MANCHESTER 1824

The University of Manchester

BELBaR

Reversibility of Bentonite-Radionuclide Interactions

Nick Sherriff,[1] Peter Ivanov,[1] Tamara Griffiths,[1] Gospodin Bozhikov,[2] Serguei Dmitriev,[2] Kath Morris[1] and Nick D. Bryan[1]

[1] University of Manchester, Manchester M13 9PL, UK
[2] Flerov Laboratory of Nuclear Reactions, JINR, 141980 Dubna, Russia

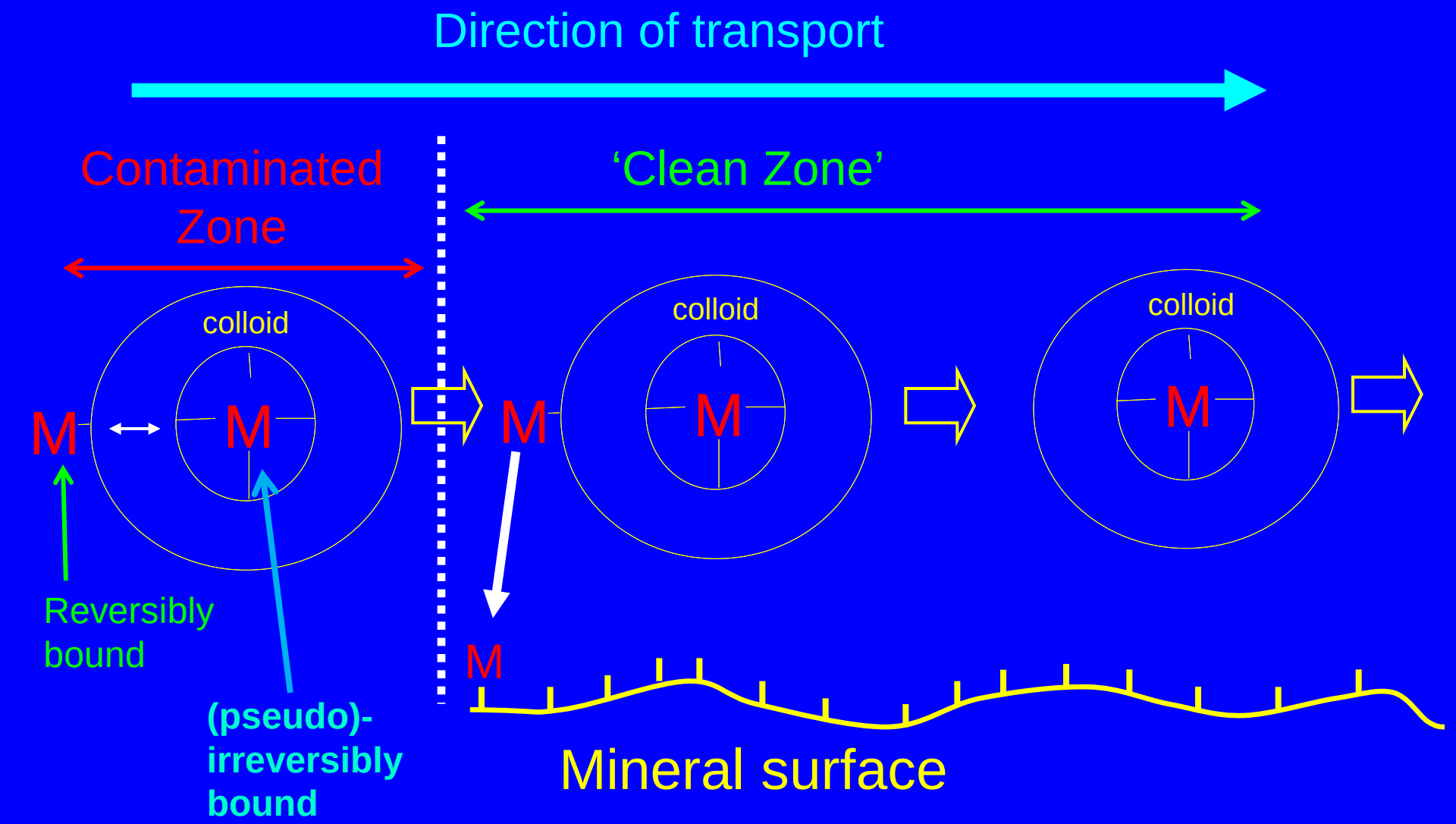
Aim of our work

Is there irreversible radionuclide binding by clay colloids (since slow dissociation will promote transport)?

Current Work:

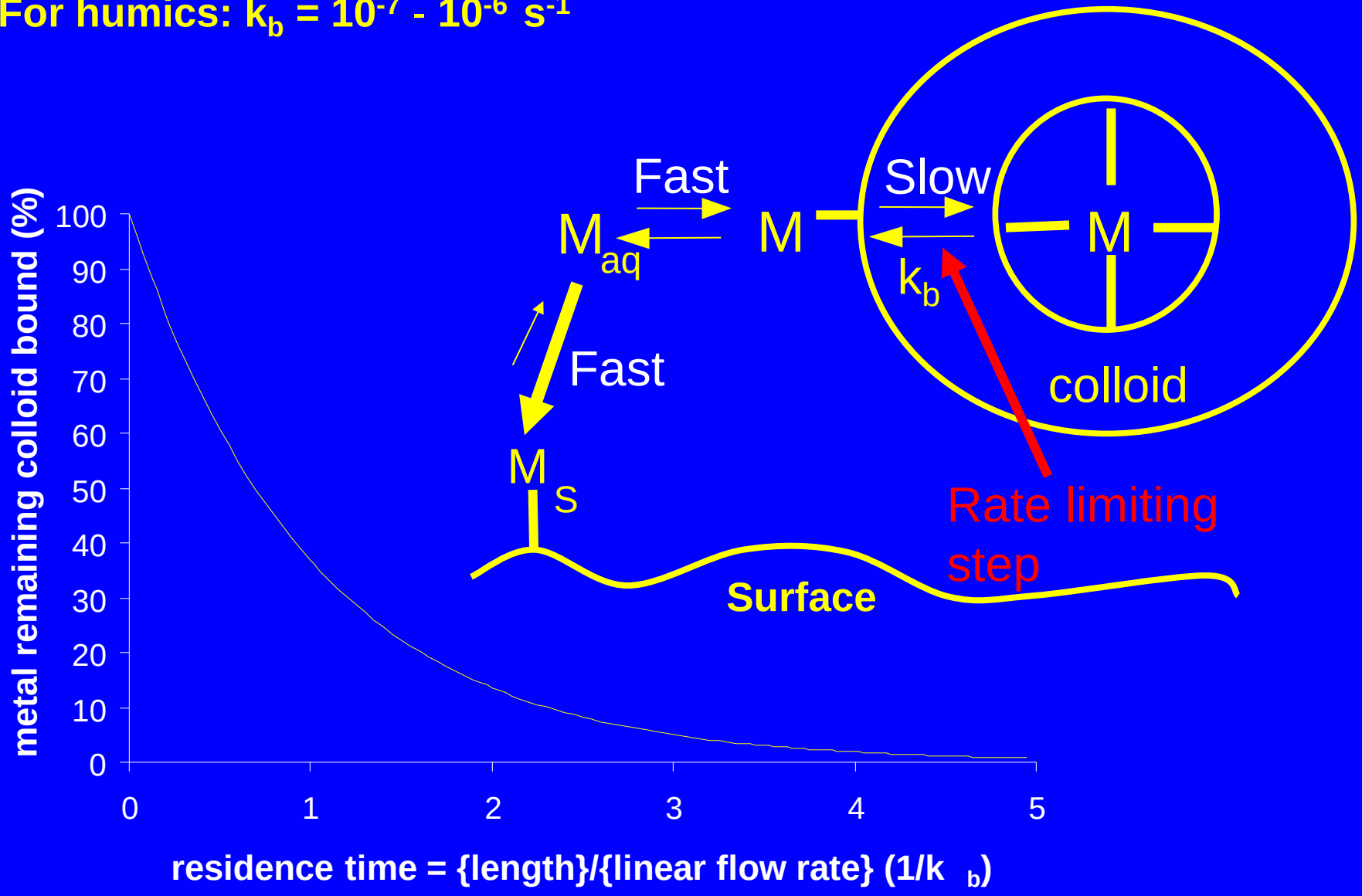
1. Developing colloidal solutions and determining radionuclide distributions between different size colloids.
2. Testing for irreversibility with bulk material (This Presentation):
    - Easier to detect irreversibility
    - Will show whether irreversibility is likely/possible with colloids.

Why does ‘irreversible’ binding matter



Effect of dissociation rate constant on transport

For humics: $k_b = 10^{-7} - 10^{-6}\ s^{-1}$



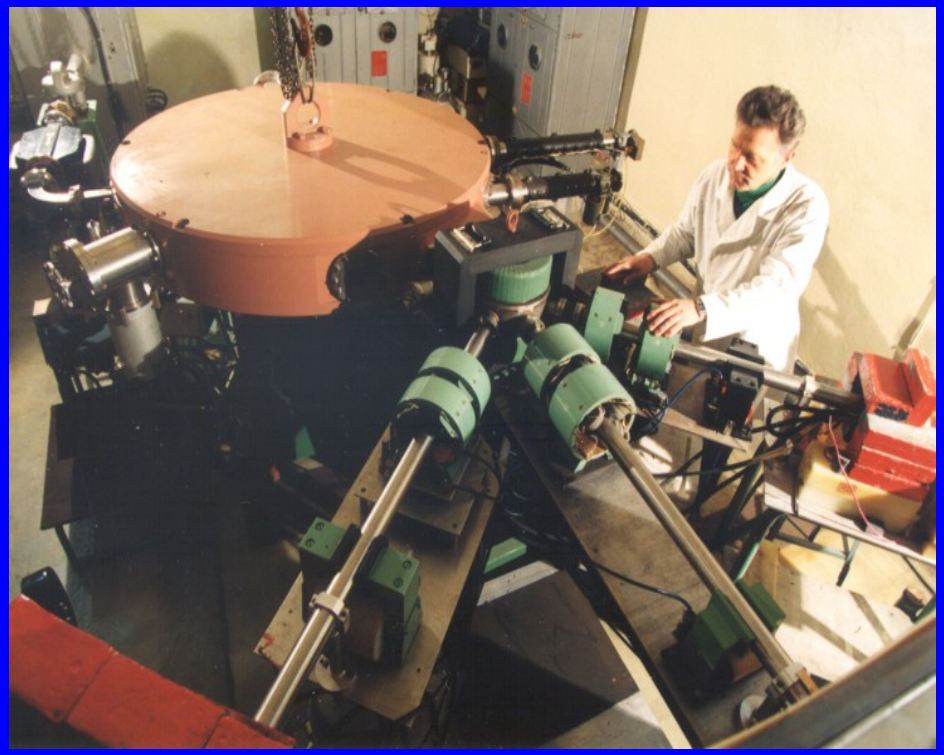
^{237}U Production

$T_{1/2}$ = 6.75 d; E_γ = 59.54 keV (34.5 %); 208.00 keV (21.2 %)

E_β endpoint = 237.25 keV (51 %); 251.06 keV (42 %)

^{238}U(VI) (γ, n) ^{237}U(III / IV)

MT-25 Electron Accelerator
E_γ = 25 MeV
Beam current: 15 µA
Target: 11 mg $^{238}UO_2(NO_3)_2$
Irradiation time: 5h
Reaction yield: 49.5 MBq / 1 mg ^{238}U



$[U]_{STOCK} = 8.6x10^{-10}$ M

$[^{237}U] = 10^{-13}$ M;

$[^{238}U] = 8.6x10^{-10}$ M

^{237}U separation from ^{238}U and FPs

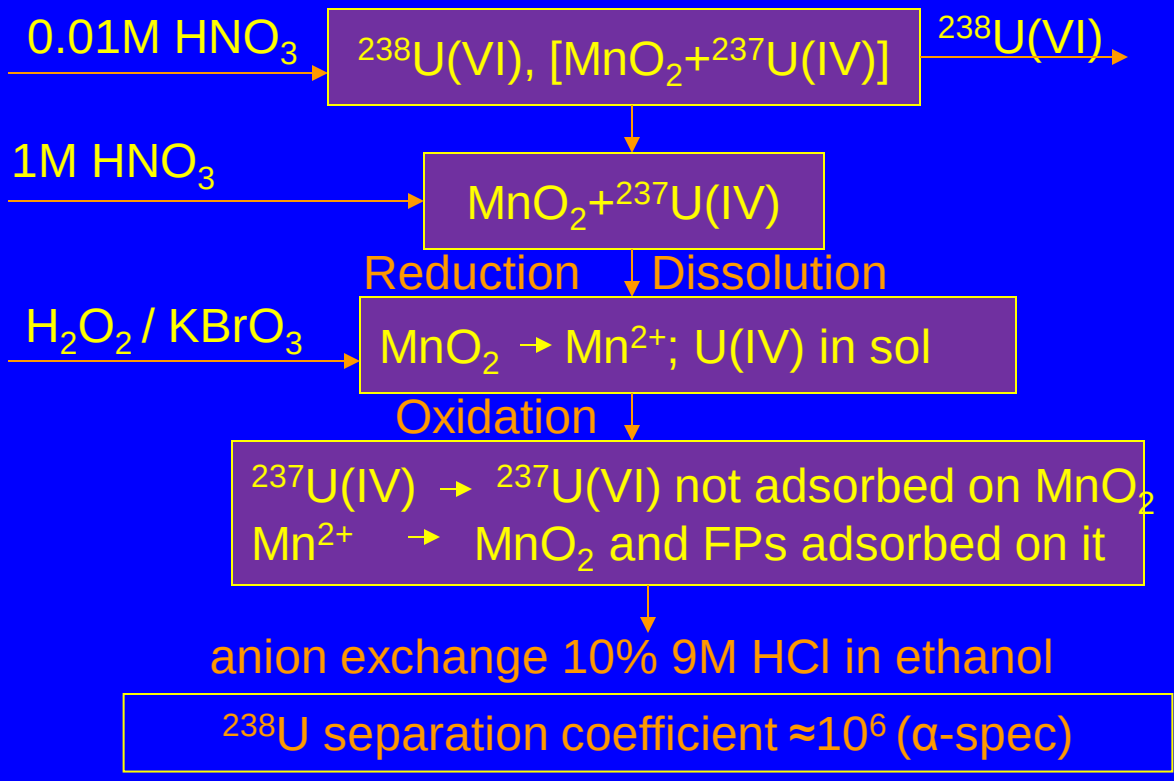
$^{238}U(VI)$ (γ, n) $^{237}U(III, IV)$

Recoil nuclei method:

Target material: $^{238}UO_2(NO_3)_2 + MnO_2$

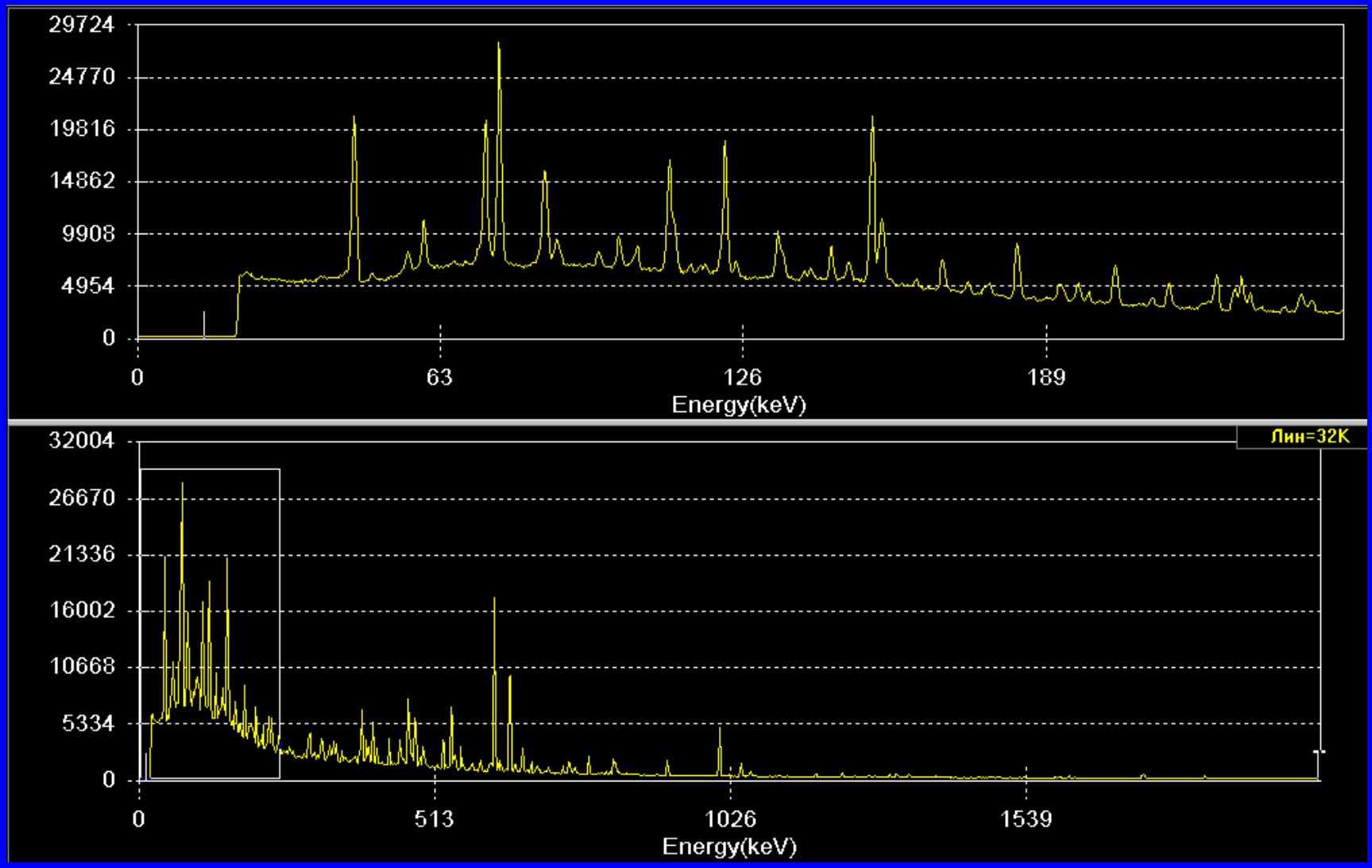
$^{237}U(III/IV)$ is sorbed onto MnO_2

(recoil nuclei collection); U(VI) has negligible sorption onto MnO_2.

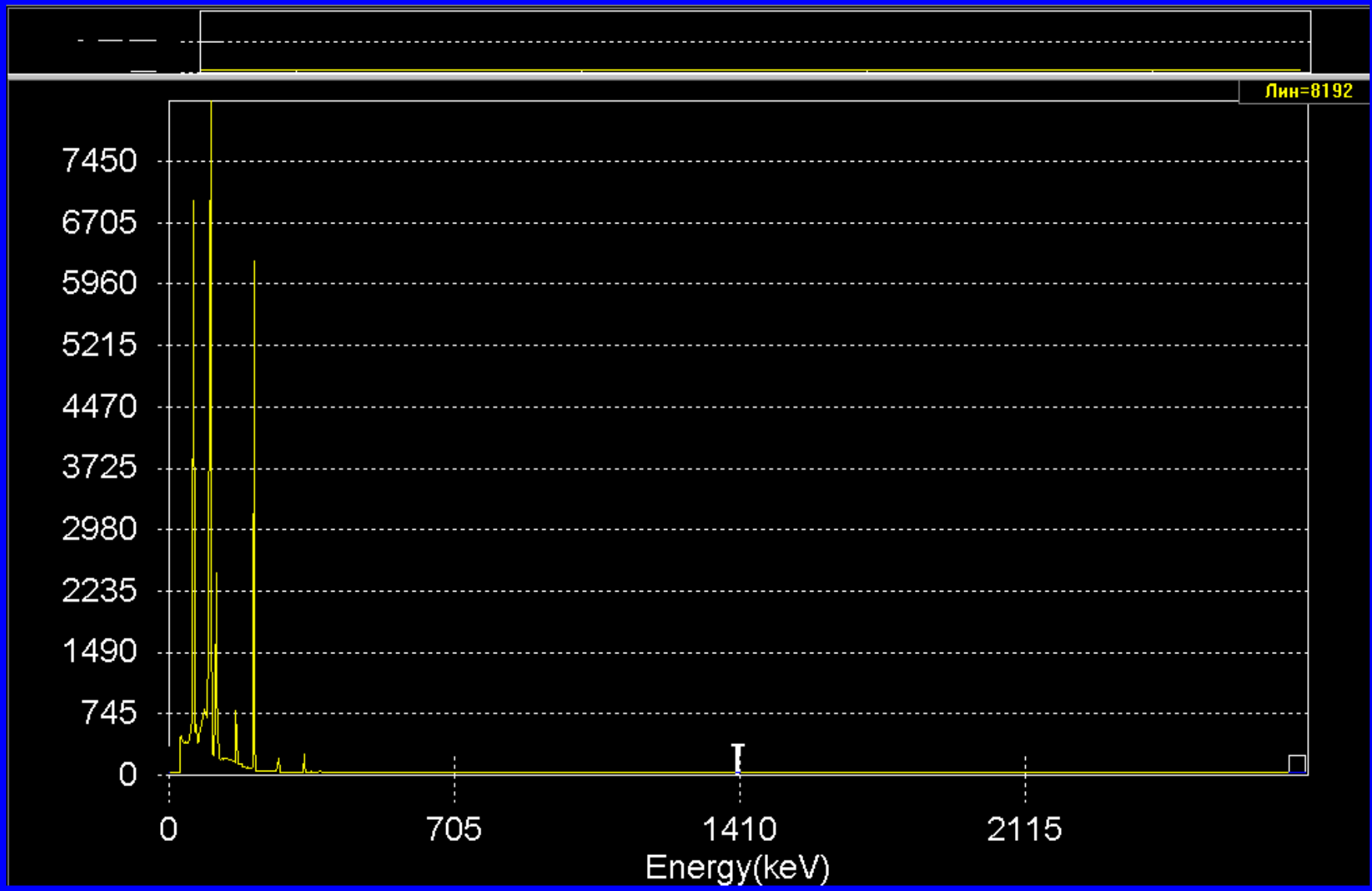


FP

^{91}Sr, ^{91m}Y, $^{95,97}Zr$, $^{95,97}Nb$, ^{99}Mo, ^{99m}Tc, ^{103}Ru, ^{105}Rh, ^{131}I, ^{132}Cs, ^{132}Te, ^{140}La, ^{140}Ba, $^{141,143}Ce$, ^{147}Nd



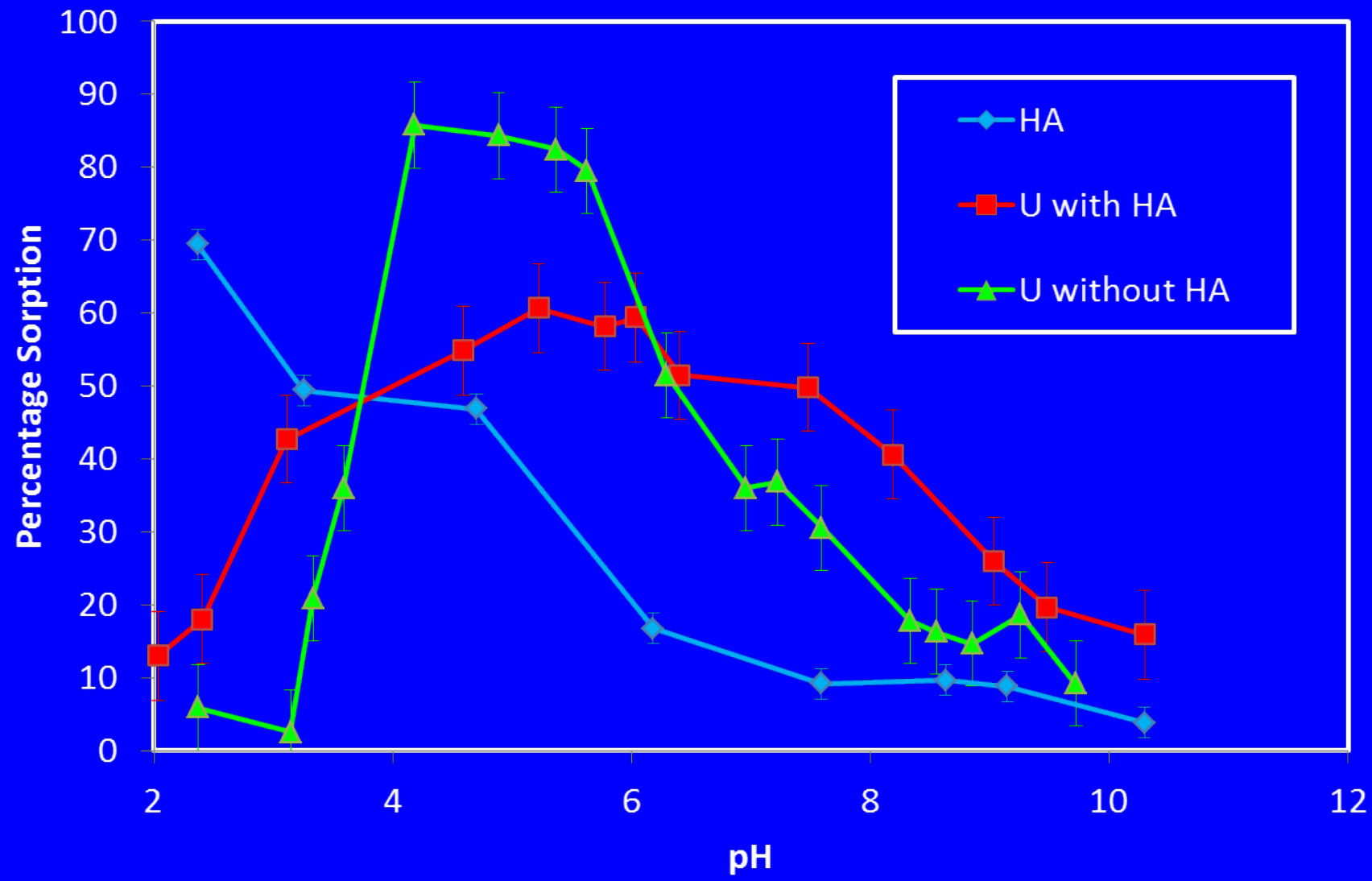
Gamma spectrum of target material before the radiochemical purification



Gamma spectrum of ^{237}U after the radiochemical purification

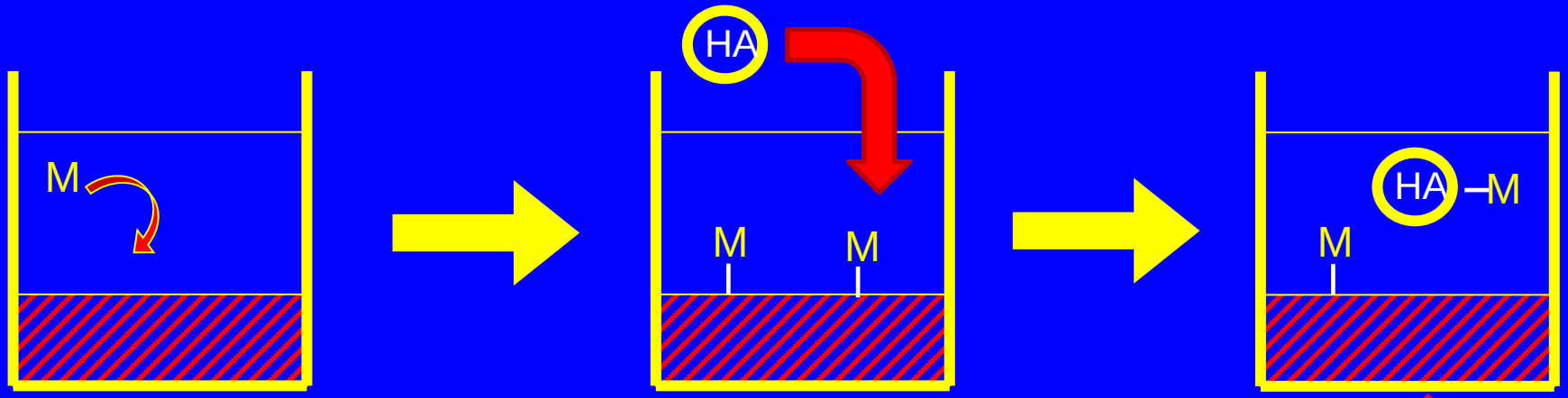
Bentonite-UO_2^{2+} Ternary System

1 g/l bentonite; [U] = 10^{-10} M [HA] = 100 ppm



Reversibility in Ternary Systems

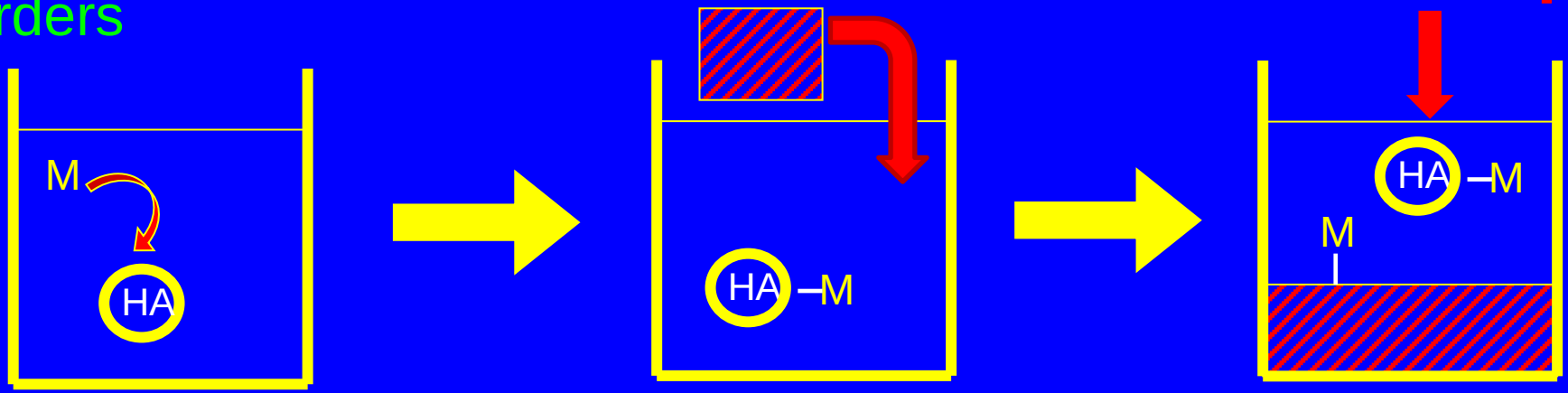
If ternary systems are ‘reversible’, then they should be insensitive to the order of addition. The time taken for systems to recover is an indication of the importance of kinetics.



Experiments with different addition orders

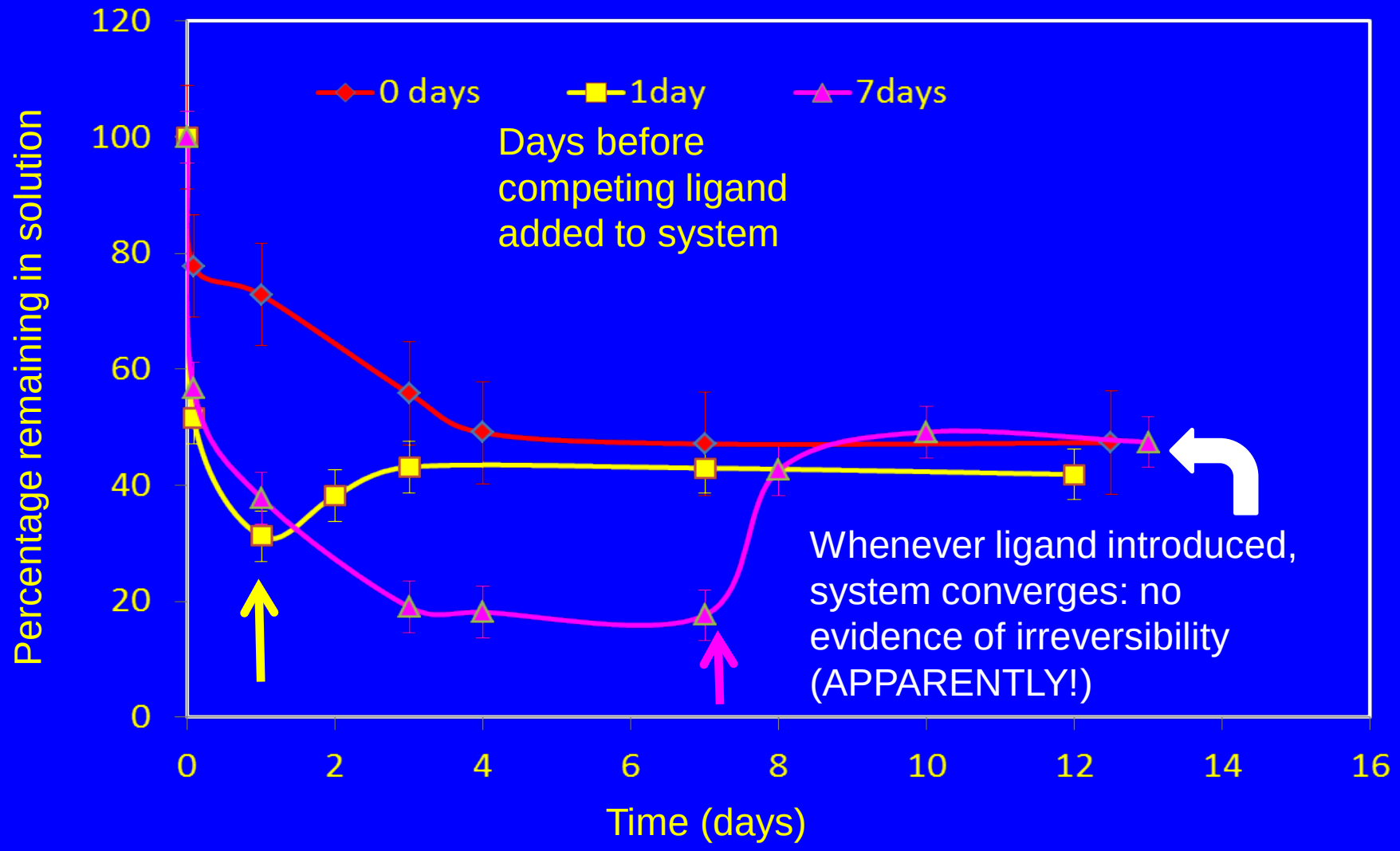
If system is reversible, then end states should be the same

= ?



U(VI) Bentonite Irreversibility test

[U] = 10^{-10} M; Effect of U/clay pre-equilibration time



Obviously need to repeat with much longer equilibration times (different isotope).

^{237}Pu Production

$T_{1/2}$ = 45.3 d

E_γ = 97.1 keV (12.5 %); 101.1 keV (20.1 %); 113.9 keV (7.6%)

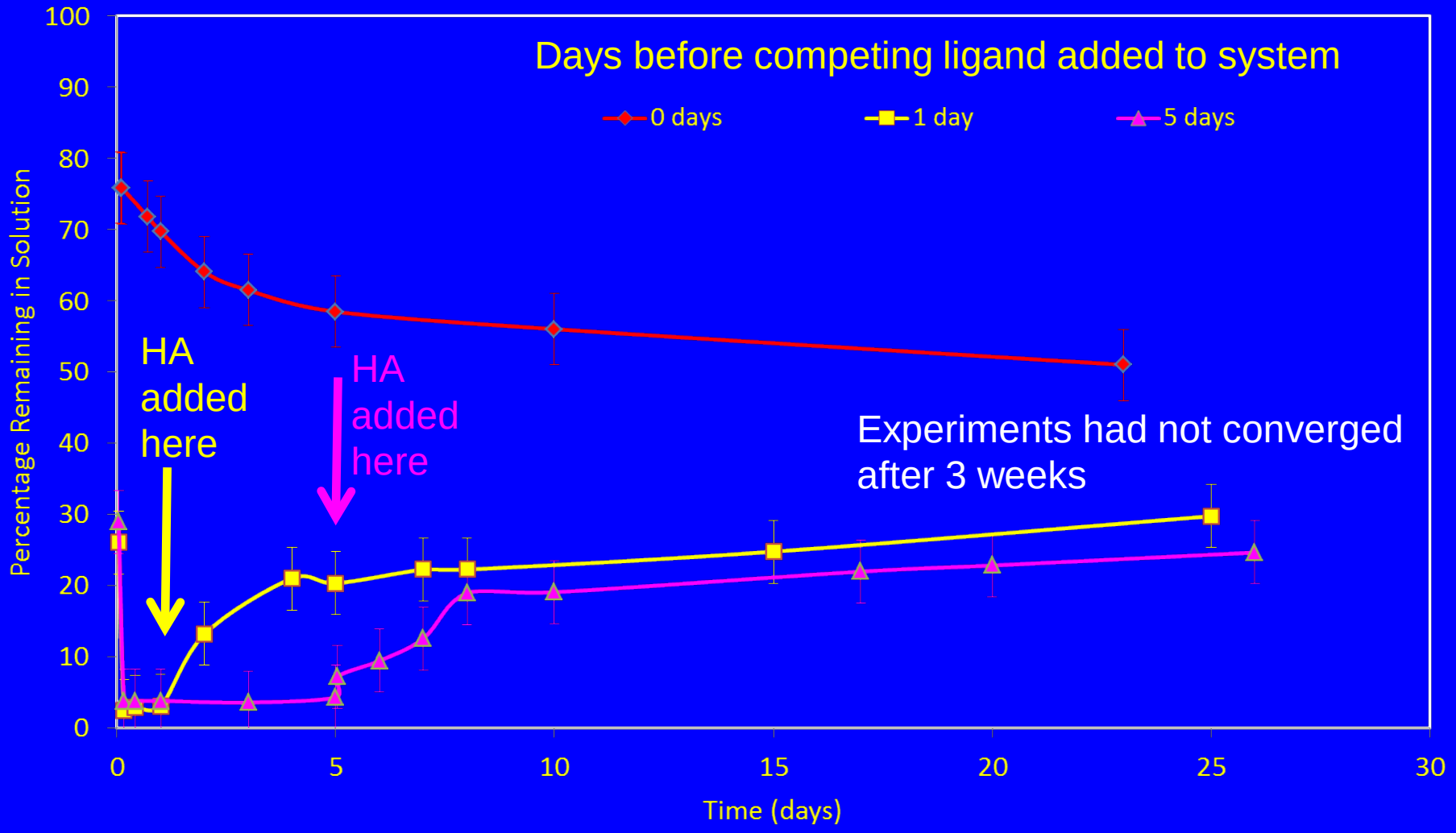
^{235}U (^{4}He, 2n) ^{237}Pu

E(^{4}He) = 25 MeV
Target: ^{235}U (U_3O_8)
Beam current : 30 μA
Yield of ^{237}Pu: 150 kBq/100 μA·h
Ratio of ^{236}Pu/^{237}Pu: 4x10^{-3} Bq/Bq

$[Pu]_T = 10^{-12}$ M

Pu(III) Bentonite Irreversibility test

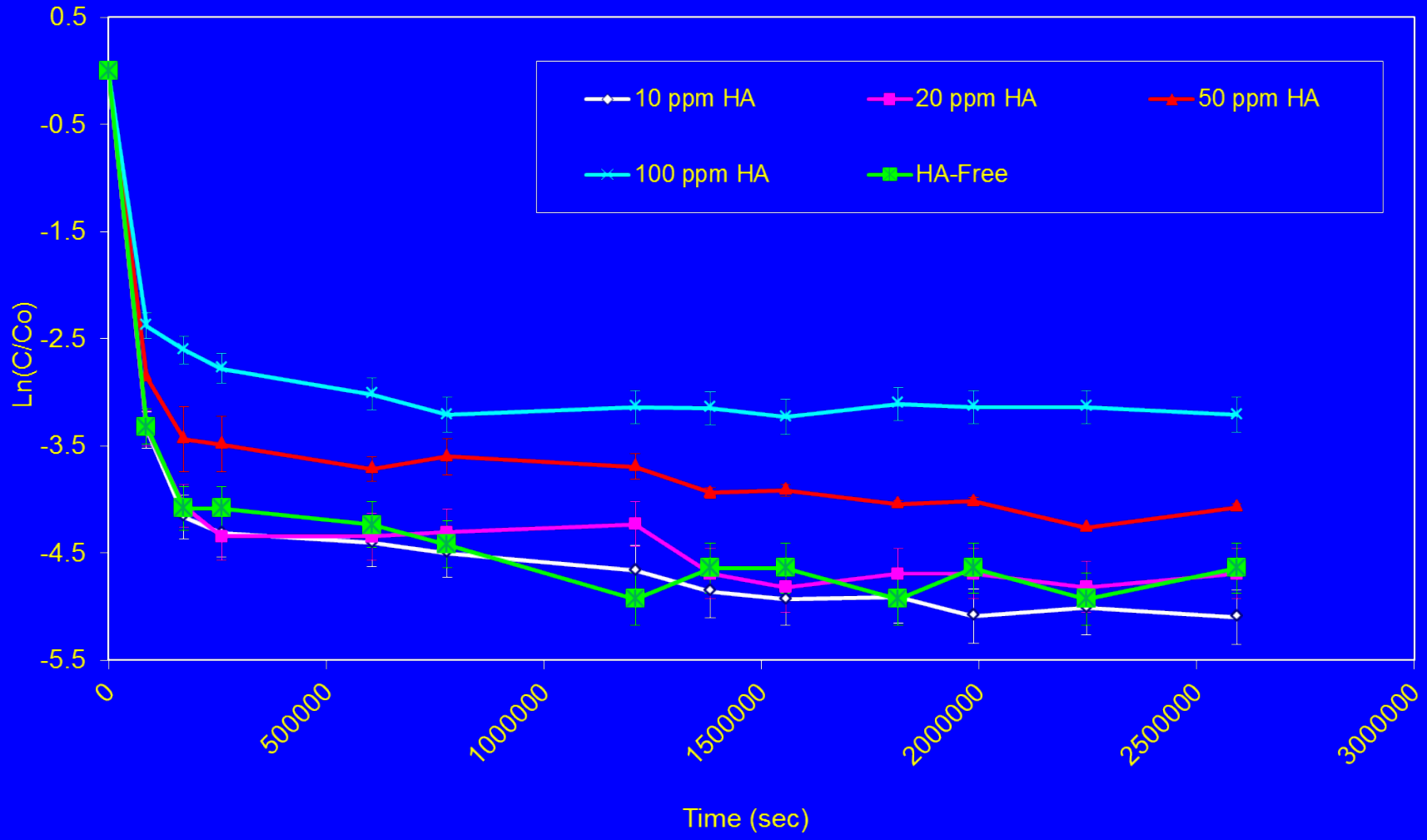
[Pu] = 3.7×10^{-11} M; Effect of Pu/clay pre-equilibration time



Some evidence for irreversibility: whether Pu 'sees' clay before addition of HA seems to make a difference.

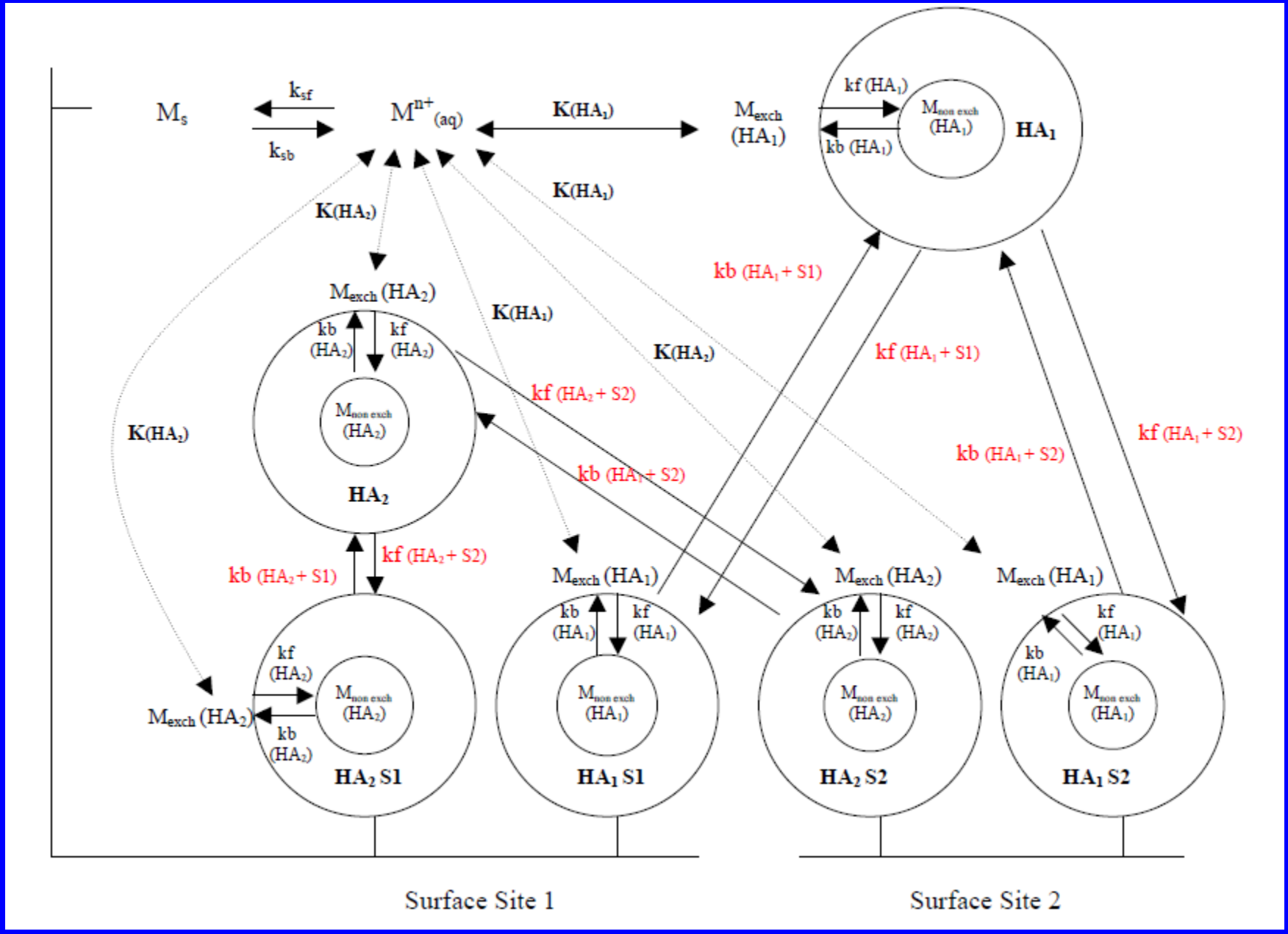
Bentonite-Eu uptake kinetics

$[Eu_T] = 7.9 \times 10^{-10}$ M; pH = 6.0

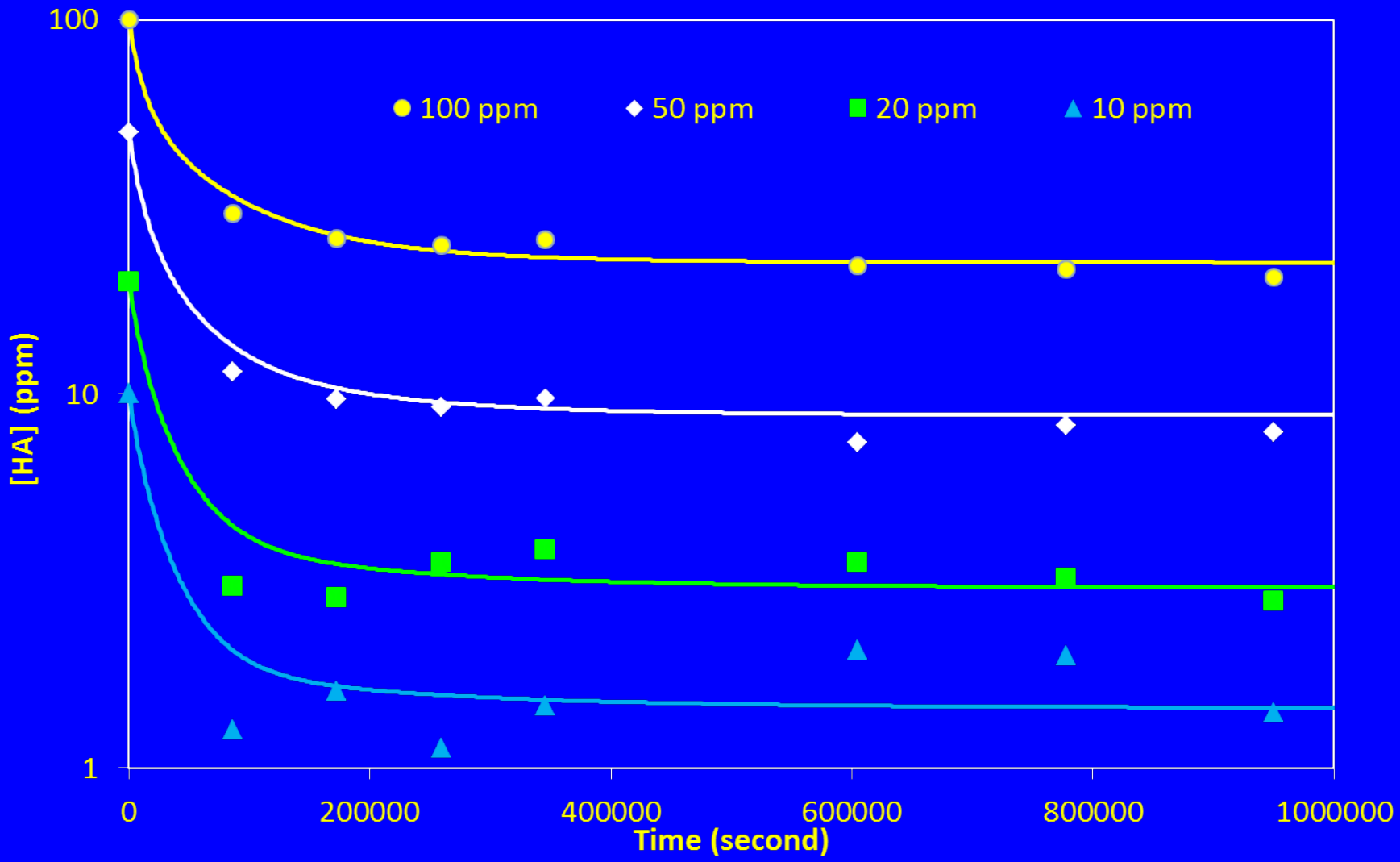


There is some evidence for slow uptake kinetics, even in the absence of a competing ligand: but the slow component is only approximately 2.5% of total bound.

Modelling of Eu(III)/Bentonite/HA experiments

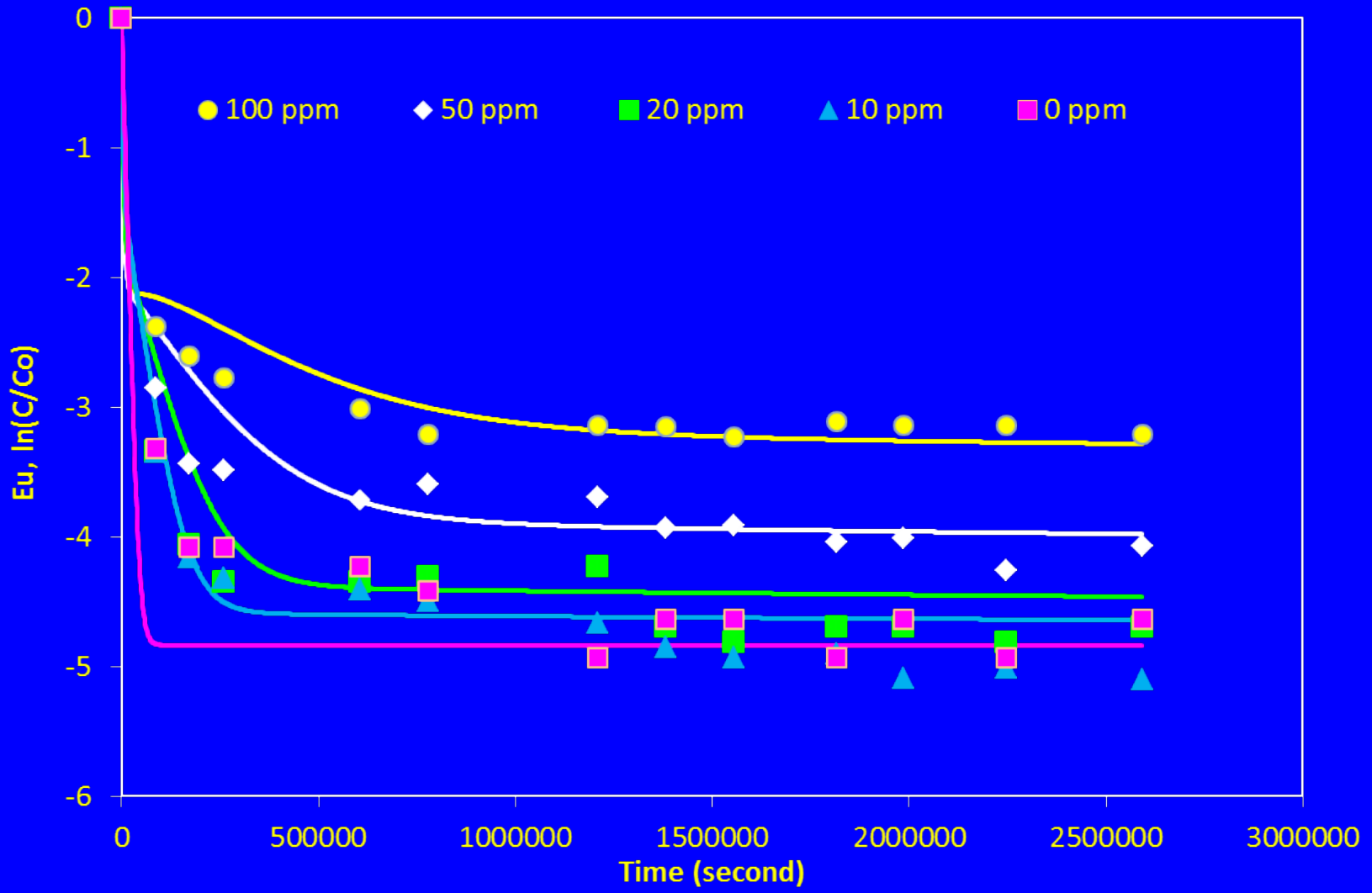


Humic Uptake on Bentonite



Eu(III) Uptake on Bentonite

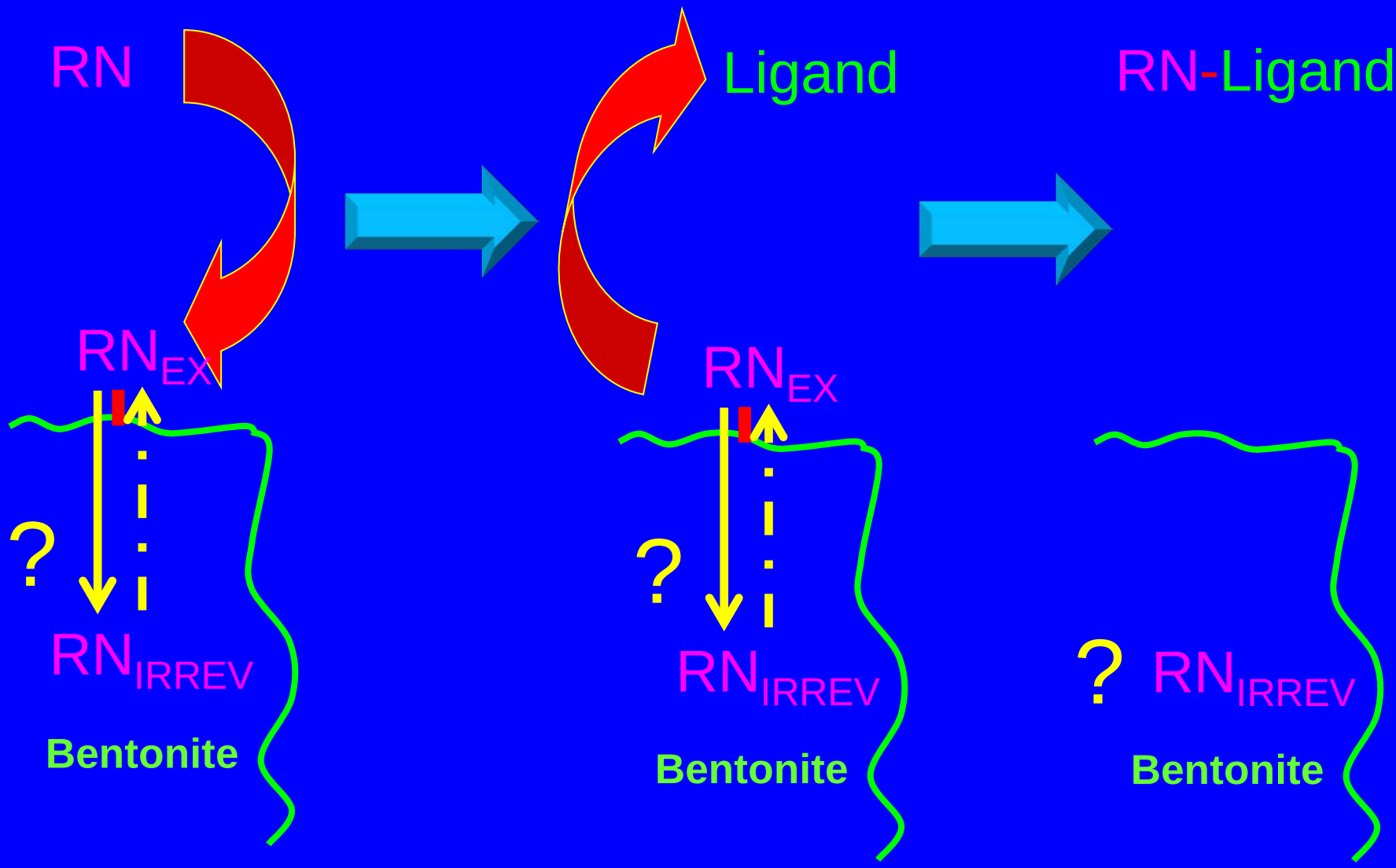
$[Eu_T] = 7.9 \times 10^{-10}$ M; pH = 6.0



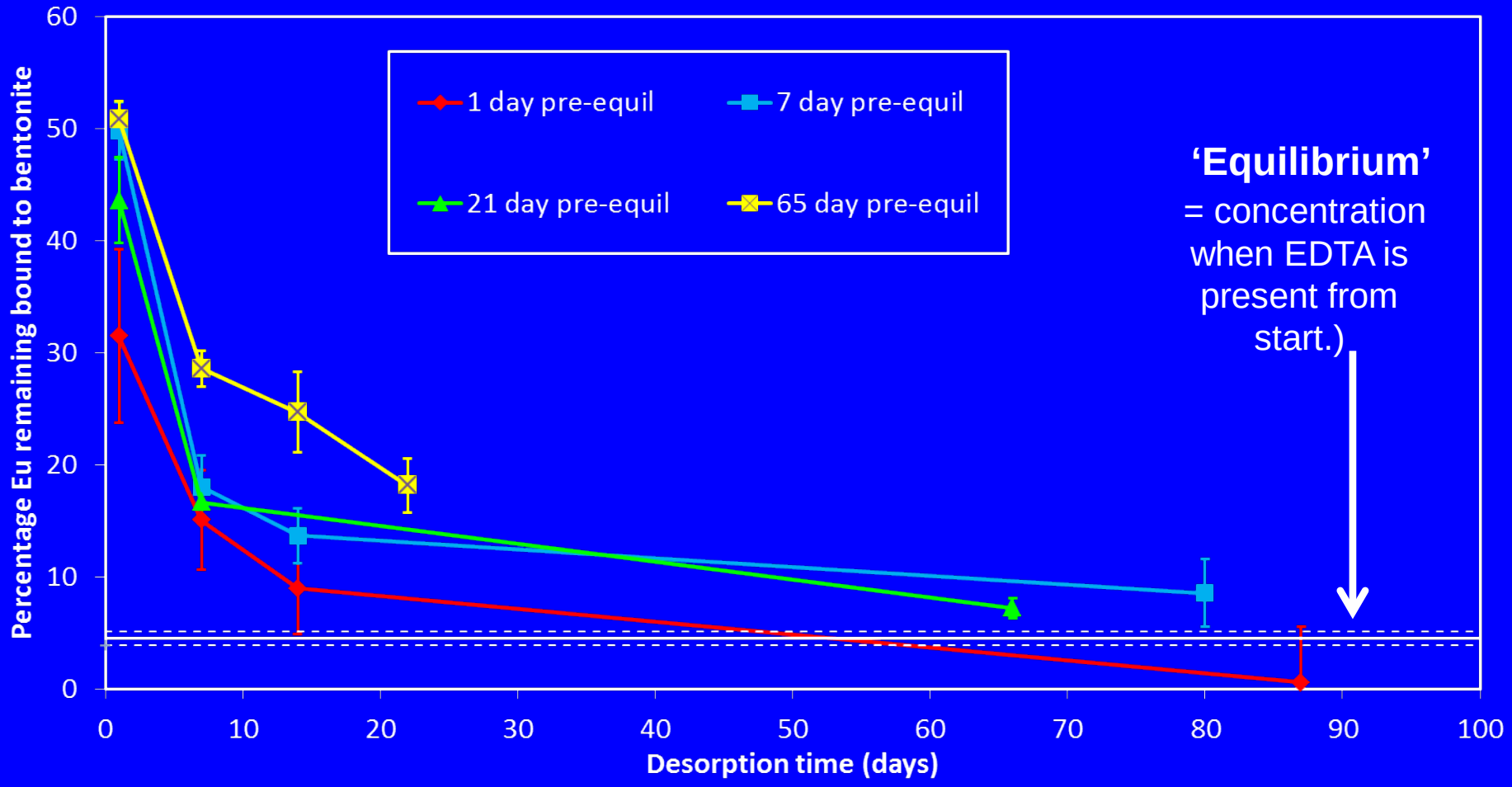
Significant chemical fractionation required in order to explain data: minor (30%) component with higher (x130) binding strength.

Irreversibility: Ligand Competition

Using ligand competition to test for irreversibility in bentonite-RN interactions: initial work has used bulk bentonite.

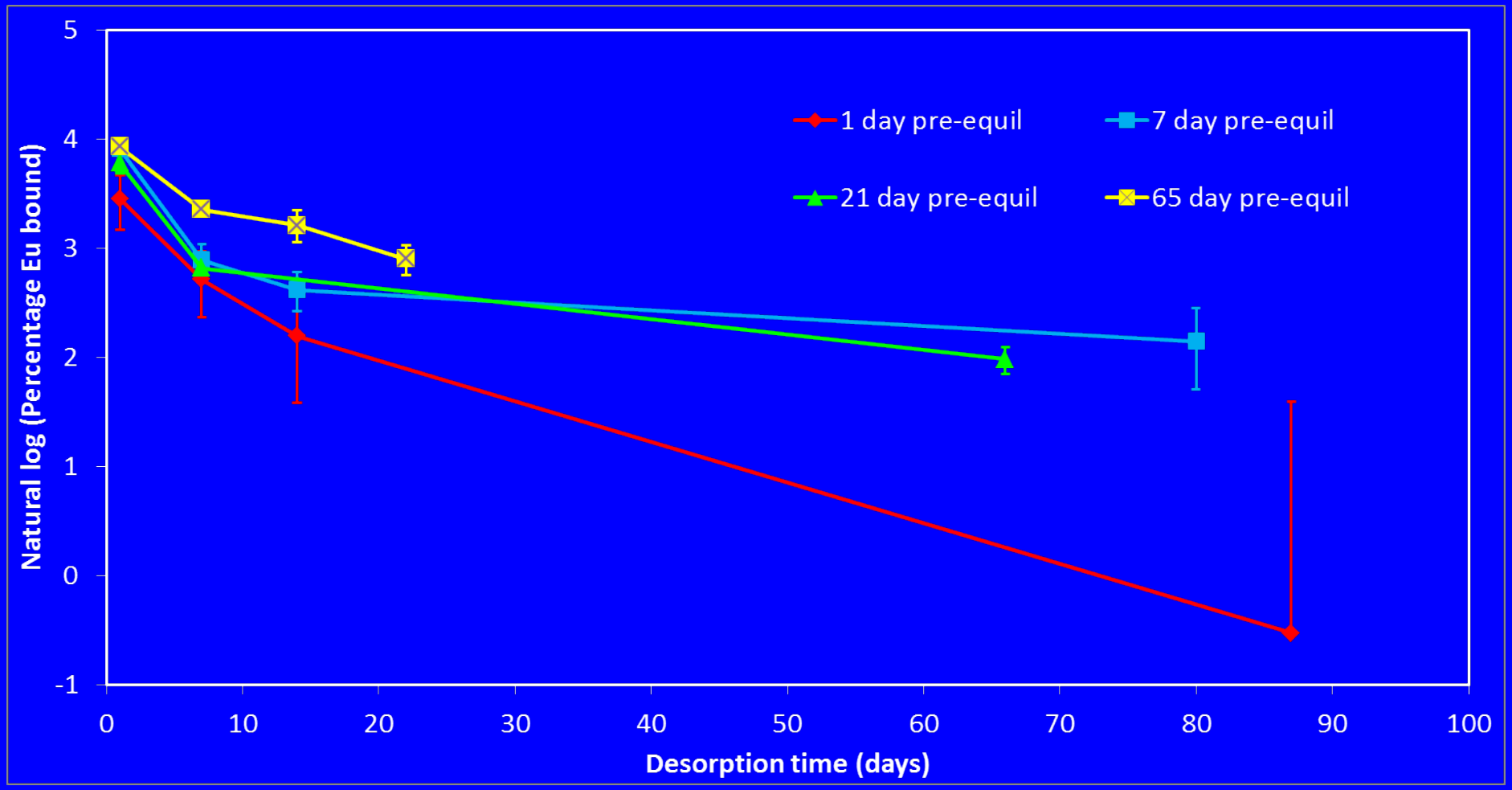


Ligand competition experiments (EDTA)



- Evidence for slow release of Eu(III) from the bentonite;
- Amount of 'non-exchangeable' Eu(III) increases with pre-equilibration time (30 – 50%); c.f . 2.5% slow uptake during sorption;
- All systems still heading towards equilibrium.

Ligand competition experiments (EDTA): log plots



- Insufficient data to determine whether dissociation rate depends upon pre-equilibration time;
- Experiments are on-going.

Preliminary Dissociation Rate Constants Eu(III)

So far, average rate constant:

$3.8 \times 10^{-7}\ s^{-1}$

(τ = 21 days)

Range:

8.2×10^{-8} - $8.6 \times 10^{-7}\ s^{-1}$

(τ = 9 - 100 days)

Same range as humic substances dissociation rates.

Implications (based on current data):

- Probably not important during diffusive transport;
- Might be important for advective transport, particularly for L/V < 100 days.*

*L = length scale of calculation; V = linear flow rate

Current/Future Work

Testing for irreversibility with bulk material with other radionuclides: $^{232}U(VI)$ and ^{228}Th.

Developing colloidal solutions and determining radionuclide distributions between different size colloids.

Use resin competition to measure radionuclide dissociation rates.

Conclusions

Preliminary work on U(VI) using ^{237}U and HA as competing ligand suggests that there may be limited kinetic effects.

Trivalent species do show slow dissociation kinetics: preliminary Eu(III) dissociation rate = 3.8×10^{-7} s^{-1} (Reaction half-time = 21 days)

So far, no evidence for ‘irreversible’ binding.

KIITOS

THANK YOU

The authors would like to thank the European Union for funding this work.