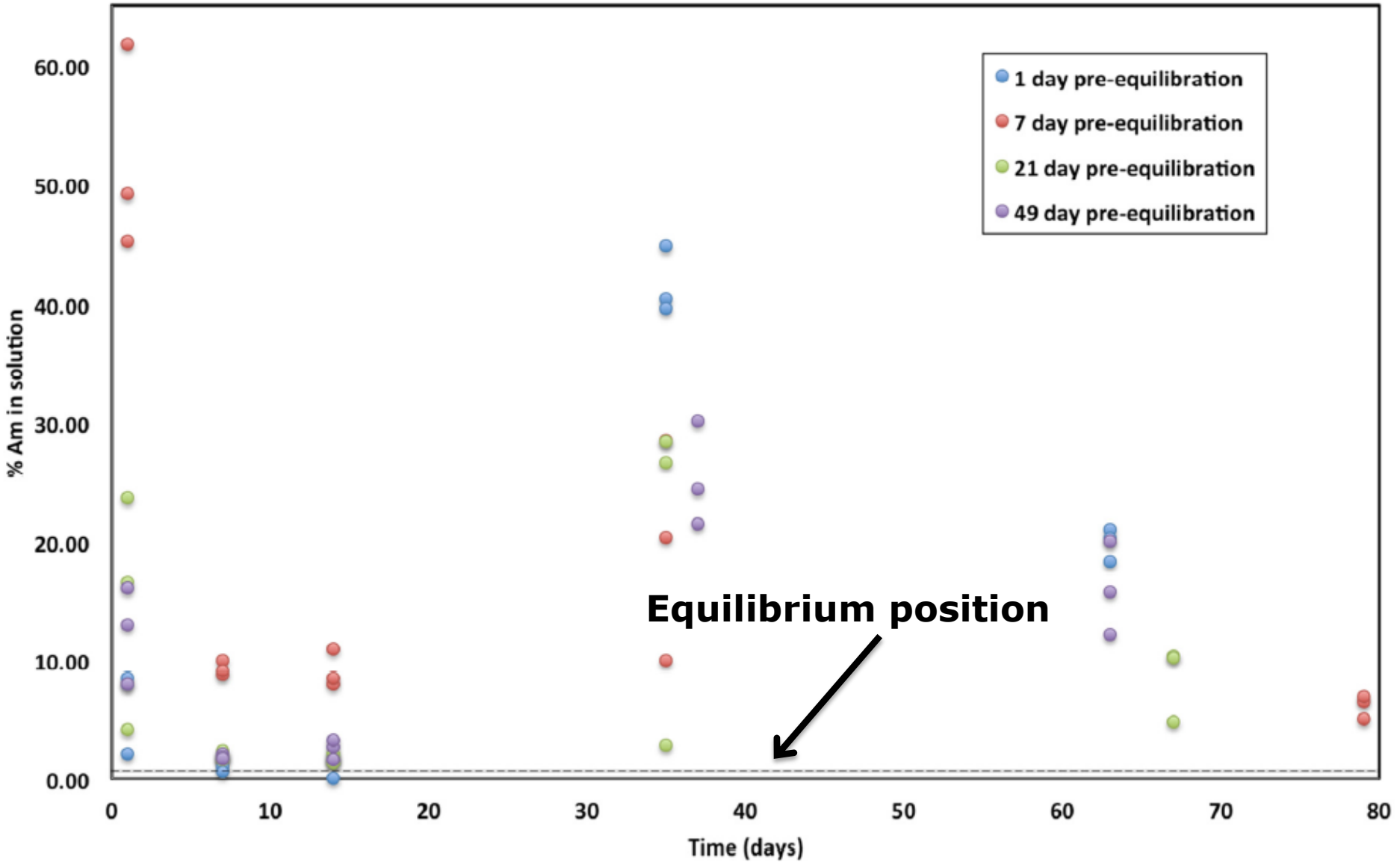
Pre-equilibration time (days)	Dissociation rate constant (s^{-1})	Amount of Eu in fraction (%)	τ (days)
1	7.8×10^{-7} ($\pm$ 5.8×10^{-7})	27.9 (+24.3; -13.0)	11
7	3.1×10^{-7} ($\pm$ 1.6×10^{-6})	20.4 (+69.7; -15.8)	25.8
21	4.6×10^{-7} ($\pm$ 2.4×10^{-7})	24.9 (+7.2; -5.6)	17.4
35	6.9×10^{-7} ($\pm$ 9.0×10^{-7})	23.7 (+33.8; -14.0)	11.7

- Even before the addition of the competing sink, only ~ 50% of the uranium was associated with the colloids.
- A fraction of the U(VI) in solution was available for release instantaneously, which was consistent with the amount of U that was not colloid associated.
- With time, the amount of U(VI) retained by the bentonite colloid reduced further, with a first order dissociation rate constant of 5.6 x 10^{-7} s^{-1} (values in the range of 3.1 x 10^{-7} – 7.3 x 10^{-7} s^{-1}).
- As for Eu(III), the pre-equilibration time of the ^{232}U(VI) with the colloids (1 – 35 days) did not affect the rate of dissociation

^{228}Th(VI) colloid bentonite dissociation



^{241}Am(III) colloid bentonite dissociation



Conclusions

- Although slow dissociation was observed for Eu(III) and U(VI) from bulk and colloidal bentonite, in no case was there convincing evidence for 'irreversible binding' of the radionuclides by the clay
- Hence, given sufficient time, the radionuclides will dissociate. Therefore, whether or not the bentonite colloids will promote transport will depend upon the transport residence time
- Dissociation of Eu(III) from bulk bentonite with time is not a single gradient; there is rapid (instantaneous) removal then a slowly dissociating fraction with two species (not surprising as bulk bentonite has many accessory mineral phases)
- Beyond the initial rapid dissociation of Eu(III) from bentonite colloids, only a single rate constant is observed (behaves much more like single phase montmorillonite)
- Therefore, cannot extrapolate colloid behaviour from bulk measurements as predicted transport residence time would be much higher
- Am(III)/Th(IV) results difficult to interpret, although data suggest that Eu(III) may not be a good analogue for Am(III)

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The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement number 295487, The BELBaR project.

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