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BELBaR

Radionuclide/Bentonite Dissociation Kinetics

(BELBaR Project)

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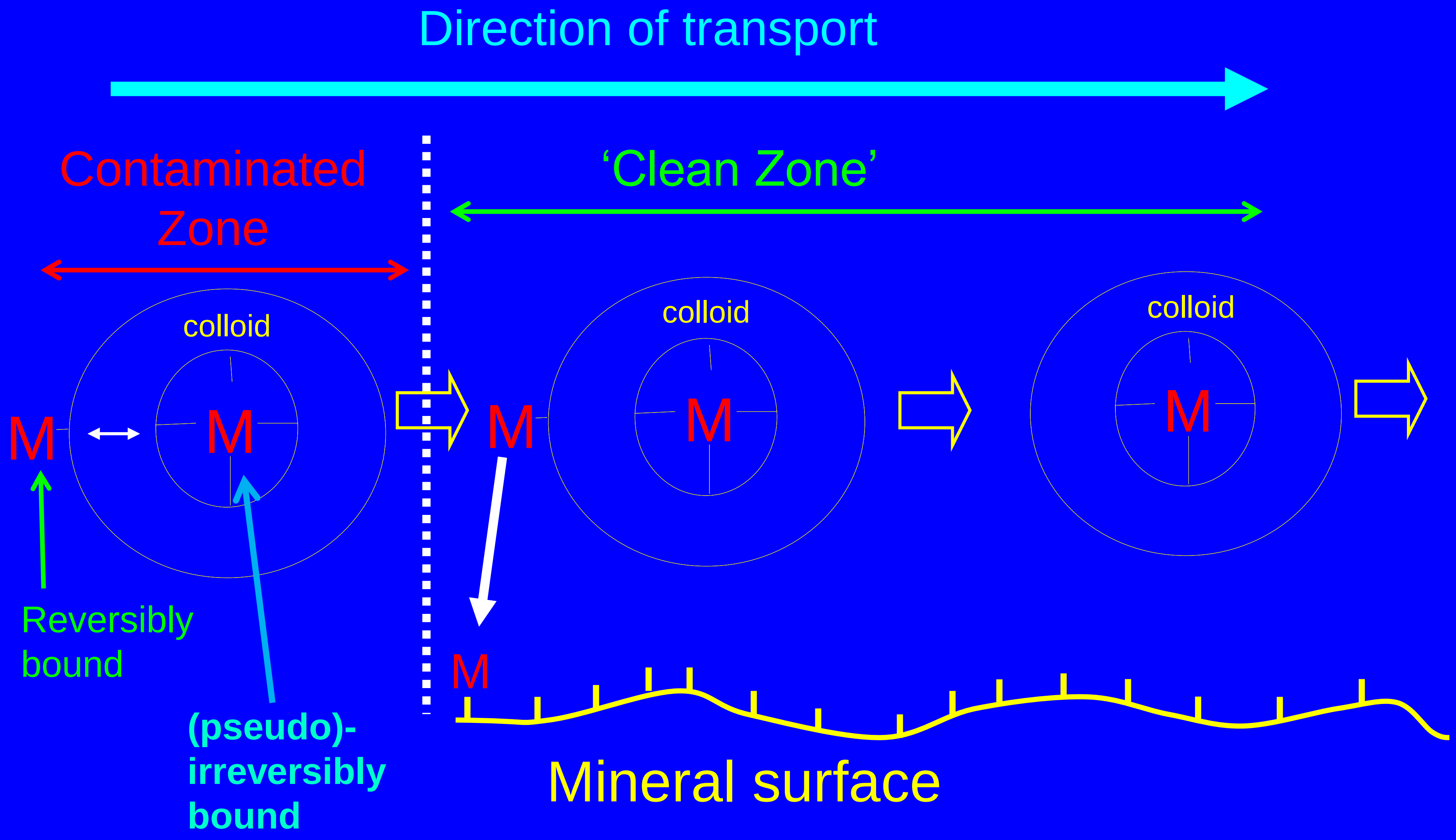
Aim of our work

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

Current Work:

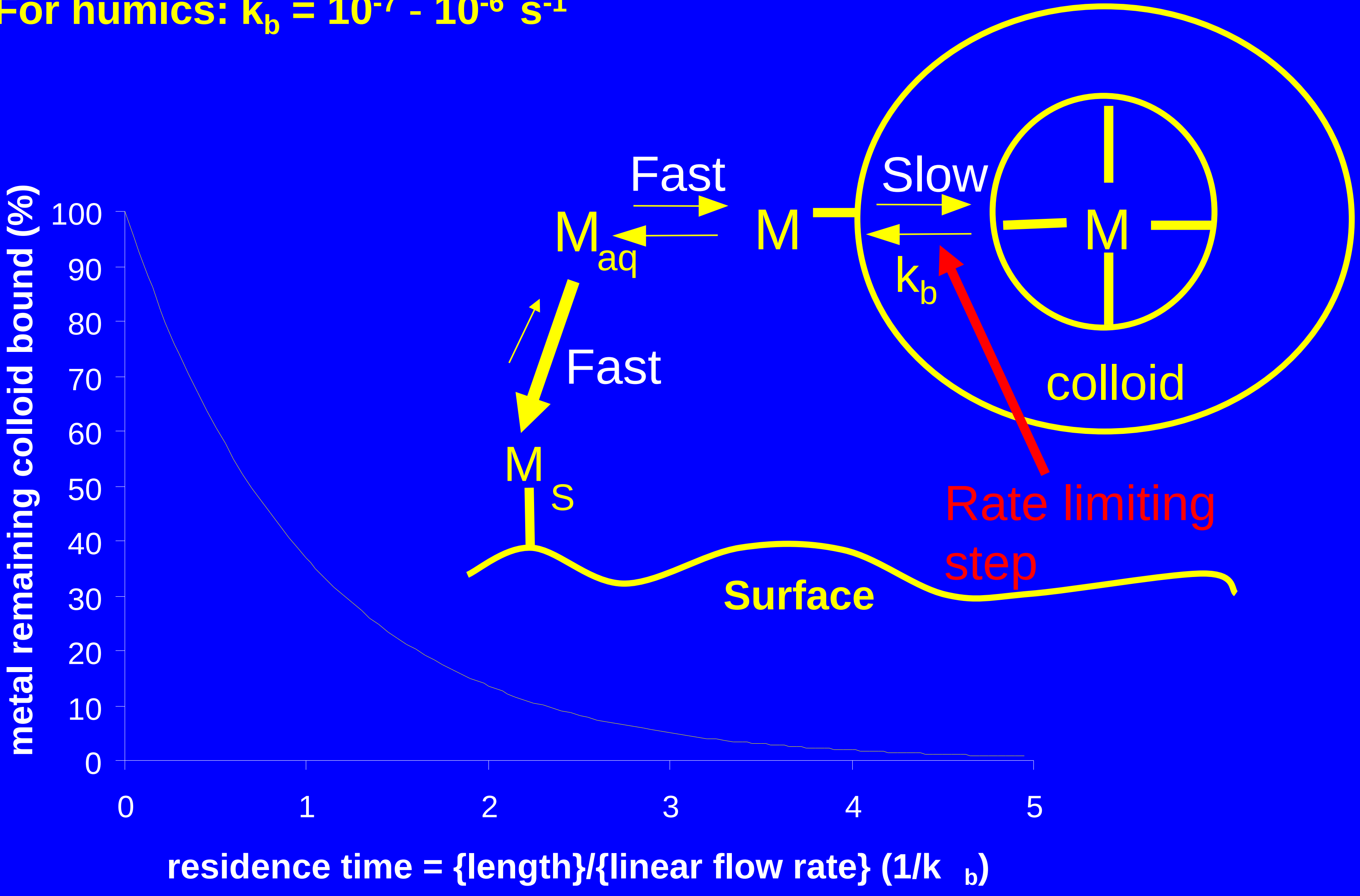
1. Sequential ultrafiltration of radionuclide and bentonite colloid mixtures.
2. Measuring dissociation kinetics for bulk and colloidal bentonite.

Why does ‘irreversible’ binding matter



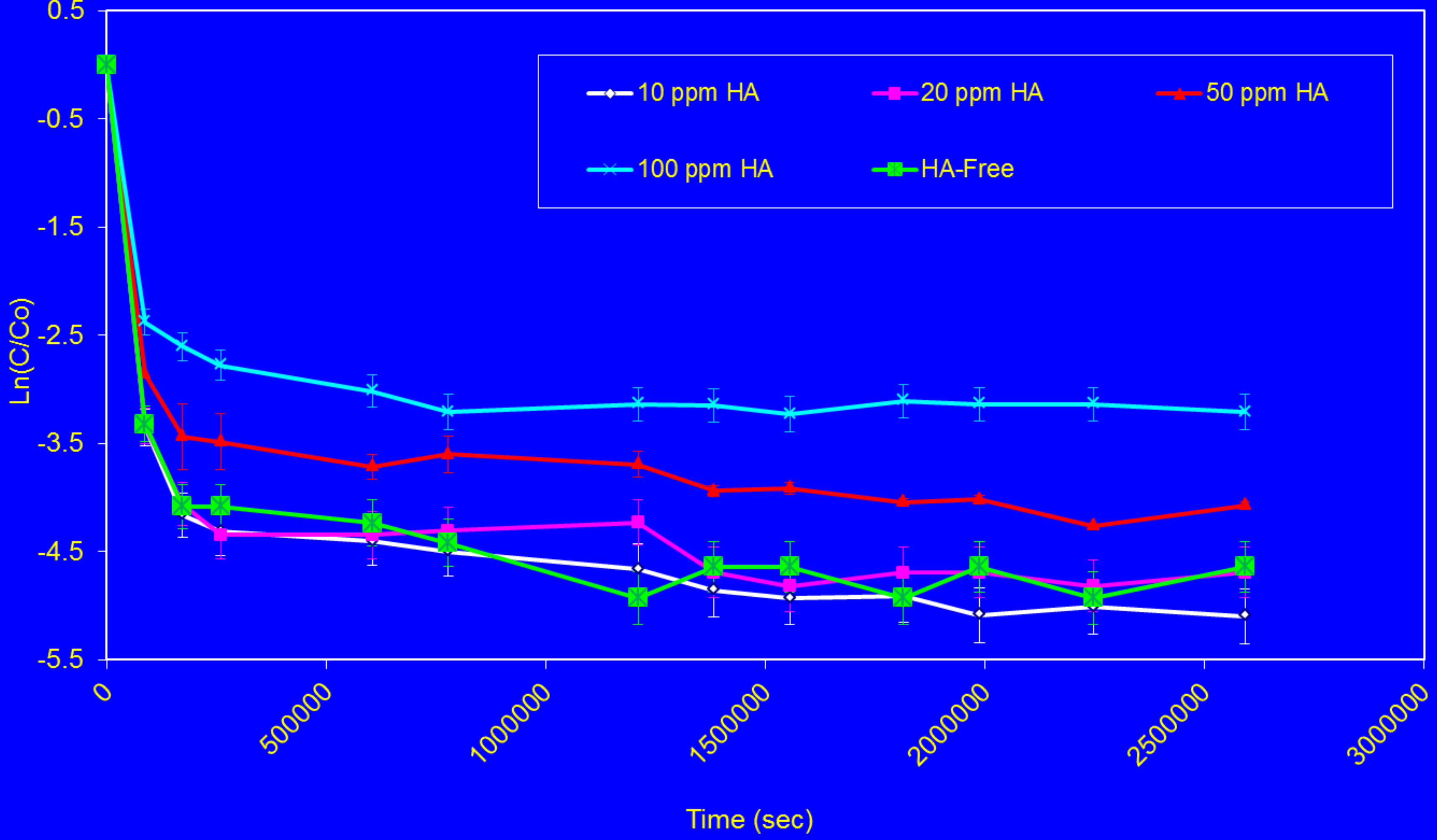
Effect of dissociation rate constant on transport

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



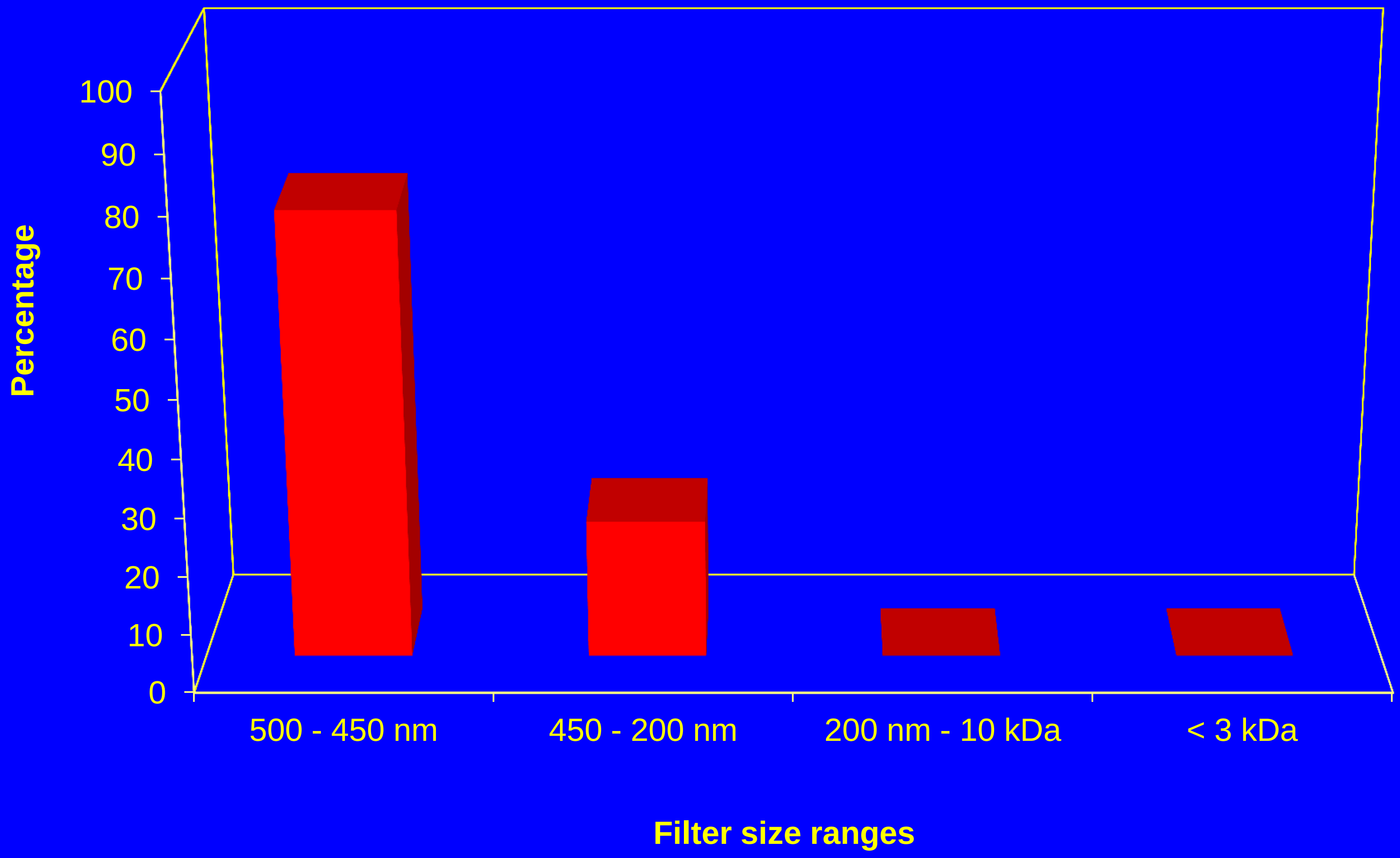
Bentonite-Eu uptake kinetics

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

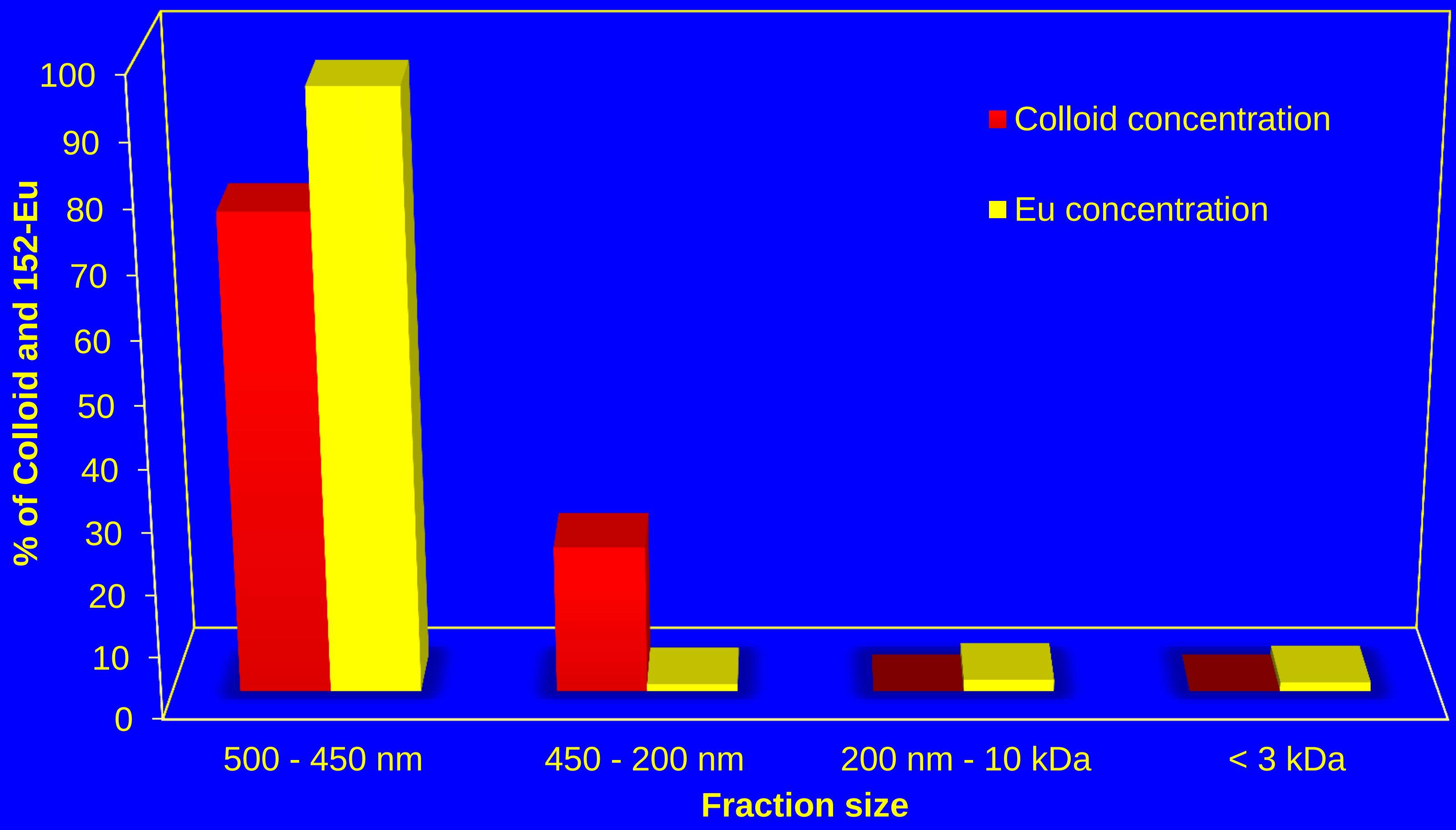


There is some evidence for slow uptake kinetics, even in the absence of a competing ligand: but the slow component is only approximately 2.5% of total bound.

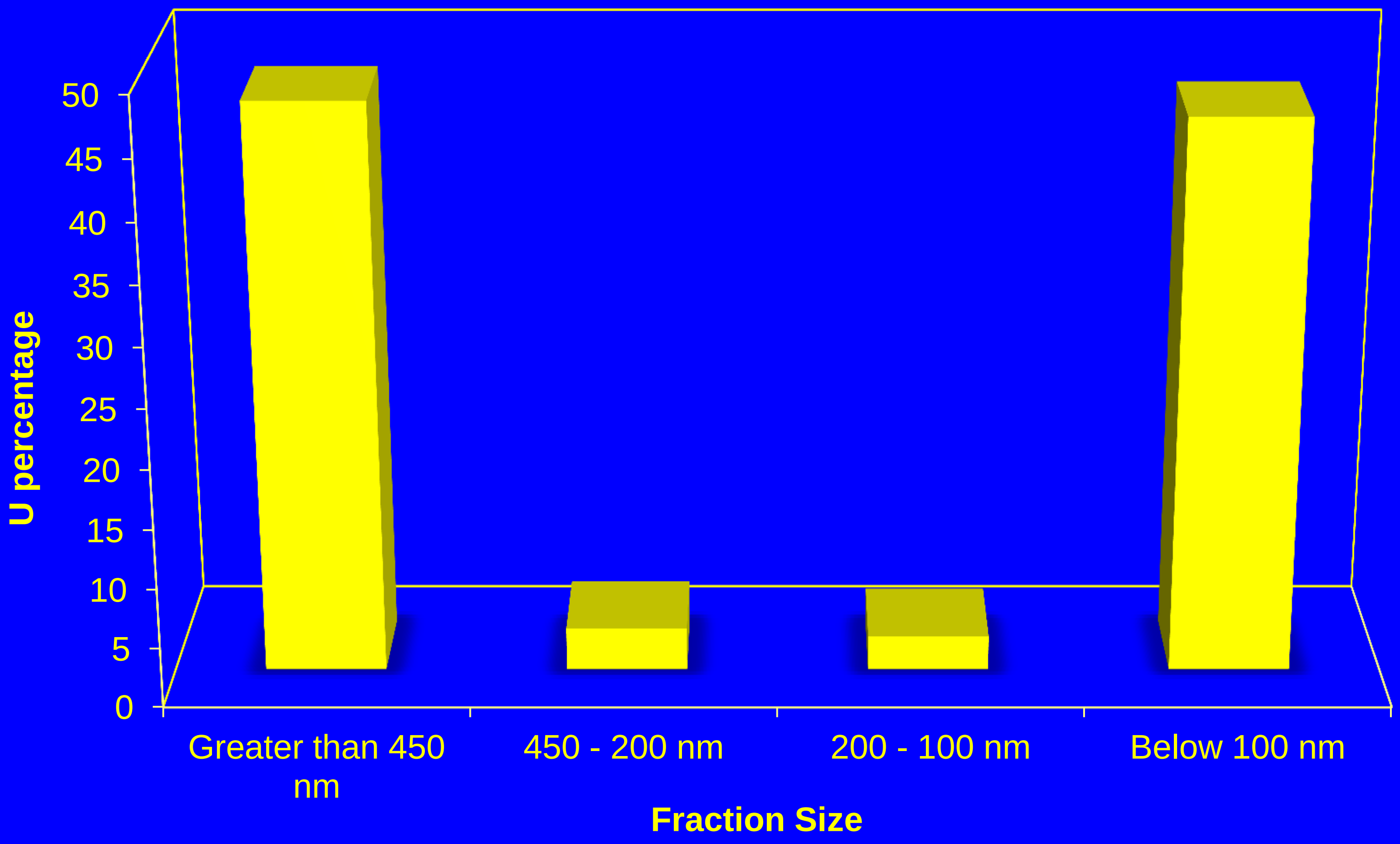
Bentonite Colloid Fractionation Data



Eu / Colloid fractionation data

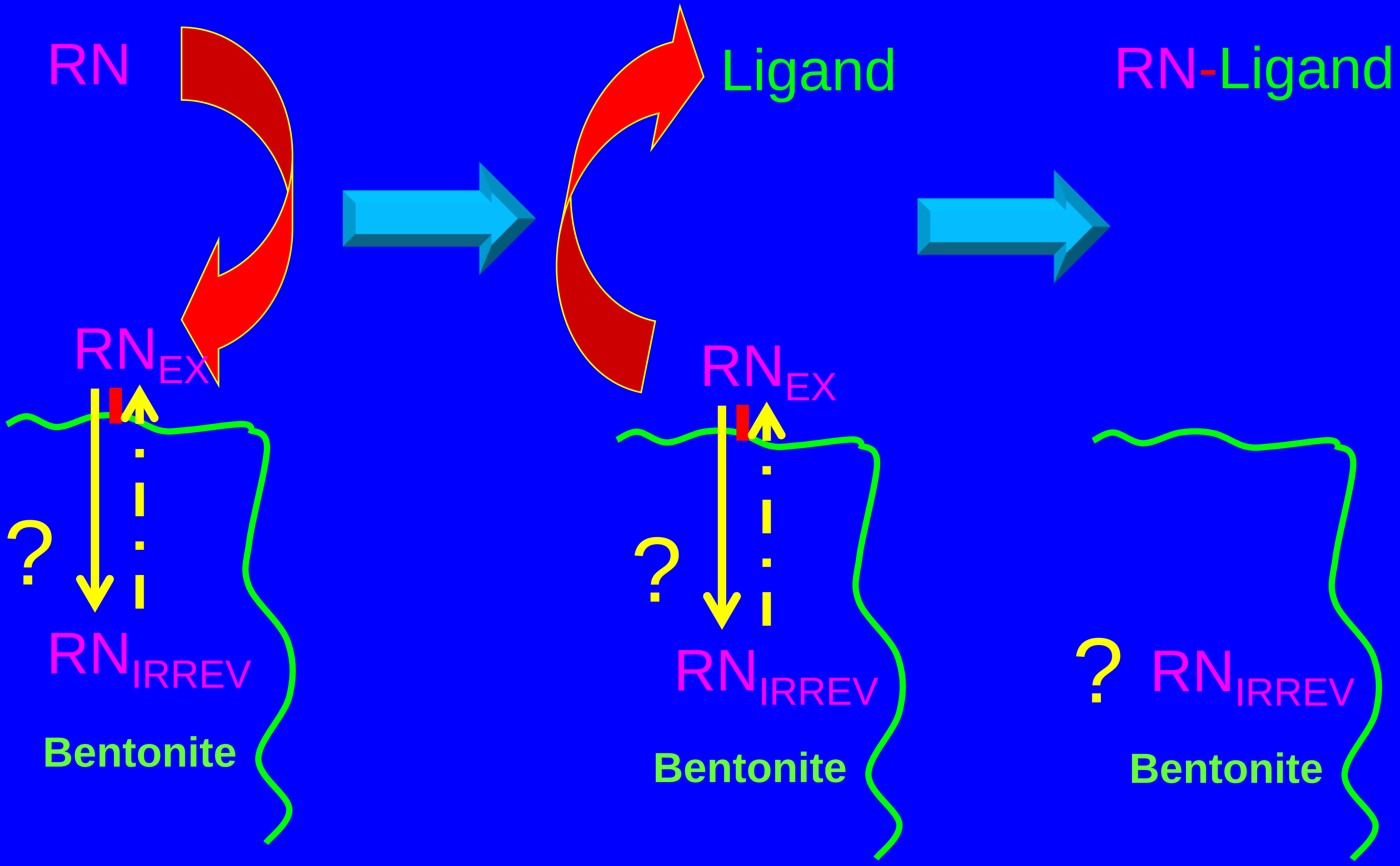


U(VI) / Colloid fractionation data

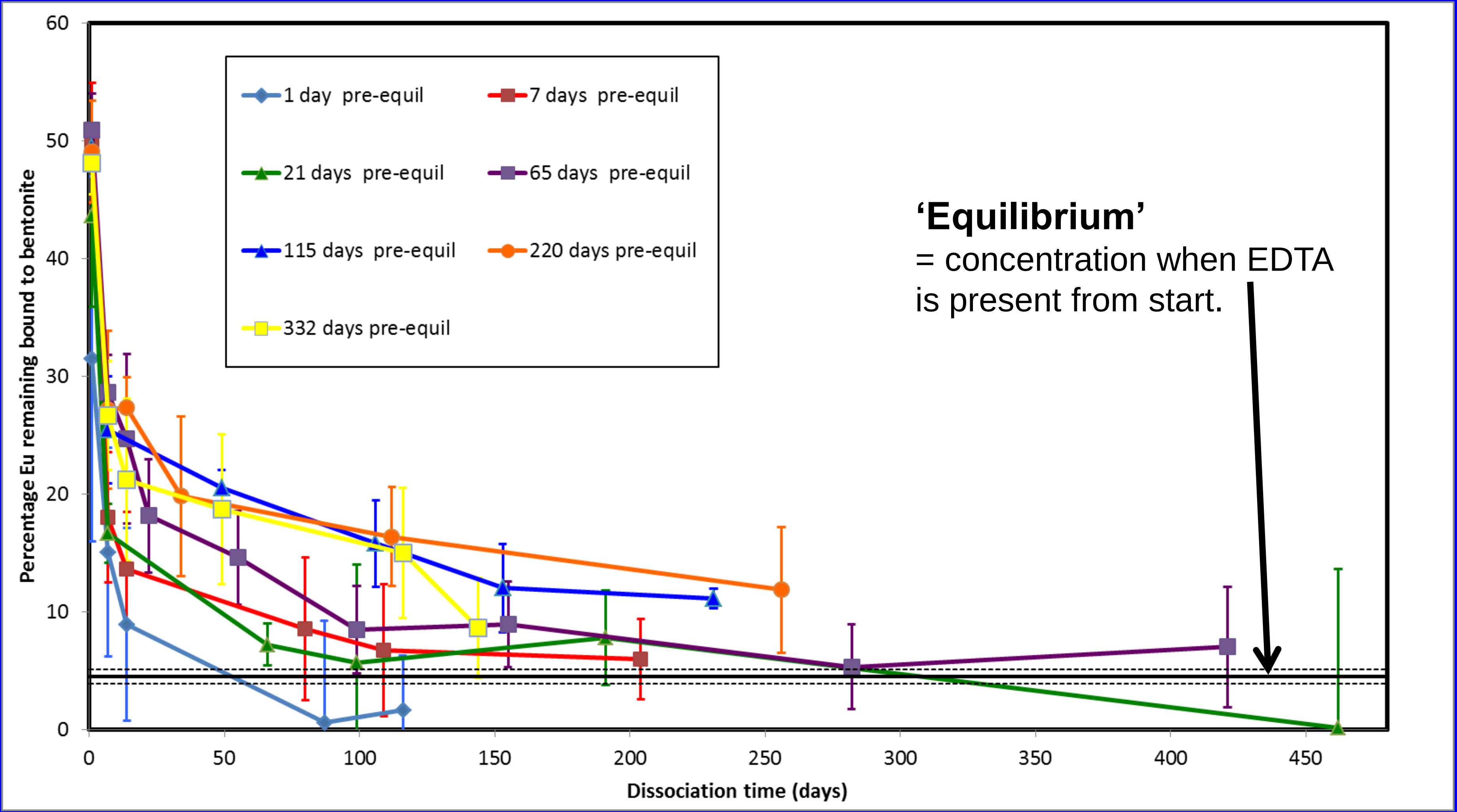


Irreversibility: Ligand Competition

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



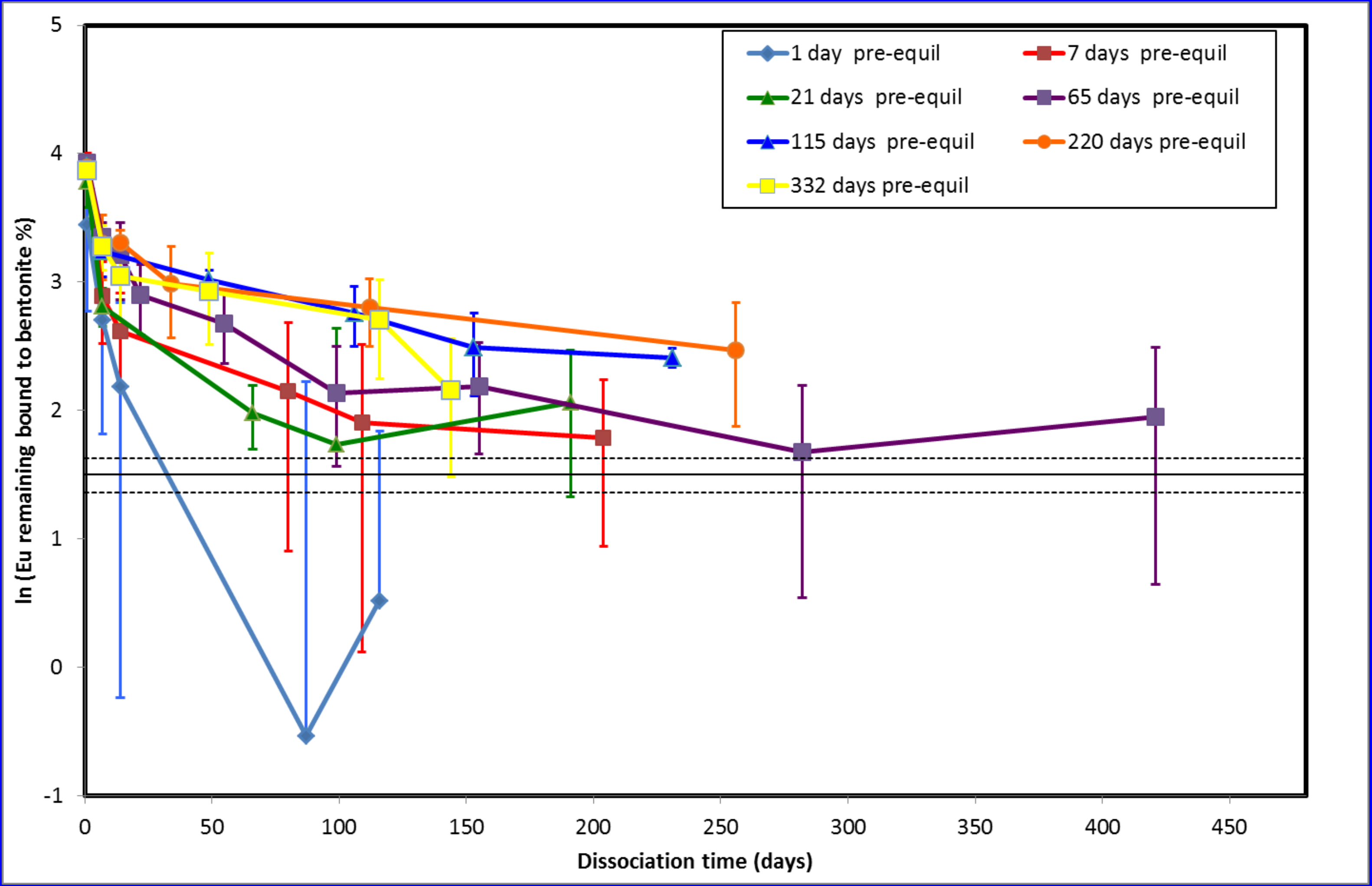
Bulk Ligand competition experiments (EDTA)



'Equilibrium'
= concentration when EDTA is present from start.

- Evidence for slow release of Eu(III) from the bentonite;
- Amount of 'non-exchangeable' Eu(III) increases with pre-equilibration time;
- All systems still heading towards equilibrium.

Ligand competition experiments (EDTA): log plots



- So far, dissociation rate constant does **not** depend upon pre-equilibration time (beyond 1 week);
- Small increase in amount slowly dissociating with time;
- Experiments are on-going.

Bulk First Order Dissociation Rate Constants

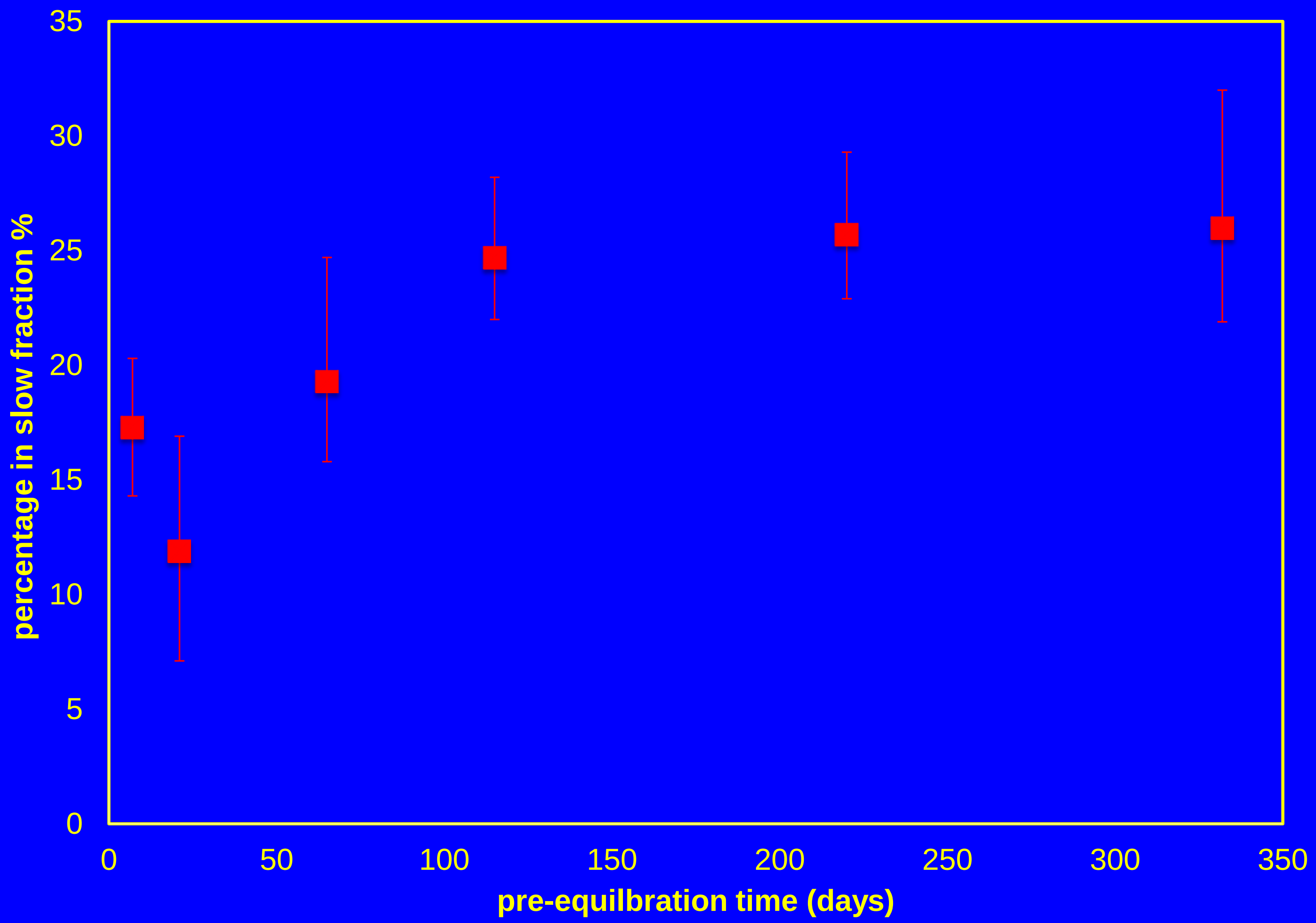
Pre-equilibration time (days)	**Dissociation rate constant (s^{-1})**	**Amount of Eu in fraction (%)**	**τ (days)**
7	1.01 X 10^{-7} (±6.23 X 10^{-8})	17.3 (±3)	79
21	4.19 X 10^{-8} (±8.51 X 10^{-8})	11.9 (+5.0)(-4.8)	192
65	3.93 X 10^{-8} (±1.35 X 10^{-8})	19.3 (+5.4)(-3.5)	204
115	4.47 X 10^{-8} (±1.06 X 10^{-8})	24.7 (+3.5)(-2.7)	179
220	3.72 X 10^{-8} (±1.14 X 10^{-8})	25.7 (+3.6)(-2.8)	215
332	7.58 X 10^{-8} (±2.55 X 10^{-8})	26.0 (+6)(-4.1)	106

For radionuclide/bentonite contact times > 1 week:

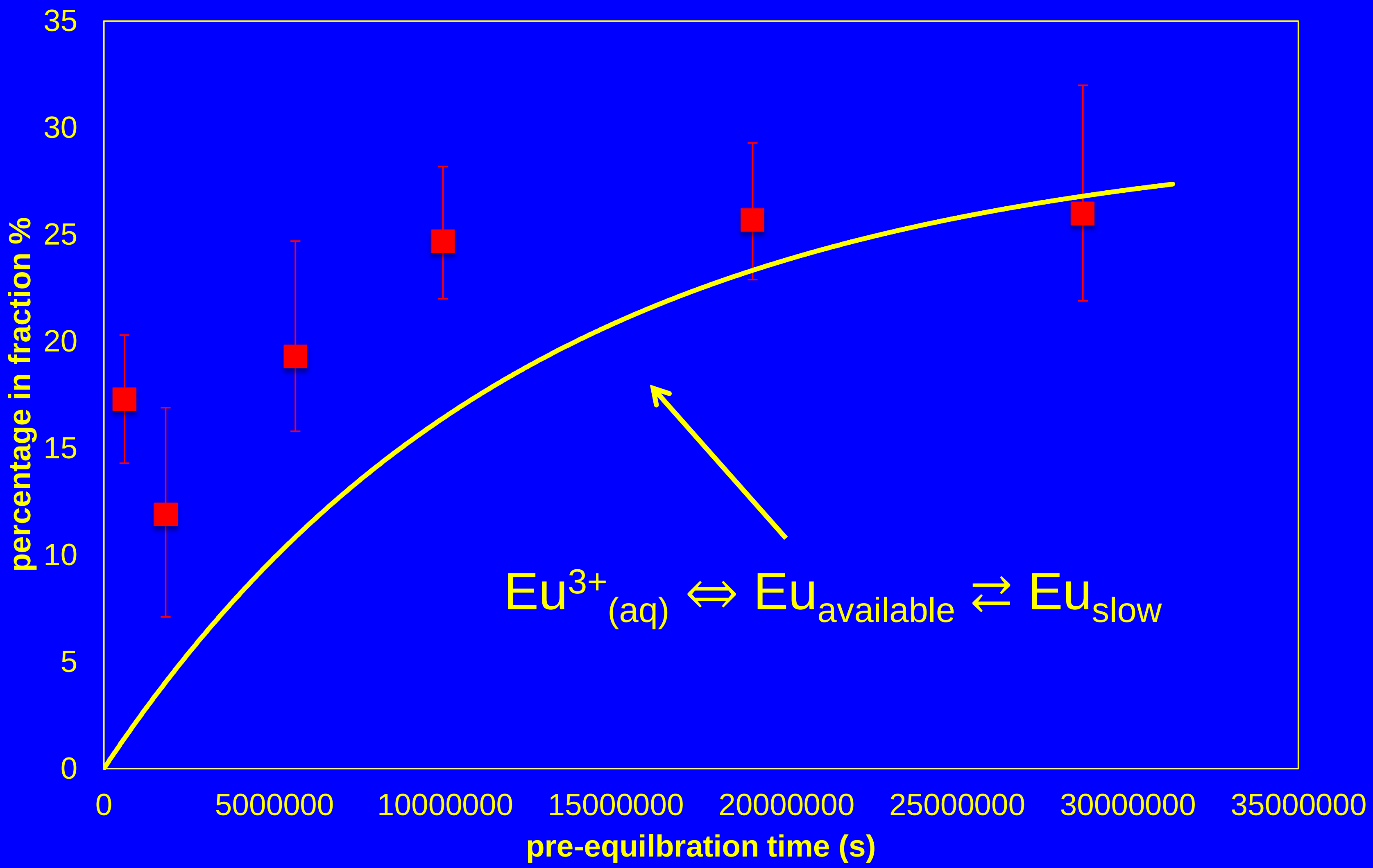
- Rapid (instantaneous) removal of 50 – 60% of clay bound material;
- Continued, but slowing dissociation over first week;
- Thereafter – no consistent variation in dissociation rate with equilibration time.

For contact times < 1 week: faster kinetics (approx 10^{-6} s^{-1}).

Amount slowly dissociating with pre-equilibration time



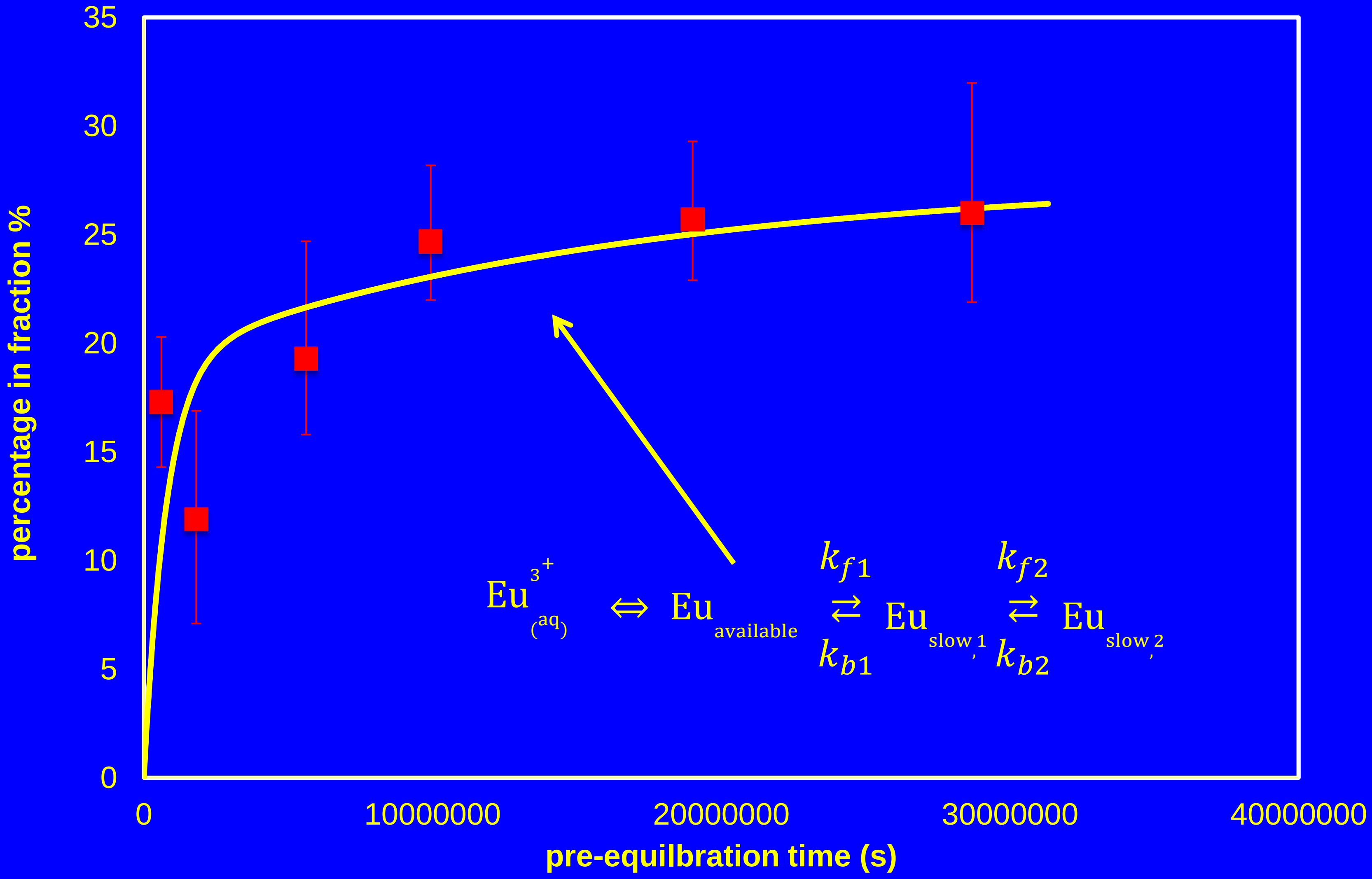
Amount in slowly dissociating with pre-equilibration time



$Eu^{3+}_{(aq)} \Leftrightarrow Eu_{available} \rightleftarrows Eu_{slow}$

Not possible to simulate data very well with just a single slow fraction. The 1 day expt also has a different dissociation rate.

Amount in slowly dissociating with pre-equilibration time



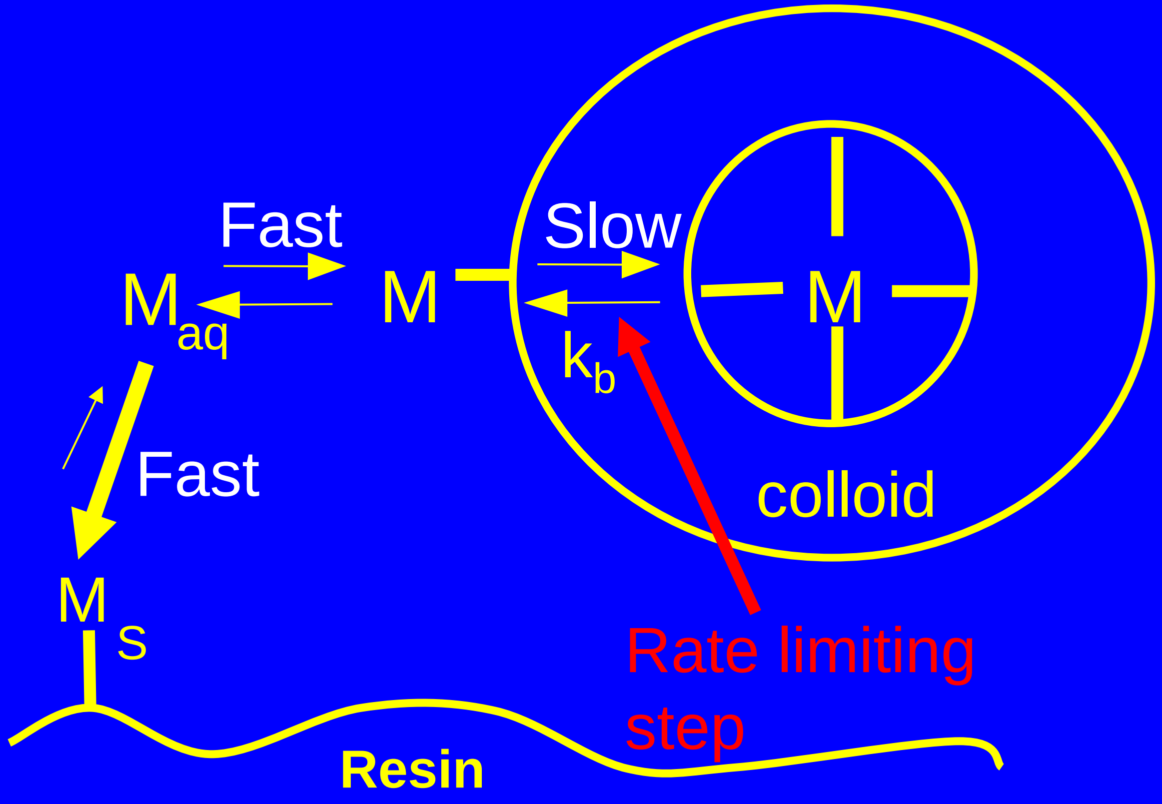
$$\mathrm{Eu}^{3+}_{(aq)} \Leftrightarrow \mathrm{Eu}_{\mathrm{available}} \underset{k_{b1}}{\overset{k_{f1}}{\rightleftarrows}} \mathrm{Eu}_{\mathrm{slow\,1}} \underset{k_{b2}}{\overset{k_{f2}}{\rightleftarrows}} \mathrm{Eu}_{\mathrm{slow\,2}}$$

A two fraction model is much more effective.

$k_{f1} = 2.5 \times 10^{-7}\ s^{-1}$; $k_{b1} = 1.0 \times 10^{-6}\ s^{-1}$; $k_{f2} = 3.0 \times 10^{-8}\ s^{-1}$; $k_{b2} = 5.67 \times 10^{-8}\ s^{-1}$

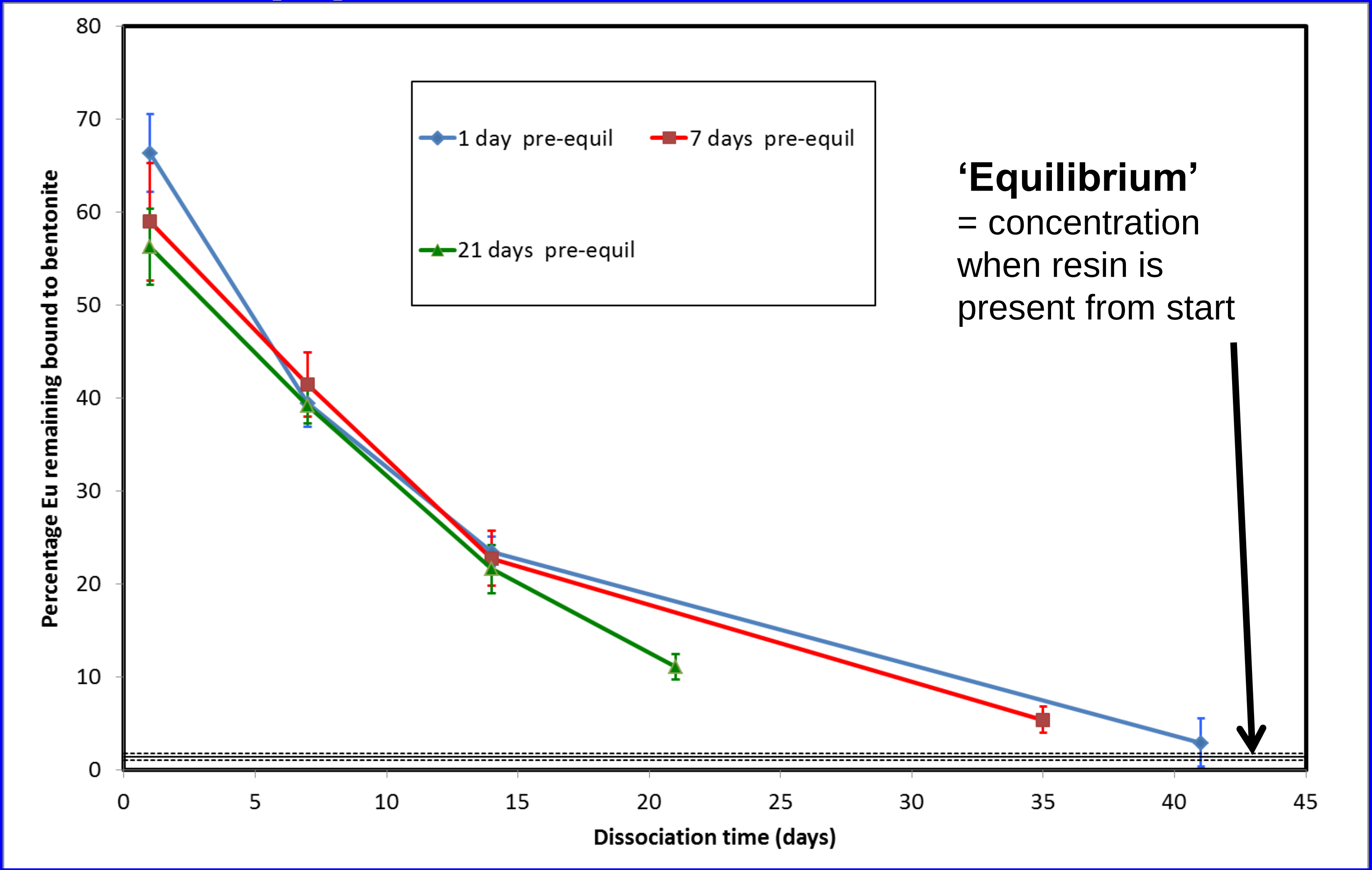
Measuring Colloid Dissociation Rates

For colloids, can’t use competing ligands, because there is no phase separation: instead we use a cation exchange resin to remove radionuclides from bentonite colloids.



We are using Dowex cation exchange resin.

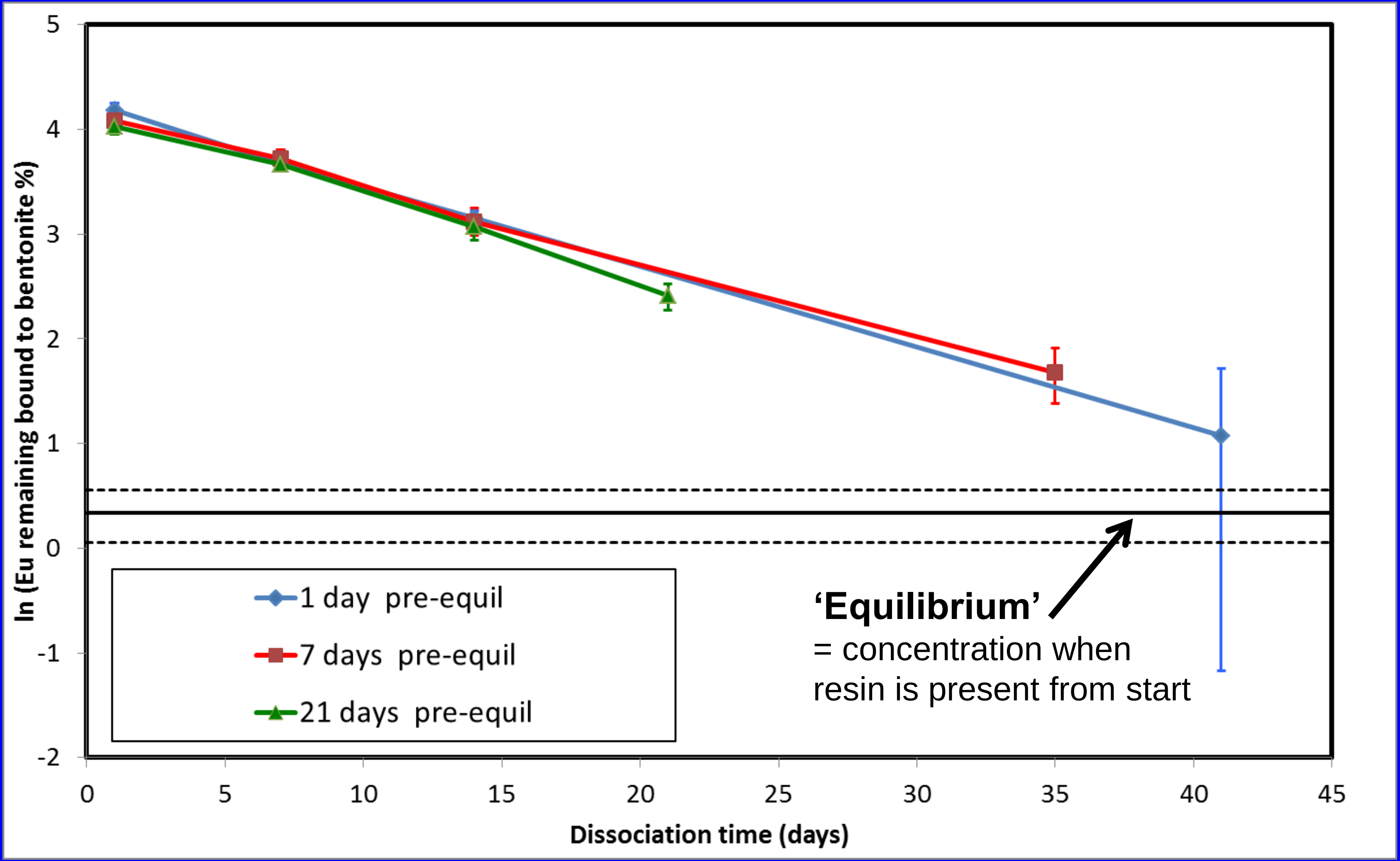
Eu(III) Colloid Dissociation Kinetics



'Equilibrium'
= concentration
when resin is
present from start

- Once again, evidence for slow release of Eu(III) from the bentonite;
- Dissociation appears similar this time;
- All systems still heading towards equilibrium.

Colloid dissociation: log plots



'Equilibrium'
= concentration when resin is present from start

- Kinetics are remarkably uniform between the different systems;
- Unlike the bulk experiments, a single dissociation rate can describe the dissociation kinetics from 1 day onwards.

Colloid First Order Dissociation Rate Constants

Pre-equilibration time (days)	**Dissociation rate constant (s^{-1})**	**Amount of Eu in fraction (%)**	**τ (days)**
1	8.97 X 10^{-7} (±2.27 X 10^{-8})	69.76 (+3.1)(-2.9)	8.94
7	8.25 X 10^{-7} (±5.05 X 10^{-8})	64.4 (+5.9)(-5.0)	9.72
21	9.47 X 10^{-7} (±1.31 X 10^{-7})	64.9 (+11.2)(-8.3)	8.47

- Very narrow range of rate constants;
- Faster dissociation than for bulk (approx order of magnitude);
- But, more in slow fraction than for bulk.

Current Dissociation Rate Constants
Eu(III)

BULK BENTONITE

Average rate constant: **5.67×10^{-8} s^{-1}**

Rate constant range: **3.7×10^{-8} - 1.0×10^{-7} s^{-1}**

Amount: approximately 25%, constant after 100 days

COLLOIDAL BENTONITE (so far)

Average rate constant:

Average rate constant: **8.9×10^{-7} s^{-1}**

Rate constant range : **8.3×10^{-7} - 9.5×10^{-7} s^{-1}**

Amount: 64 – 70%, independent of pre-equil’ time

Colloid Kinetics in a Safety Case (1)

The division between equilibria and kinetics is artificial.

Whether a reaction is ‘equilibrium’ or ‘kinetic’ or whether radionuclide binding appears ‘irreversible’ will depend upon the conditions of the observation:

- for example, flow rate, distance, total time.

For a given flow rate, distance, time etc. there will be just three classes of reaction:

1. Fast enough to be effectively equilibria;
2. So slow that they do not take place (**irreversibility**);
3. Intermediate (need a kinetic description).

Damkohler Numbers

$$D = \frac{L}{V} k_b$$

For colloid dissociation kinetics, we can use Damkohler numbers to assess the importance of kinetics: e.g.,

1. Assume instantaneous reversiblity at large D, e.g., $D > 100$

   CAUTION: NOT INHERENTLY CONSERVATIVE !

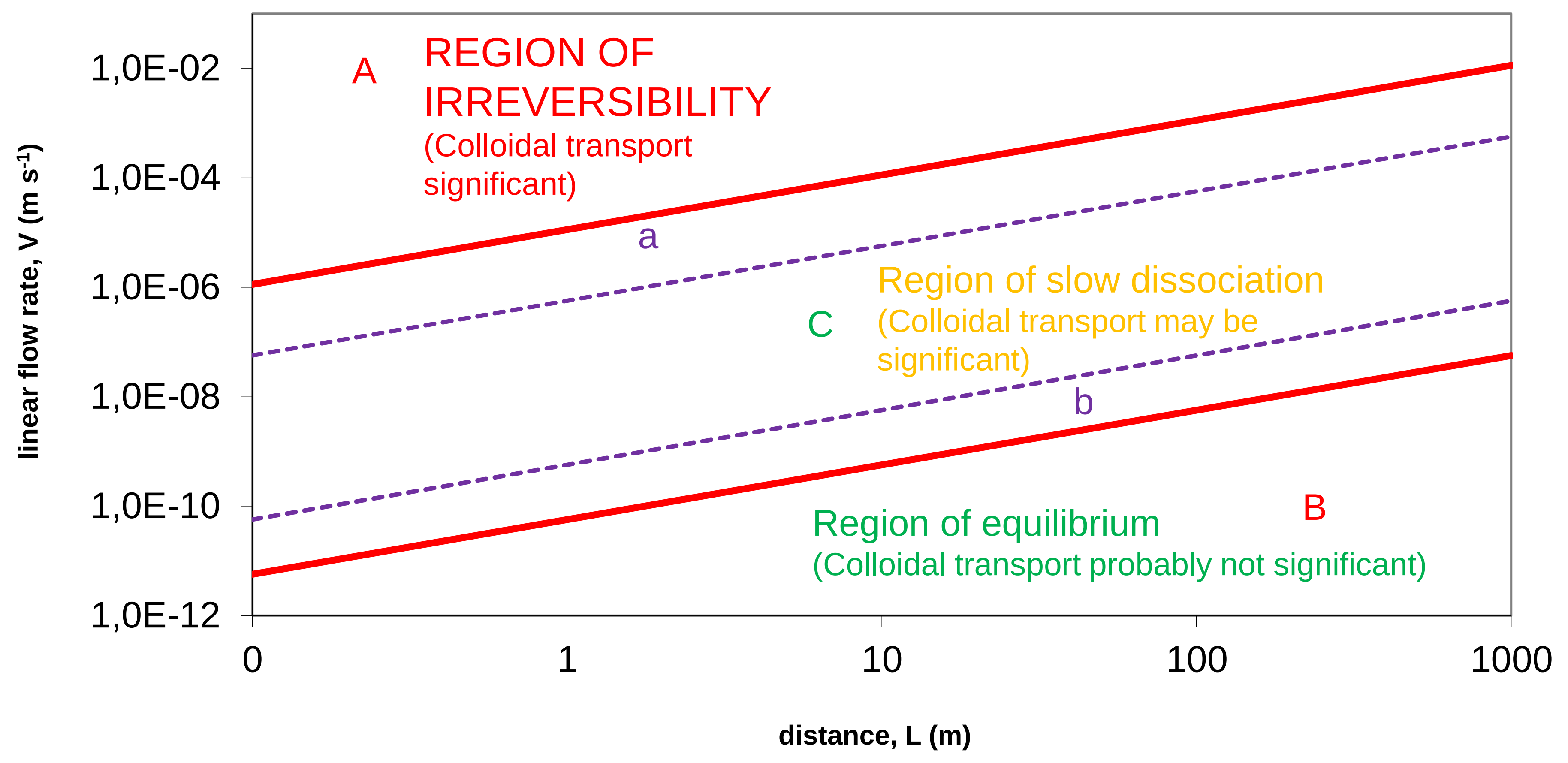
2. Assume complete ‘irreversibility’ at small D, e.g., $D < 0.01$

   INHERENTLY CONSERVATIVE ✓

3. Use kinetic calculation at intermediate D

   CONSERVATIVE ✓

Bulk Damkohler Numbers: limits



A: Assume irreversibility

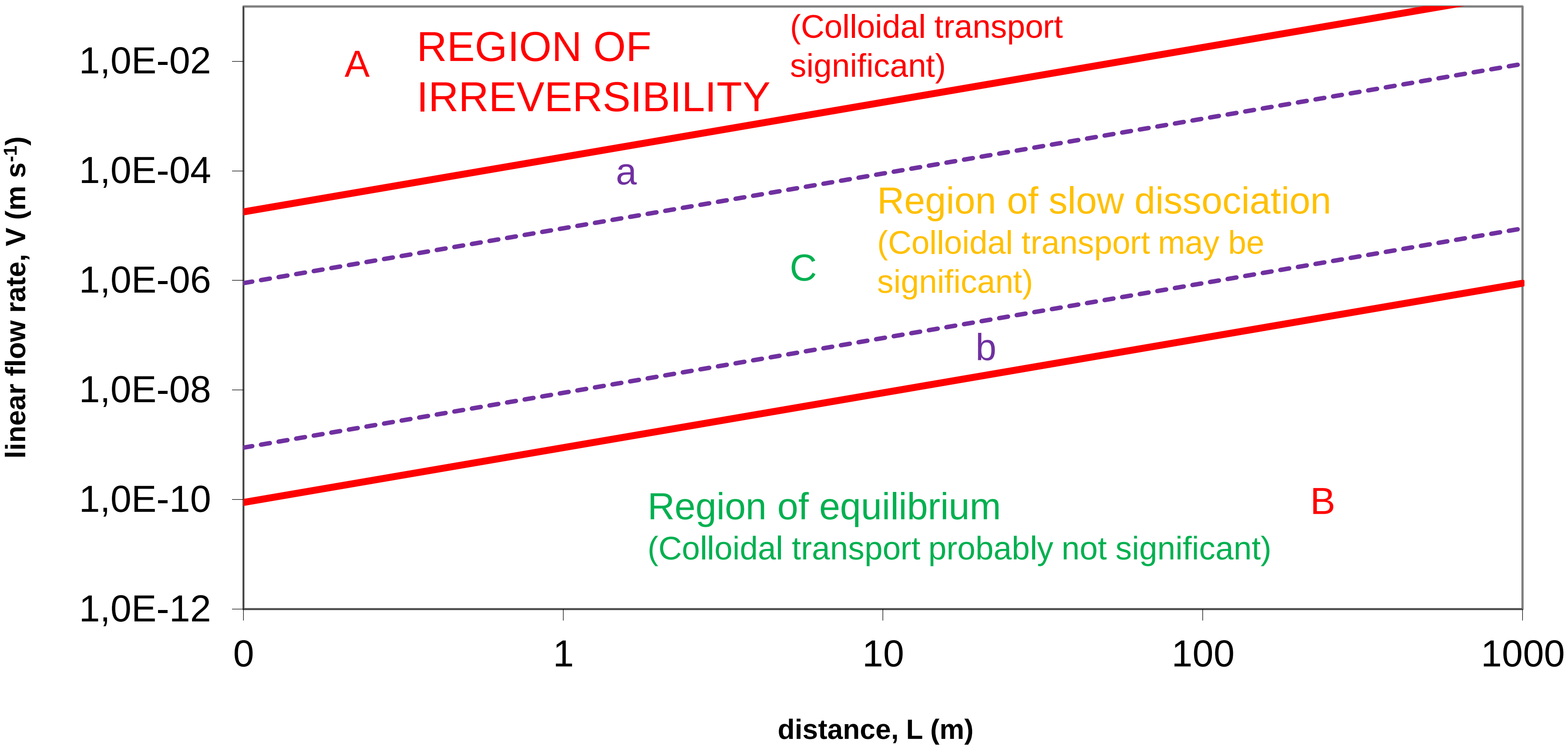
a: Assume irreversibility with care

B: Assume equilibrium (**care**) ?

b: Assume equilibrium (**extra care!**)?

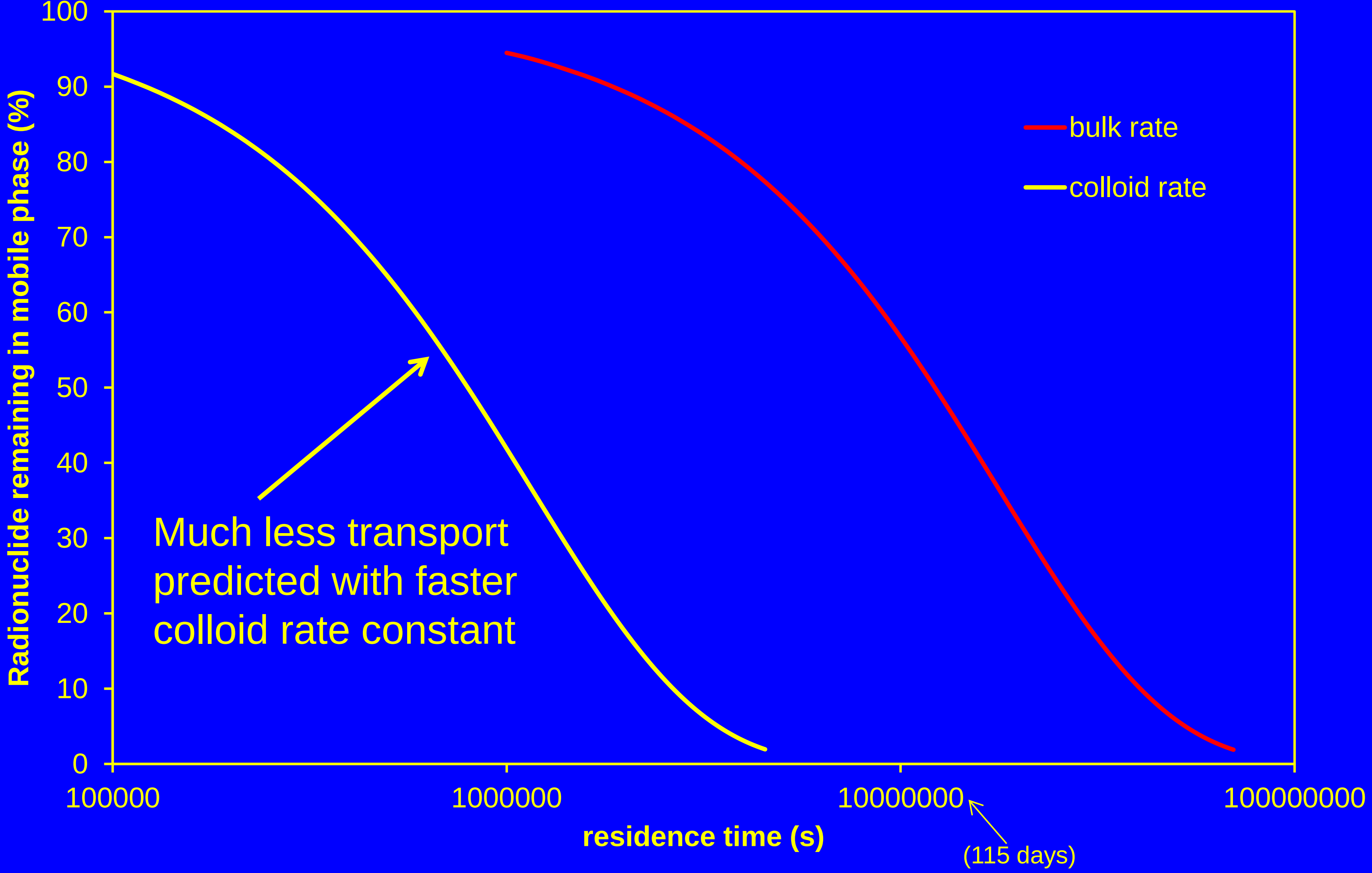
C: Full kinetics or dimensionless approximation

Colloid Damkohler Numbers: limits



Changing the rate constant makes a significant difference to the region where colloidal transport may be significant.

Implications of First Order Rate constants



Much less transport predicted with faster colloid rate constant

Calculations assume that rock surface can outcompete colloid thermodynamically

Conclusions

Trivalent species do show slow dissociation kinetics:
current Eu(III) dissociation rates:
Bulk bentonite = **5.67×10^{-8} s^{-1}** ;
Colloidal bentonite = **8.9×10^{-7} s^{-1}**

More Eu(III) dissociates slowly for colloids than bulk (surprising?), but dissociation is faster (expected?).

Kinetics are simpler for colloids (compared to bulk).

For the colloid rate constant, a residence time of 60 days should reduce the amount colloid bound to < 1%.

Remaining questions (amongst others)

What about tetravalents (experiments underway)?

What is the mechanism? Really need to be able to explain the observed behaviour.

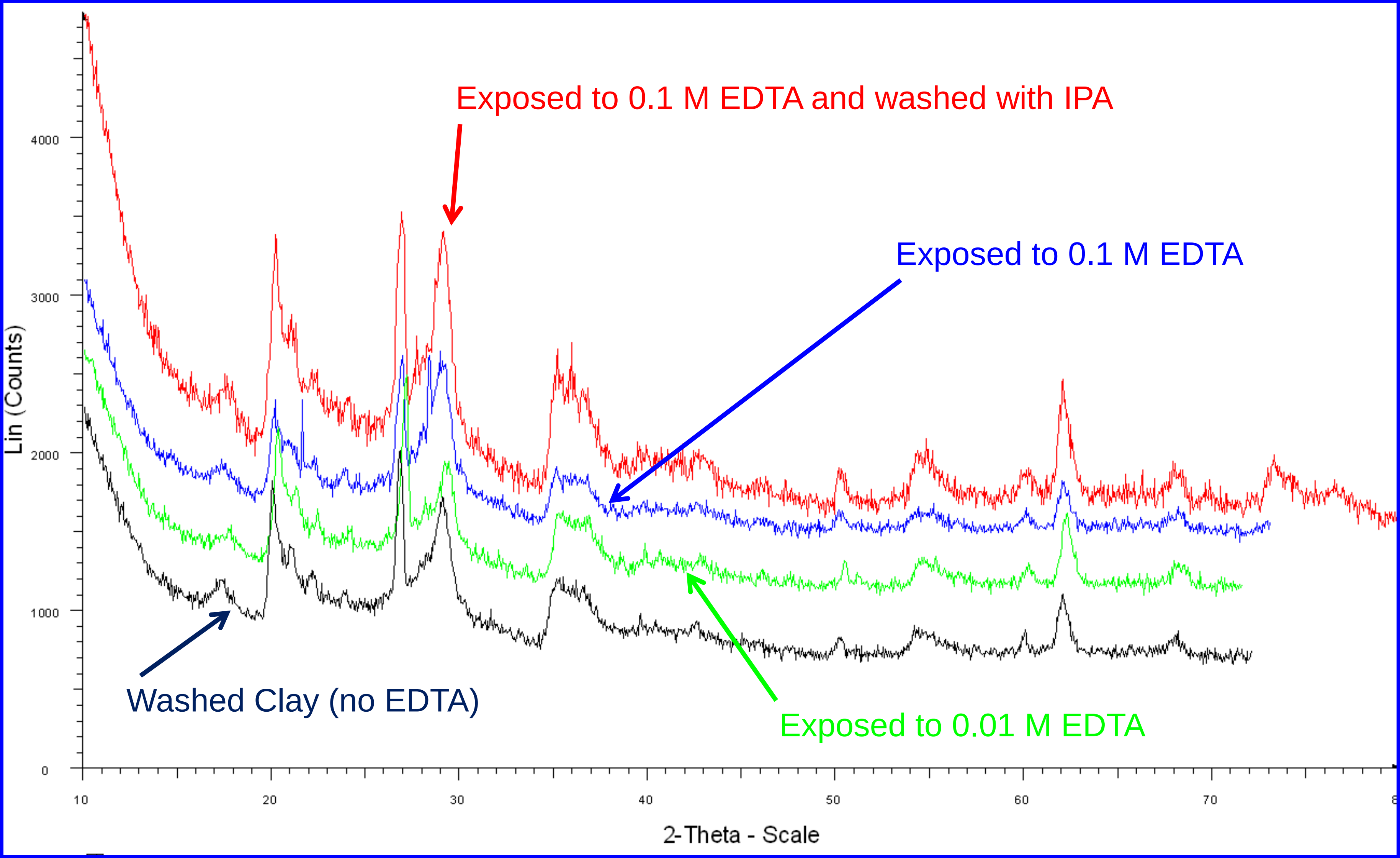
Need to confirm position of thermodynamic equilibrium with (e.g.) fracture material (to confirm that we can ignore exchangeably bound radionuclides.

Acknowledgements

RWM

European Union, BELBaR project

Effect of EDTA on Bentonite: p-XRD



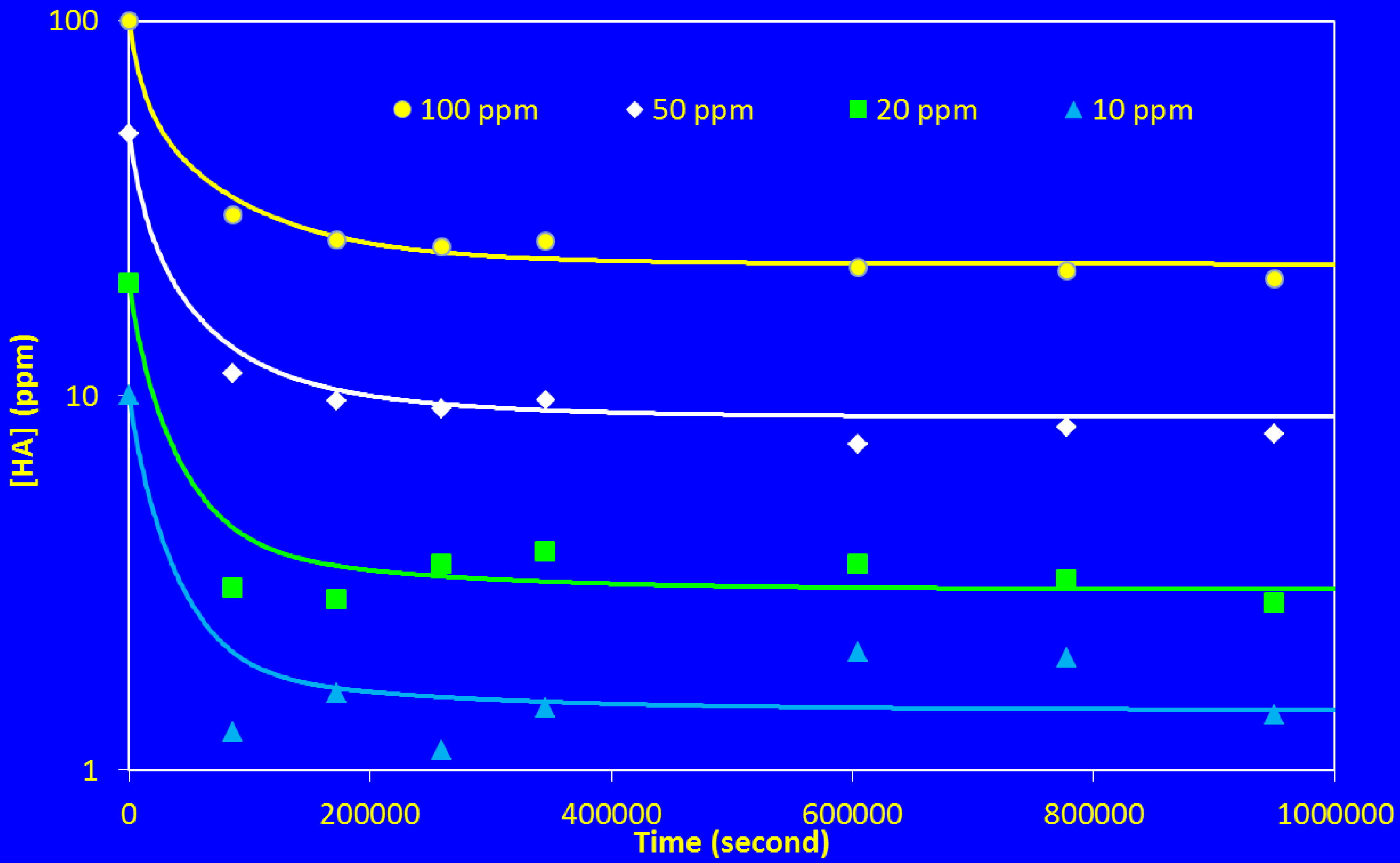
Exposed to 0.1 M EDTA and washed with IPA

Exposed to 0.1 M EDTA

Washed Clay (no EDTA)

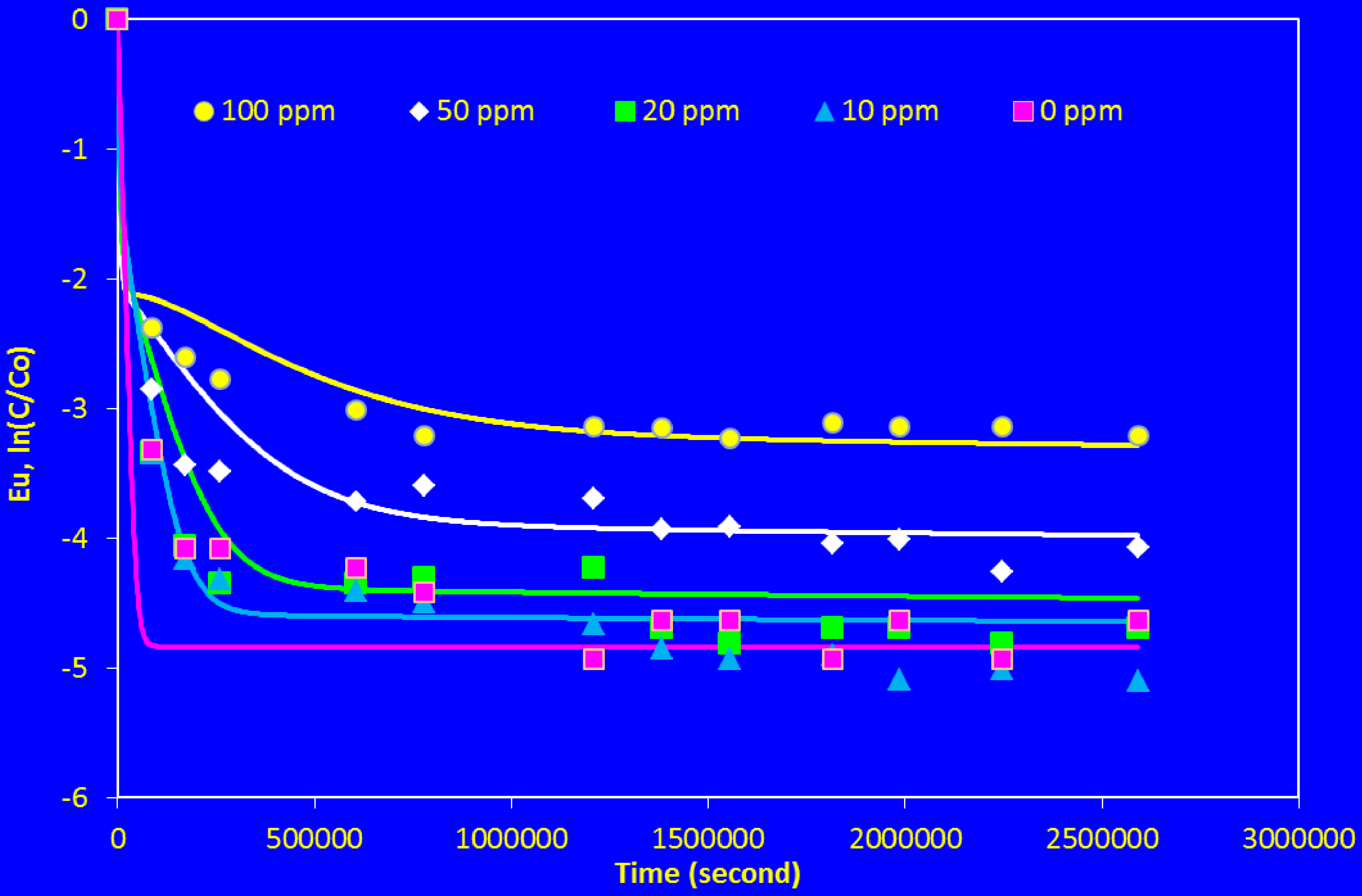
Exposed to 0.01 M EDTA

Humic Uptake on Bentonite



Eu(III) Uptake on Bentonite

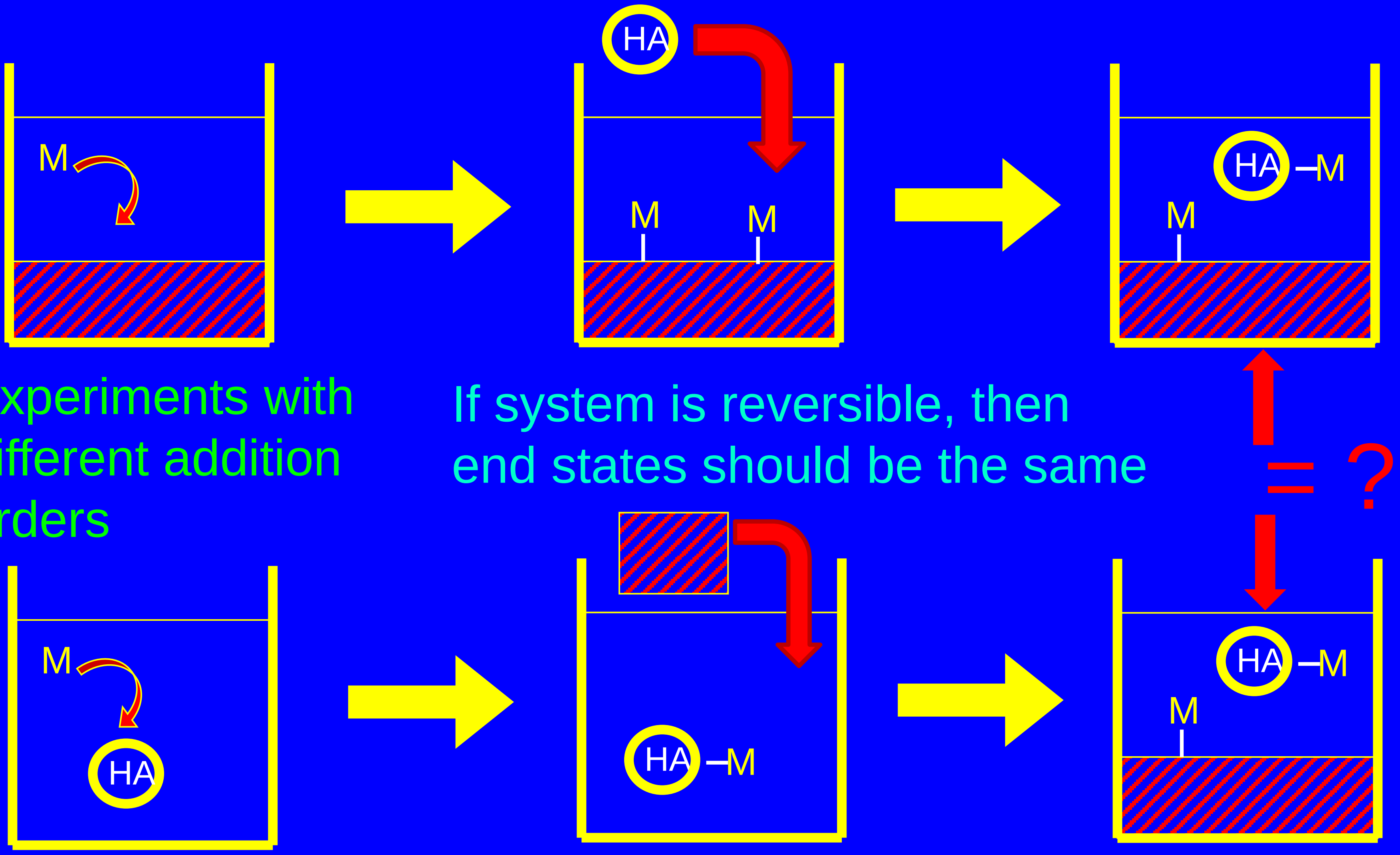
$[Eu_T] = 7.9 \times 10^{-10}$ M; pH = 6.0



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

Reversibility in Ternary Systems

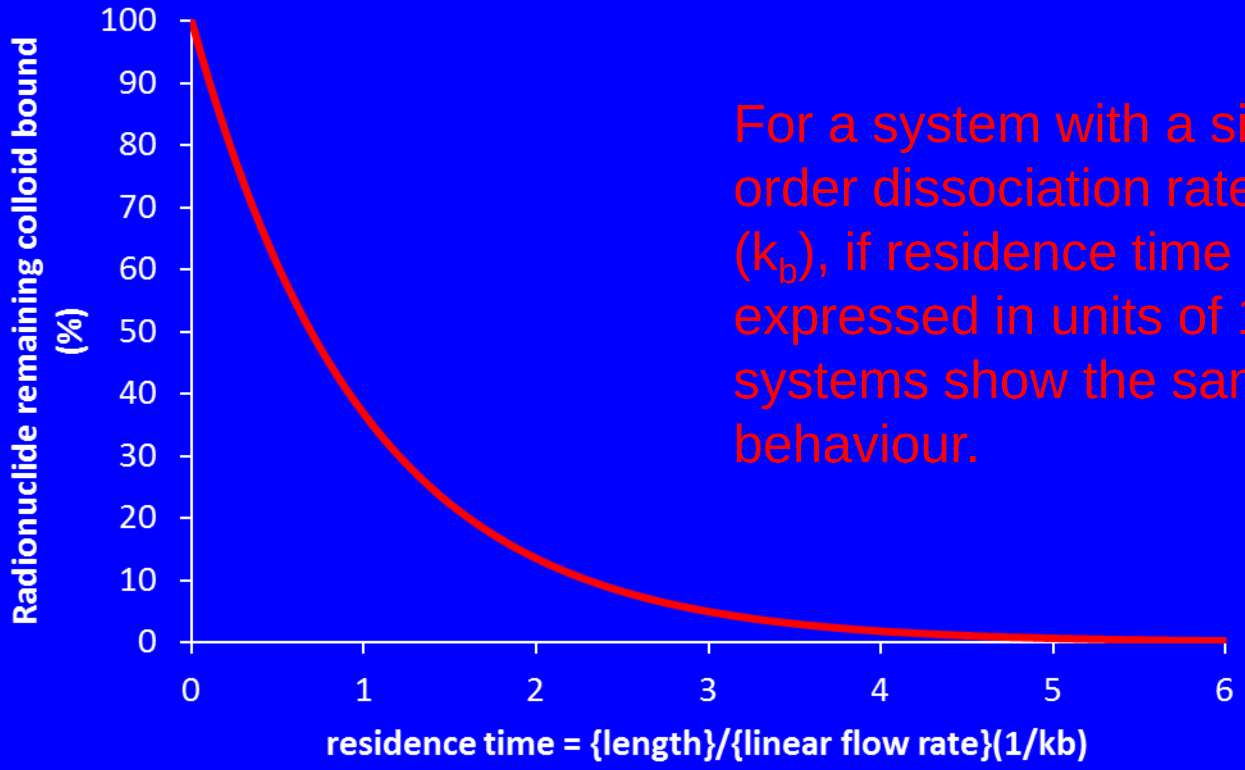
If ternary systems are ‘reversible’, then they should be insensitive to the order of addition. The time taken for systems to recover is an indication of the importance of kinetics.



Experiments with different addition orders

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

Damkohler Numbers (1)



For a system with a single first order dissociation rate constant (k_b), if residence time is expressed in units of $1/k_b$, then all systems show the same behaviour.

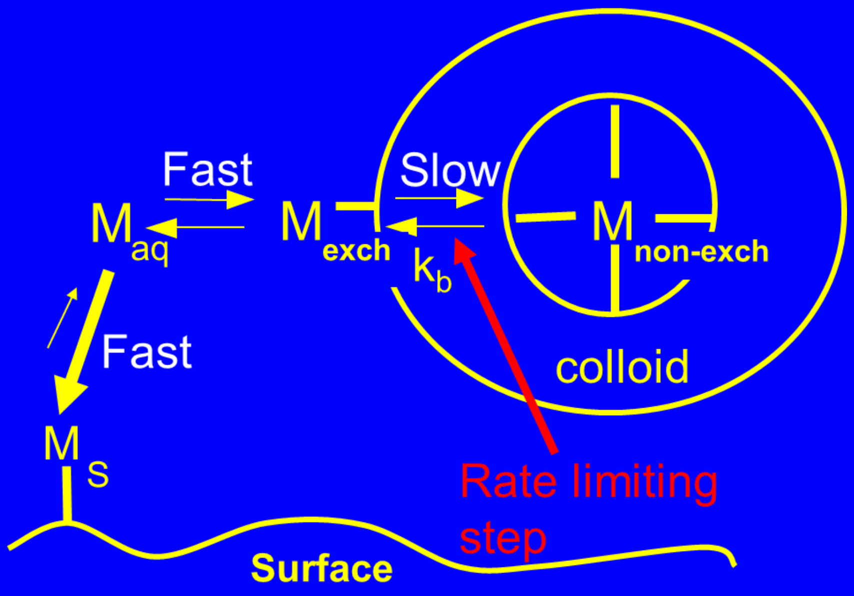
We can define a ‘Damkohler Number’ for each system/reaction:

$$D = \frac{L}{V} k_b$$

L = distance; V = linear velocity

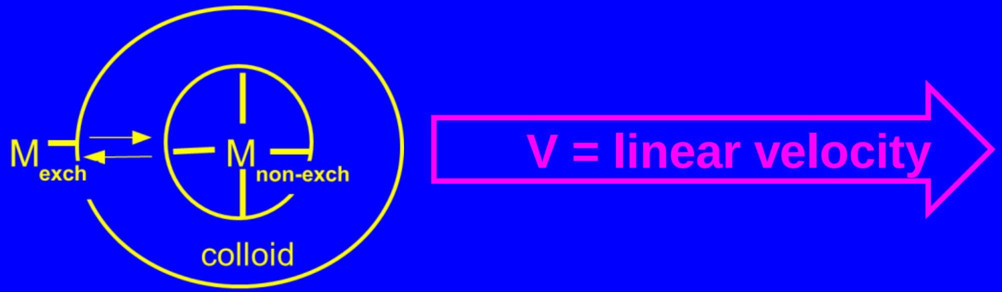
The value of D is a measure of the importance of the kinetics in a given calculation.

Damkohler Numbers in Colloidal Transport



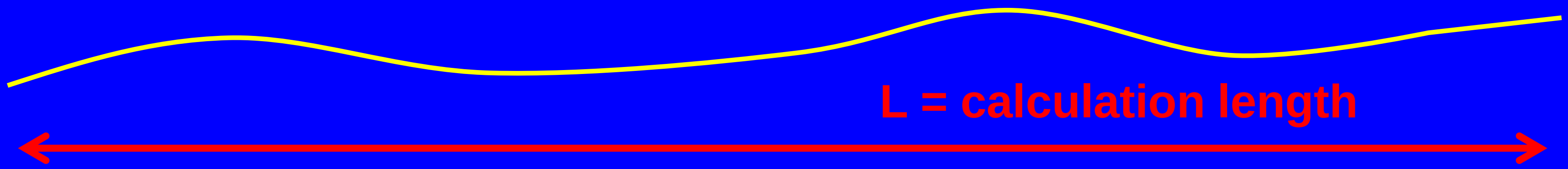
$$M_{exch} \overset{k_b}{\underset{\rightarrow}{\leftarrow}} M_{non-exch}$$

$$\frac{d[M_{non-exch}]}{dt} = k_f[M_{exch}] - k_b[M_{non-exch}]$$

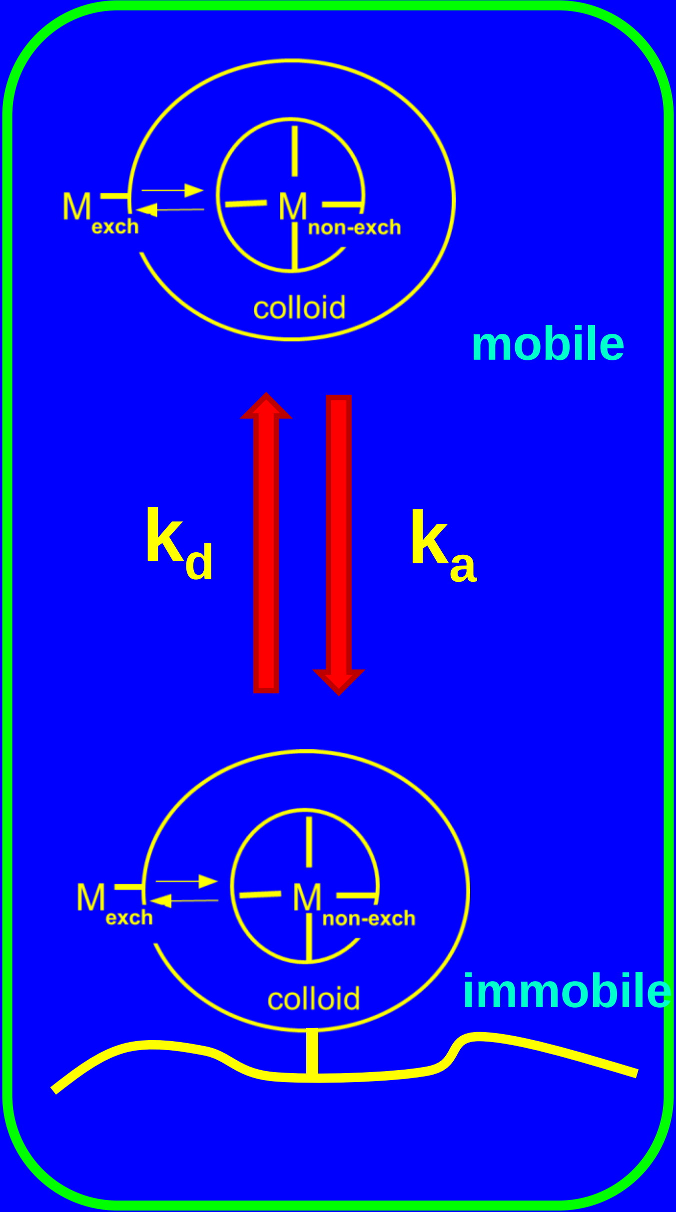


$$t_{res} = \frac{L}{V}$$

$$D_M = \frac{L}{V}k_b$$



Effect of Colloid Sorption on Damkohler Numbers



Interaction of the colloid with a surface will affect transport. For a simple first order attachment/dissociation mechanism:

$$\text{Coll}_{\text{mobile}} \rightleftarrows \text{Coll}_{\text{immobile}}$$

$$\frac{d[\text{Coll}_{\text{immobile}}]}{dt} = k_a[\text{Coll}_{\text{mobile}}] - k_d[\text{Coll}_{\text{immobile}}]$$

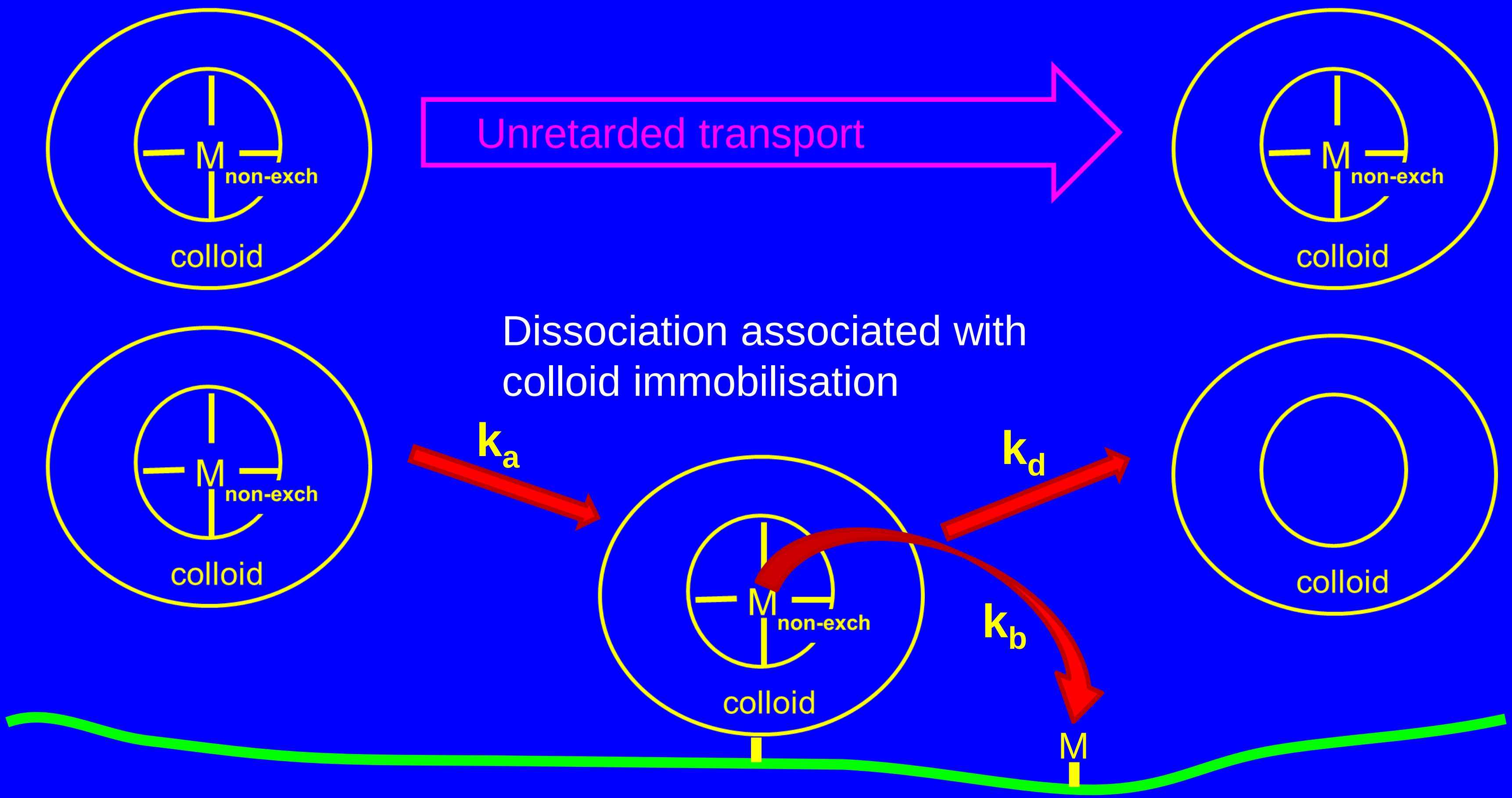
$$K_C = \frac{k_a}{k_d}$$

There will be direct retardation, but there could also be an indirect effect due to the increased residence time.

We can define a Damkohler number for the colloid immobilisation reaction:

$$D_C = \frac{k_a L}{V}$$

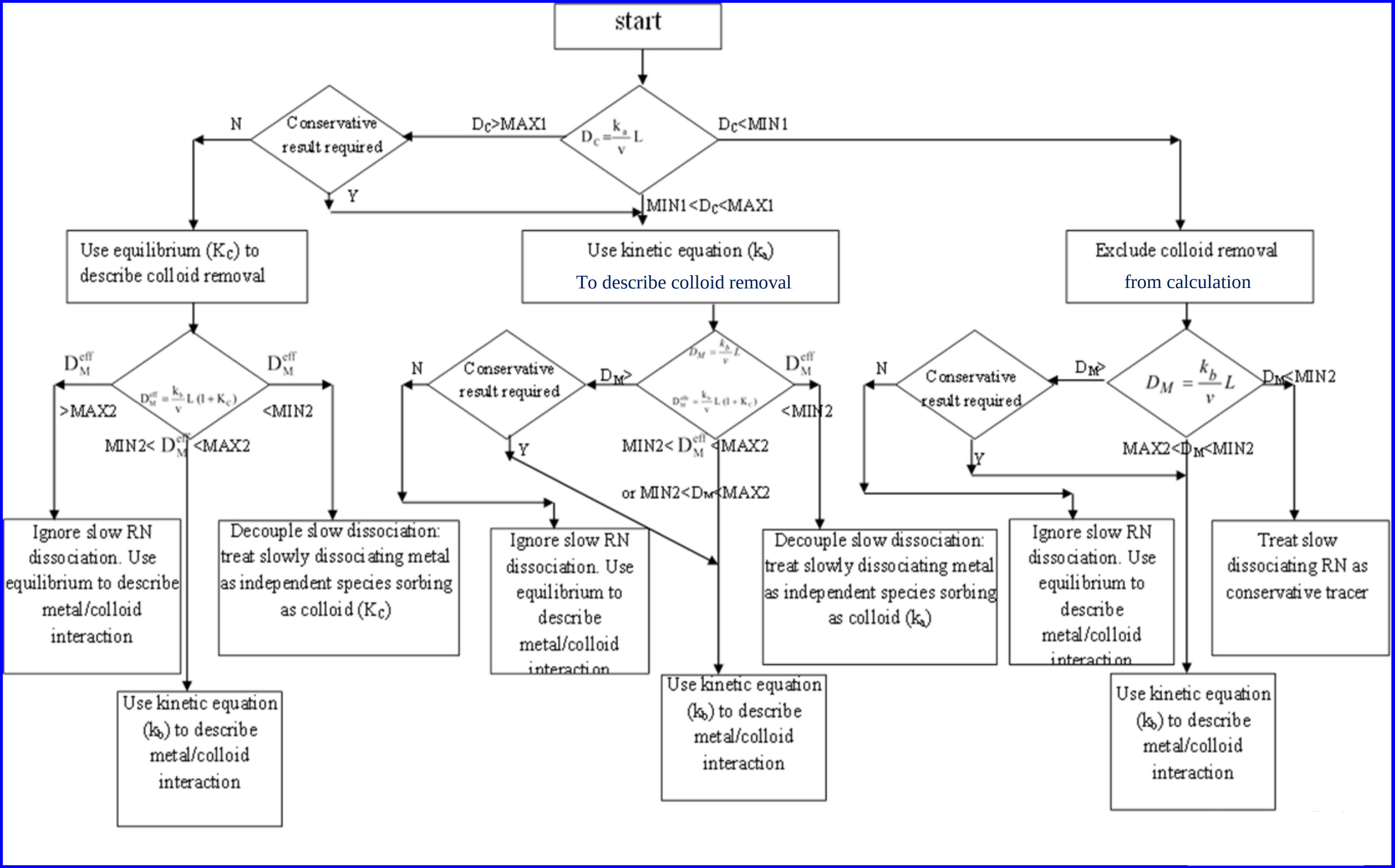
Effect of Colloid Sorption on Radionuclide Transport



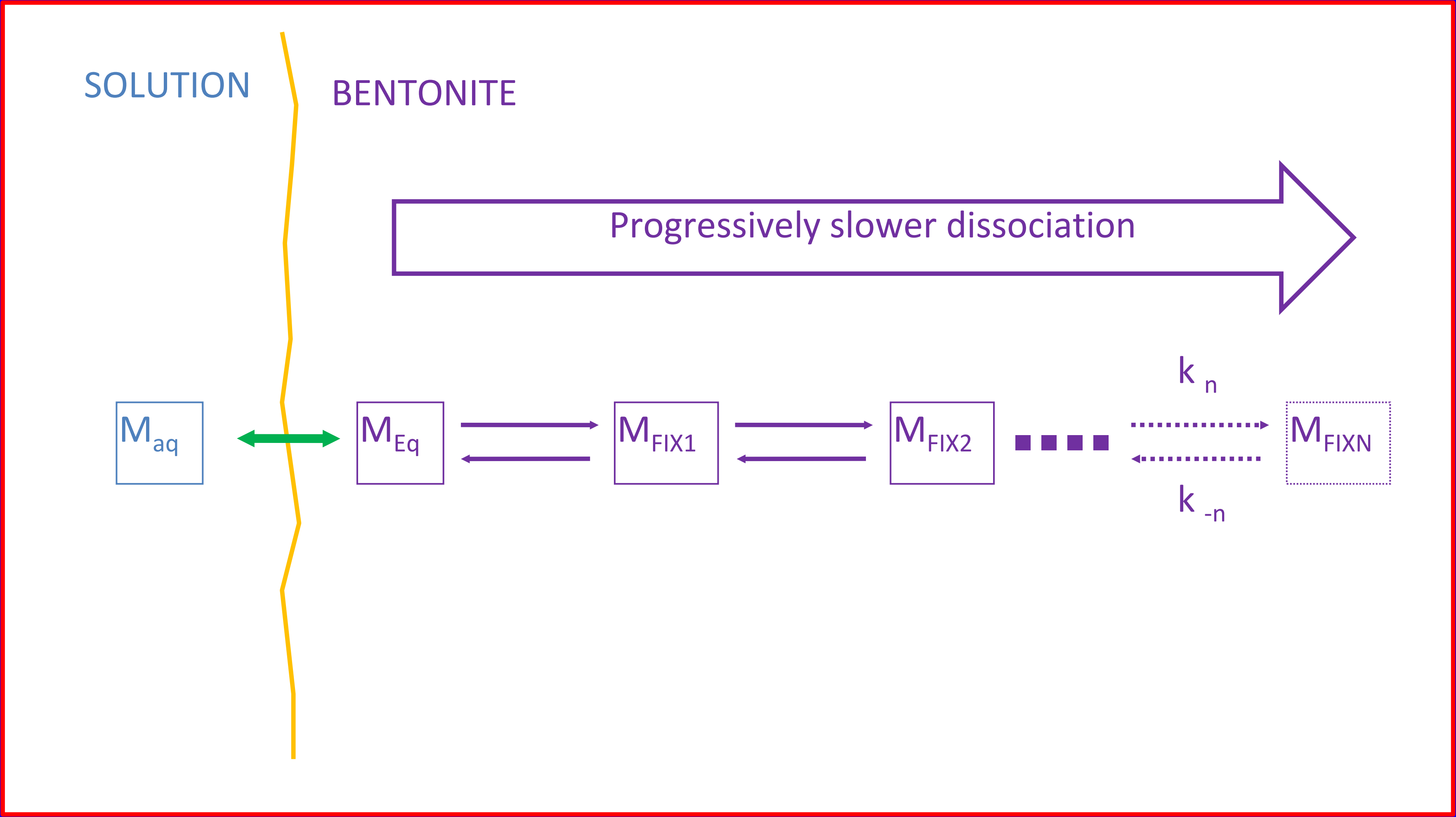
Dissociation associated with colloid immobilisation

$$D_M = \frac{k_b}{V}L\Big|_{D_C\to 0} \xrightarrow{D_C\ \text{increasing}} D_M^{eff} = \frac{k_b}{V}L(1+K_C)\Big|_{D_C\to\infty}$$

Colloid Kinetics in Transport Calculations

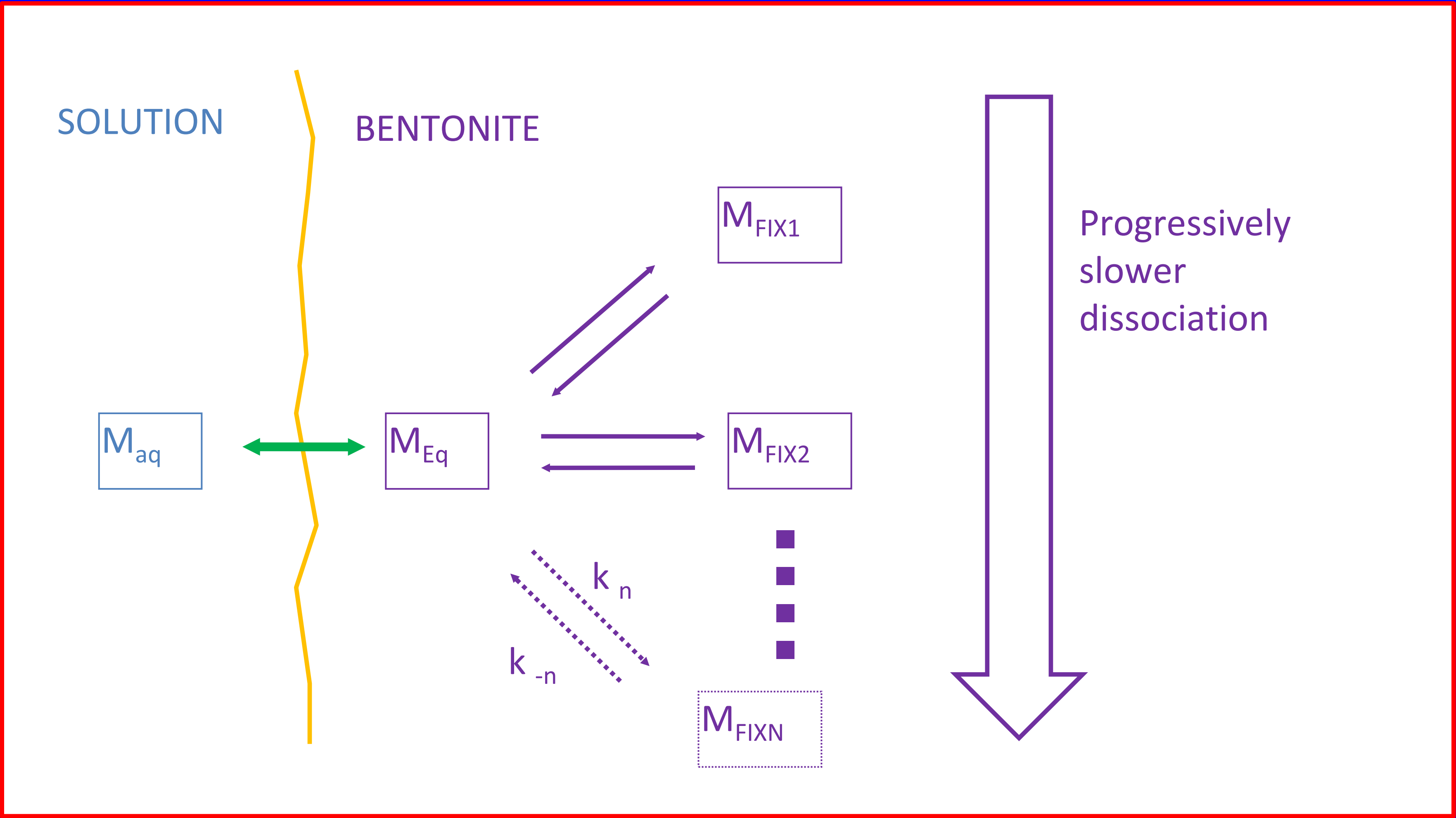


Complications:
multiple slow dissociating fractions (in series).

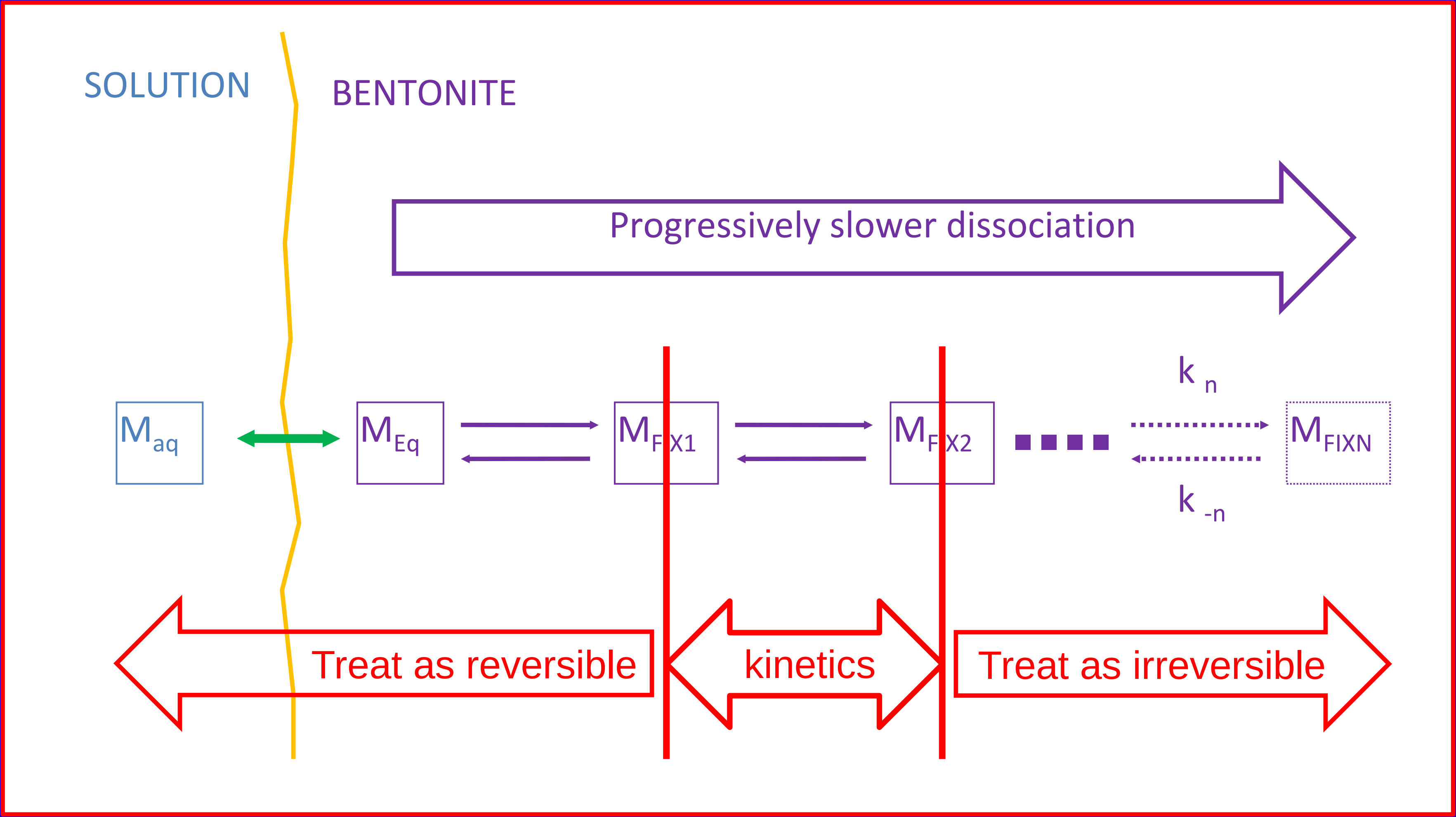


Complications:

multiple slow dissociating fractions (or parallel).



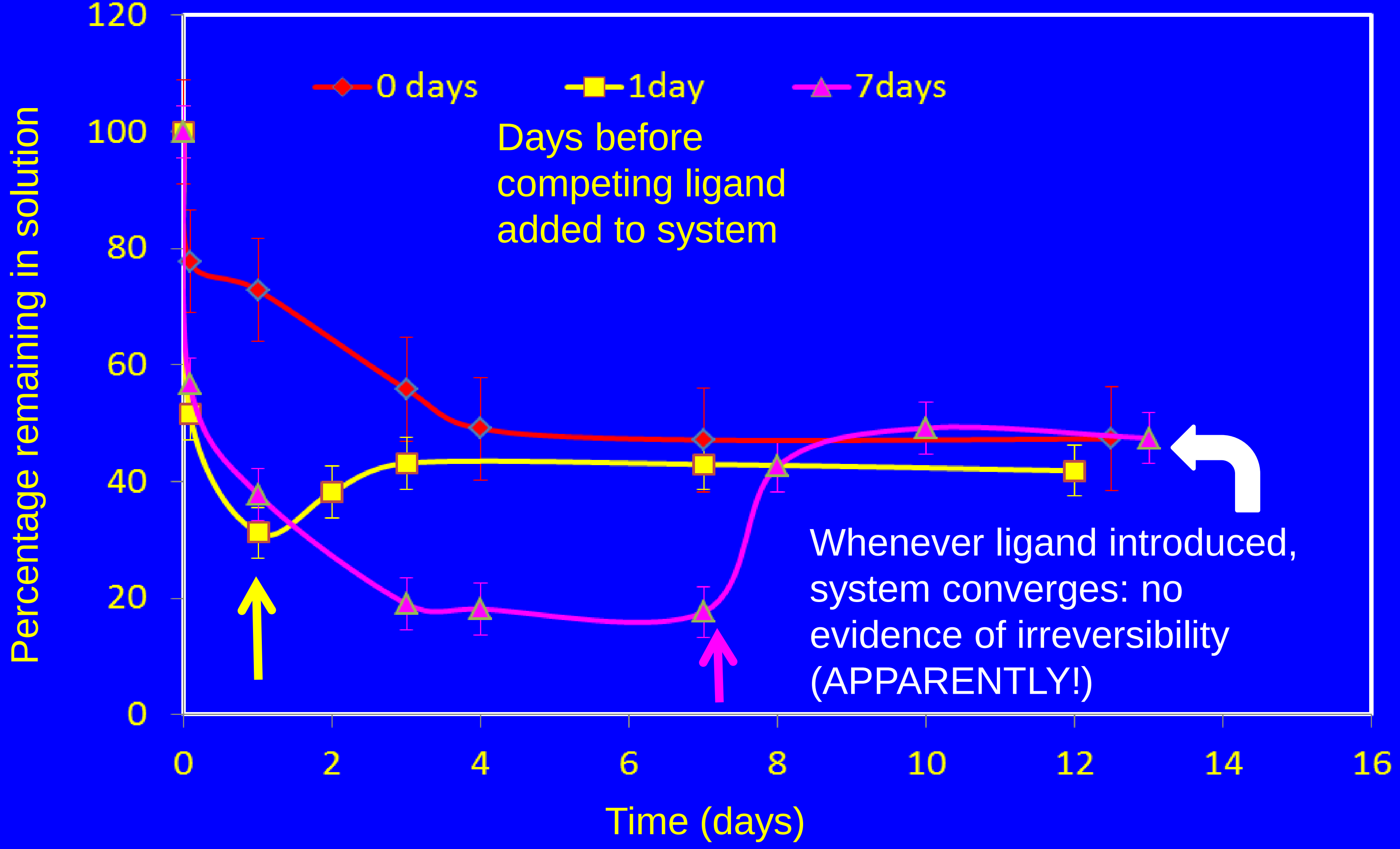
Multiple Slow Dissociating Fractions:



Even in a system with multiple fractions, it is still possible to use the Damkohler procedure to partition the reactions.

U(VI) Bentonite Irreversibility test

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



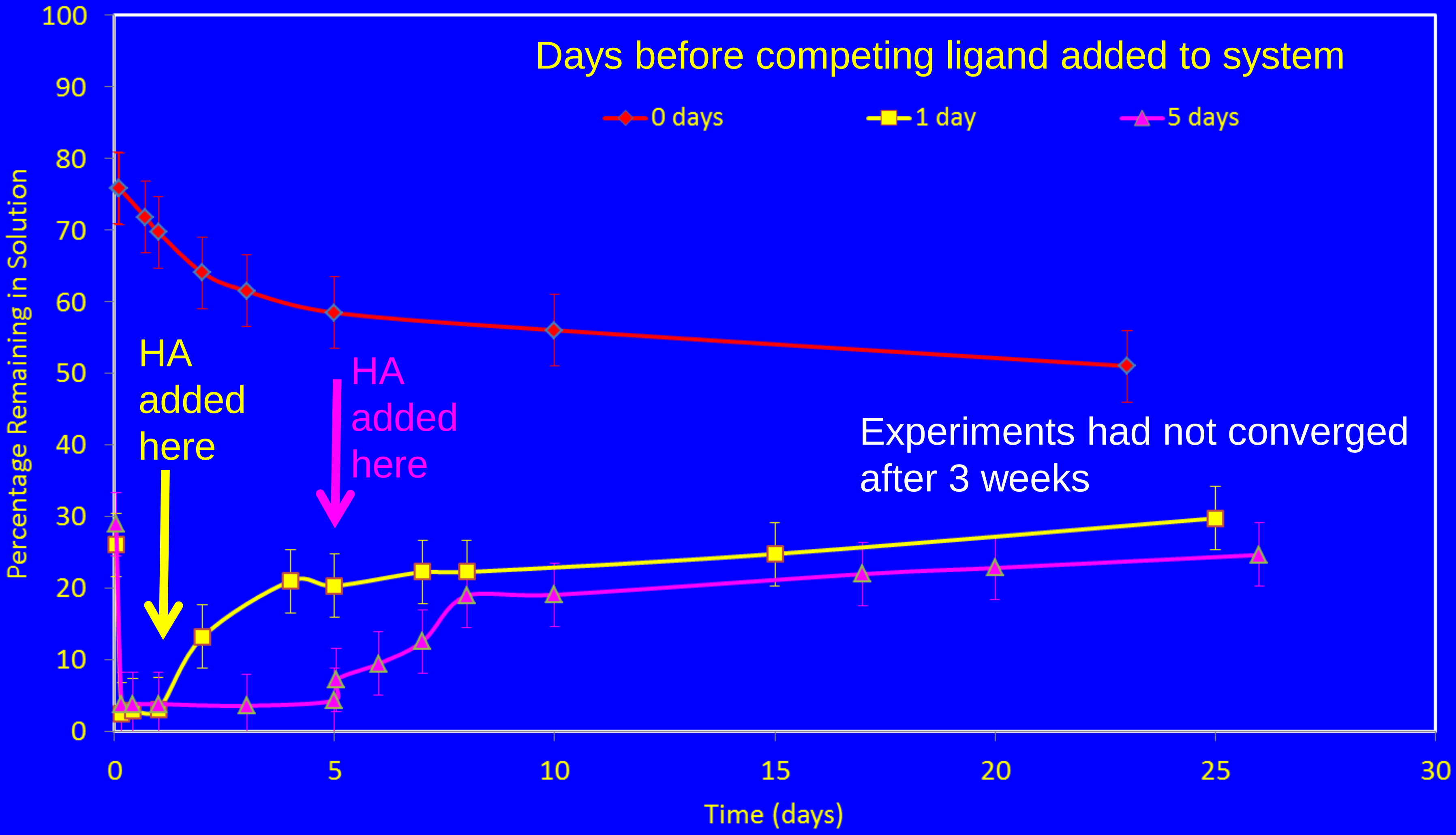
Days before competing ligand added to system

Whenever ligand introduced, system converges: no evidence of irreversibility (APPARENTLY!)

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

Pu(III) Bentonite Irreversibility test

[Pu] = 3.7x10^{-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.

Colloid Kinetics in a Safety Case (2)

For a given flow rate, distance, time etc. there will be just three classes of reaction:

1. Fast enough to be effectively equilibria;
2. So slow that they do not take place (irreversibility);
3. Intermediate (need a kinetic description).