Modeling of Glass Performance in Repository Environments — An International Perspective

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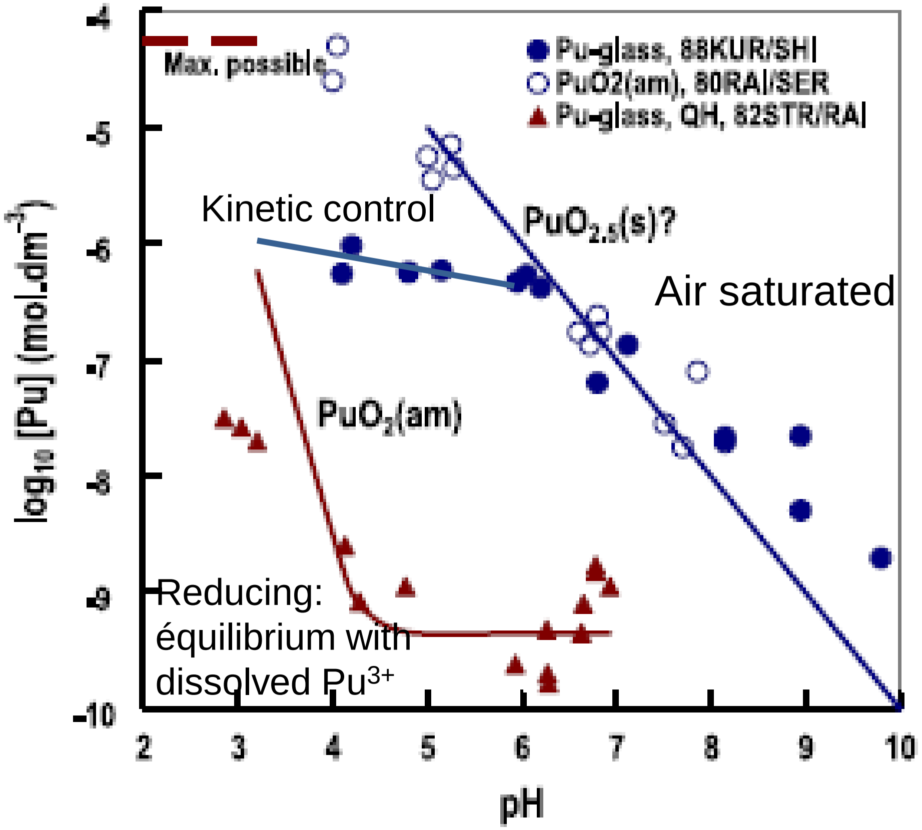
SUBATECH, France

Controls for radionuclide release during glass dissolution

- Radionuclide concentrations adjacent to a slowly dissolving glass may be controlled by the
  - **kinetics of glass dissolution**
  - **Sorption on solid reaction products**
  - **Solubility constraints of secondary phases (pure phases or solid solution)**
- Which mechanism dominates, depends on radionuclide and environmental conditions, soluble radionuclides are kinetically controlled
- Solubility constraints are difficult to assess since frequently solid solutions are formed and solid phases are amorphous or poorly crystalline.
  - However: often simple solid reaction products describe well solution behavior
- Exemple
  - Cs is more soluble than the actinides, hence, Cs release might be controlled by glass dissolution kinetics, while actinide release is controlled by solubility constraints
- Glass model in Report ANL-EBS-MD-00016 ignores radionuclide solubilities
  - “The release rate of a particular radionuclide can be calculated by multiplying the glass dissolution rate by the total surface area of glass that can be contacted by water and by the inventory of that radionuclide in the glass (e.g., Curies per g glass). The radionuclide inventory must be obtained from Initial Radionuclide Inventories (BSC 2004 [DIRS 170022]))”.
  - It is not « **defense in depth** », it is unrealistic
  - The reference pH 10 is not conservative related to actinides

Solubility control for Pu release from borosilicate glass powder



Lowest Pu solubility at pH 10

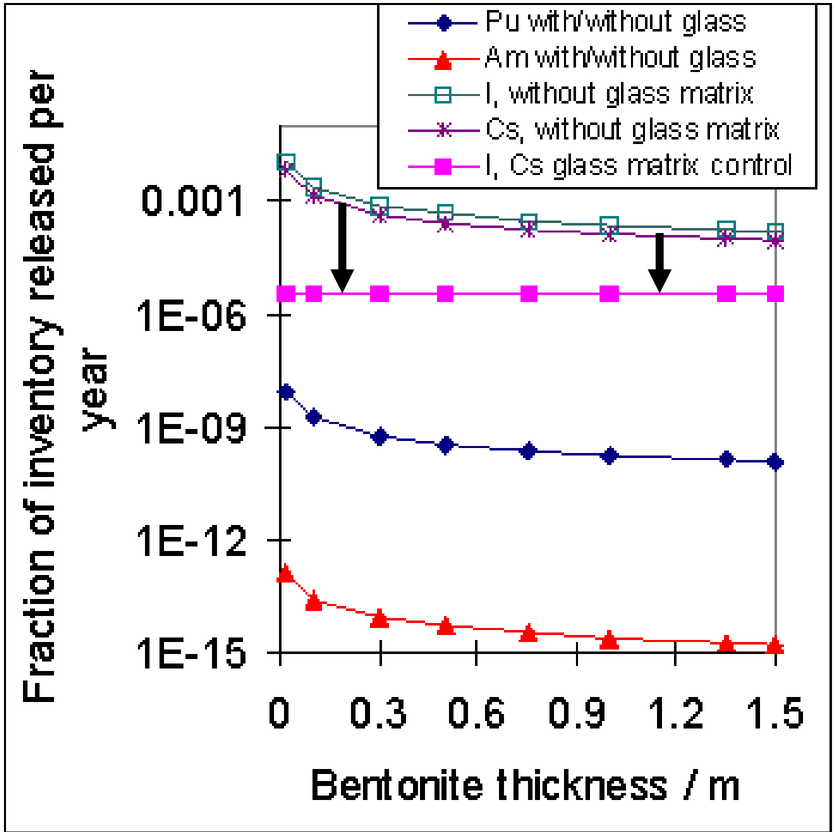
For Pu release at pH>4 under reducing conditions, the glass dissolution rate is insignificant

(Rai, Yui, Grambow 2011)

Fig. 6 Comparison of aqueous Pu concentrations in solutions from (1) Pu-doped glass (Kuroha et al. [42], *solid circles*) equilibrated with 0.1 mol·L^{-1} $NaNO_3$ for >151 days in air, and (2) PuO_2(am) (Rai et al. [43], *open circles*) equilibrated with 0.0015 mol·L^{-1} $CaCl_2$ for 90 days in air. The data in Kuroha et al. [42] may be interpreted based on equilibrium with $PuO_{2.5}$(s) (shown by the *upper solid line* based on data in Table 2) or PuO_2(am), see text for details. The *lower solid line* portrays predicted Pu^{3+} concentrations in equilibrium with PuO_2(am) (Table 2) for Strickert and Rai's [41] data (*solid triangles*), see text for details. The *line labeled "Max. possible"* corresponds to maximum Pu concentrations achievable if all of the Pu present in the glass is solubilized under the experimental conditions of Strickert and Rai [41]

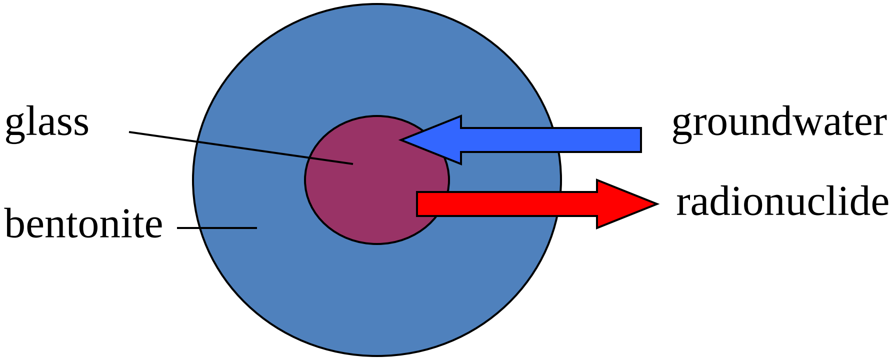
Relative importance of barriers :

- Glass corrosion rate
- Diffusion of RN in bentonite
- Weak solubility of Am, Pu
- Sorption



What limits release more effectively

Glass or bentonite ?



Conclusion:

Decay of Pu, Am within few cm

Glass important for Cs, I, …

Coupling of glass dissolution, Pu solubility and near field transport of Pu and Cs

- Fully radioactive waste glass sourrounded by compacted bentonite. Diffusion of ^{239}Pu and ^{137}Cs. Experimental and model data are similar, using a K_d of 0.01 for Cs and 10 m^3/kg for Pu (Ashida 1998)

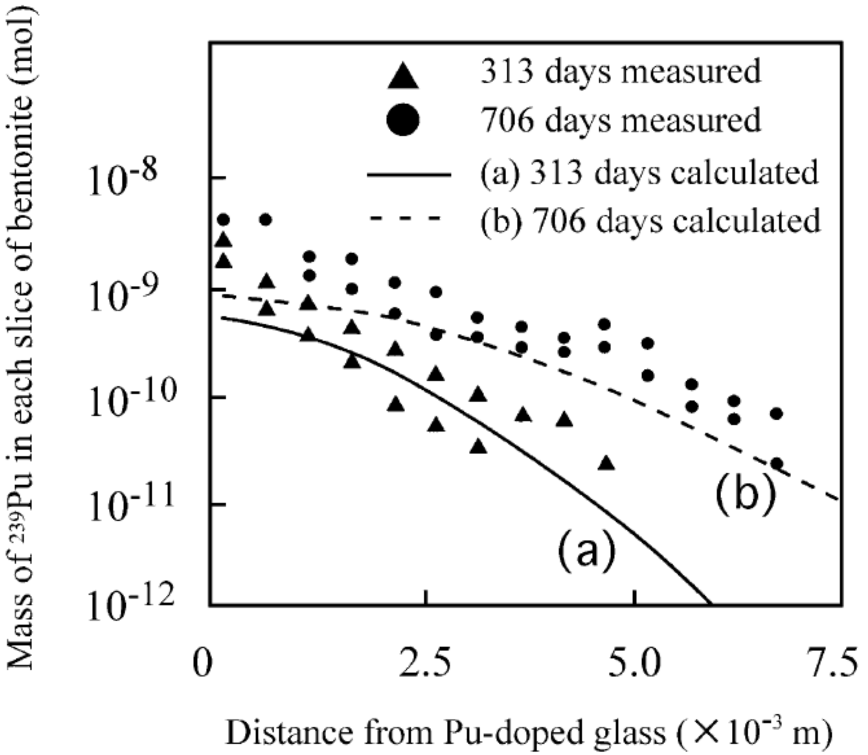


Fig. 5. Measured profiles of quantity of ^{239}Pu in each slice of bentonite and results of independent transport blind predictions (the thickness of each slice: 0.5 mm).

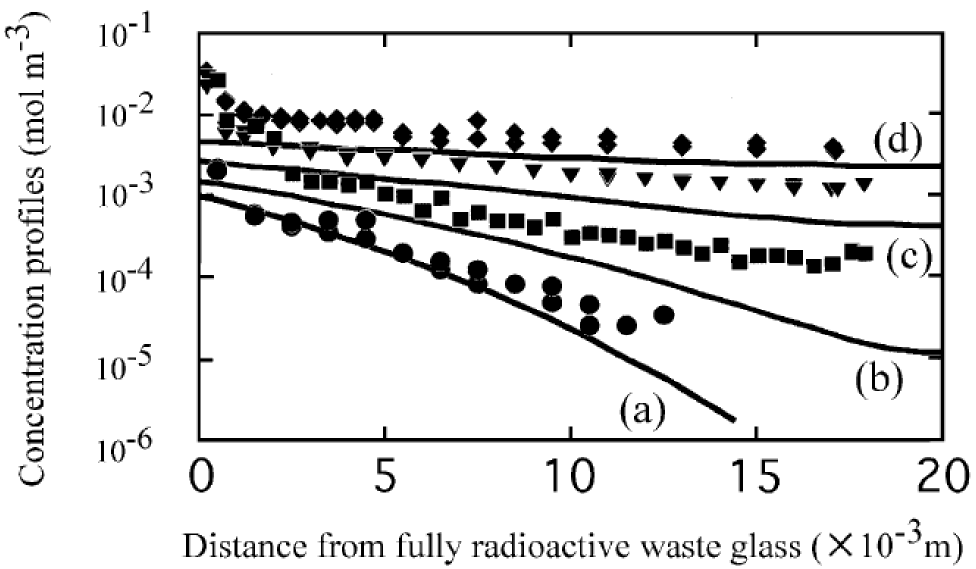


Fig. 6. Measured concentration profiles for ^{137}Cs in compacted bentonite at experimental periods of 15(●), 35(■), 110(▼) and 300(◆) days and modeling results for a dry density of 1000 kg m^{-3}. Concentration profiles by independent calculation are represented as lines (a)–(d) for each period.

Defense in depth

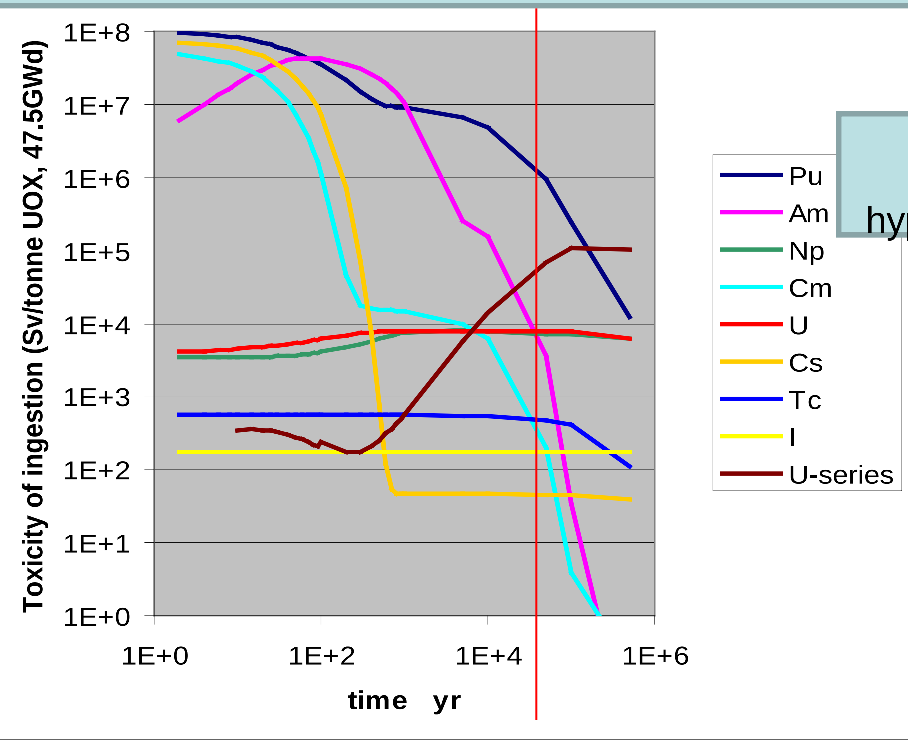
- In many PA of repository concepts, glass dissolution rates control only dose contribution of few (if any) radionuclides
- For dose contributions of other radionuclides, it is sometimes suggested that glass may provide an additional (redundant) barrier: ***defense in depth***

- ***….but….***
    - Controls like solubility or sorption are very solid concepts, if they are not reliable to the extend to abandon them, the glass will help neither
    - The burden loaded on glass would be way to high if one would assume that the kinetics of glass dissolution controlls actinide and Tc release

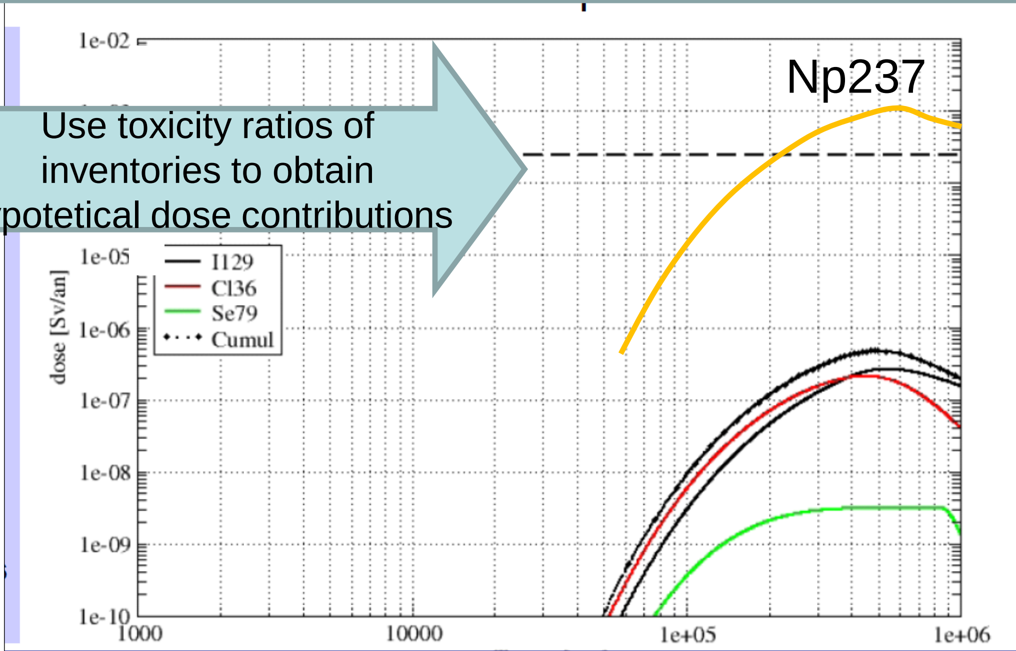
What would happen if all radionuclides would behave like iodine? Release control by glass:

1) Toxicity of various radionuclides relative to Iodine

2) Analysis of dose from glass by ANDRA considering the whole repository barrier chain and that only 1% of Iodine from waste is in the glass



Use toxicity ratios of inventories to obtain hypotetical dose contributions



Nuclear waste glass, Bure, Dossier 2005 ANDRA

Safety case : **weak contribution of actinides to disposal risk in clay**

- decay of Pu, Np and Am in near field and weak solubility and strong retention and filtration of colloids

- Actinides and Tc would be very close to release limits if they whould behave like Iodine : the kinetics of glass dissol.contributes insufficiently to defense in depth in clay rock

Question 1

- 1a) What are the various approaches to modeling glass corrosion in repository environments
- 1b) and how do different countries take account of glass corrosion and radionuclide release in repository performance assessments?

Question 1a

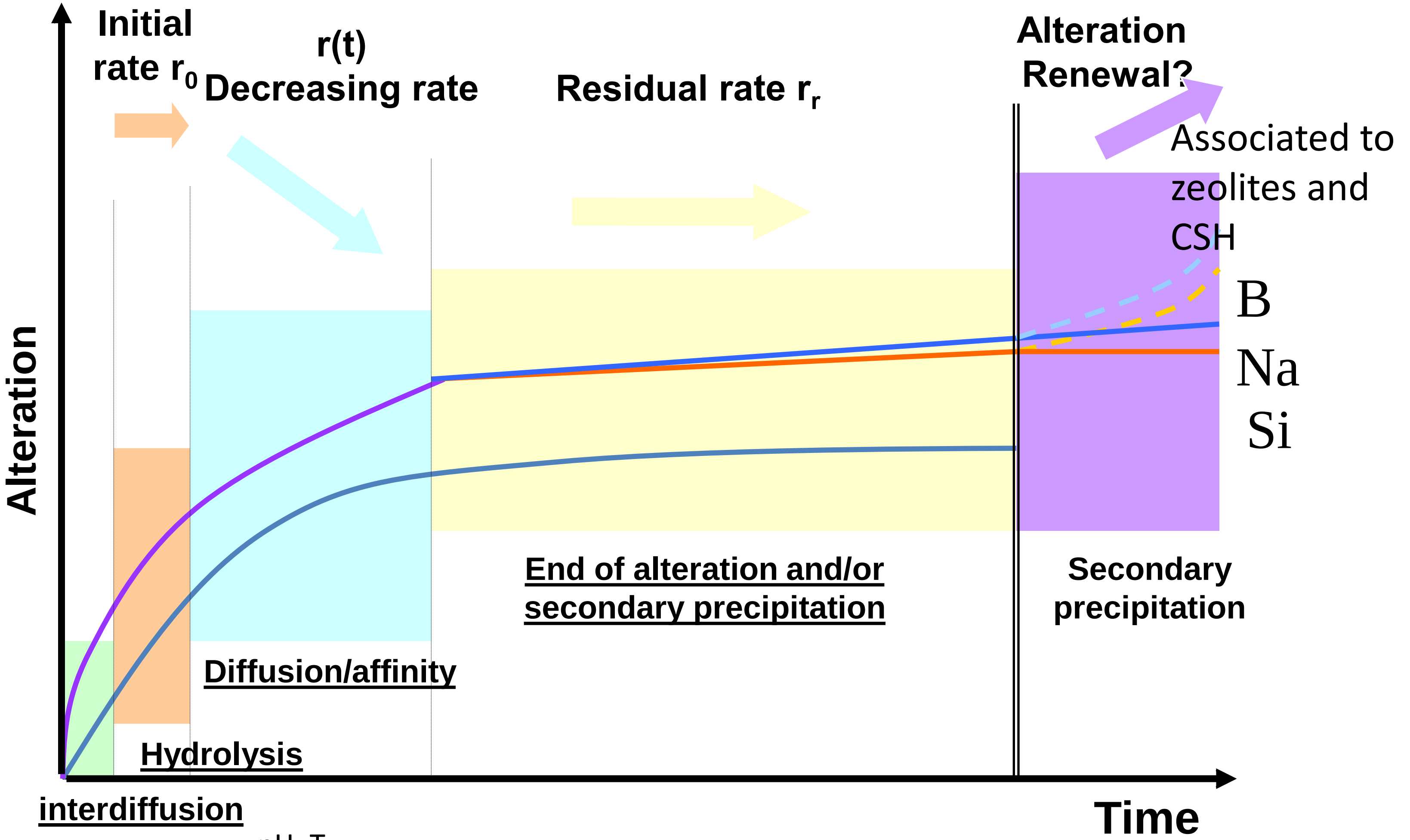
- What are the various approaches to modeling glass corrosion in repository environments ?

Dissolution mechanisms of HLW glass – General scheme

Knowlege base + ++ 2000-2006 strong dispute today accord on interplay of both processes

still only empirical knowledge with qualitative explanations

may only exist for specific glass types and environments (alkaline?)



Initial rate r_0

r(t) Decreasing rate

Residual rate r_r

Alteration Renewal?

Associated to zeolites and CSH

<u>interdiffusion</u>

<u>Hydrolysis</u>

<u>Diffusion/affinity</u>

<u>End of alteration and/or secondary precipitation</u>

Secondary precipitation

Repository environment

pH, T, glass

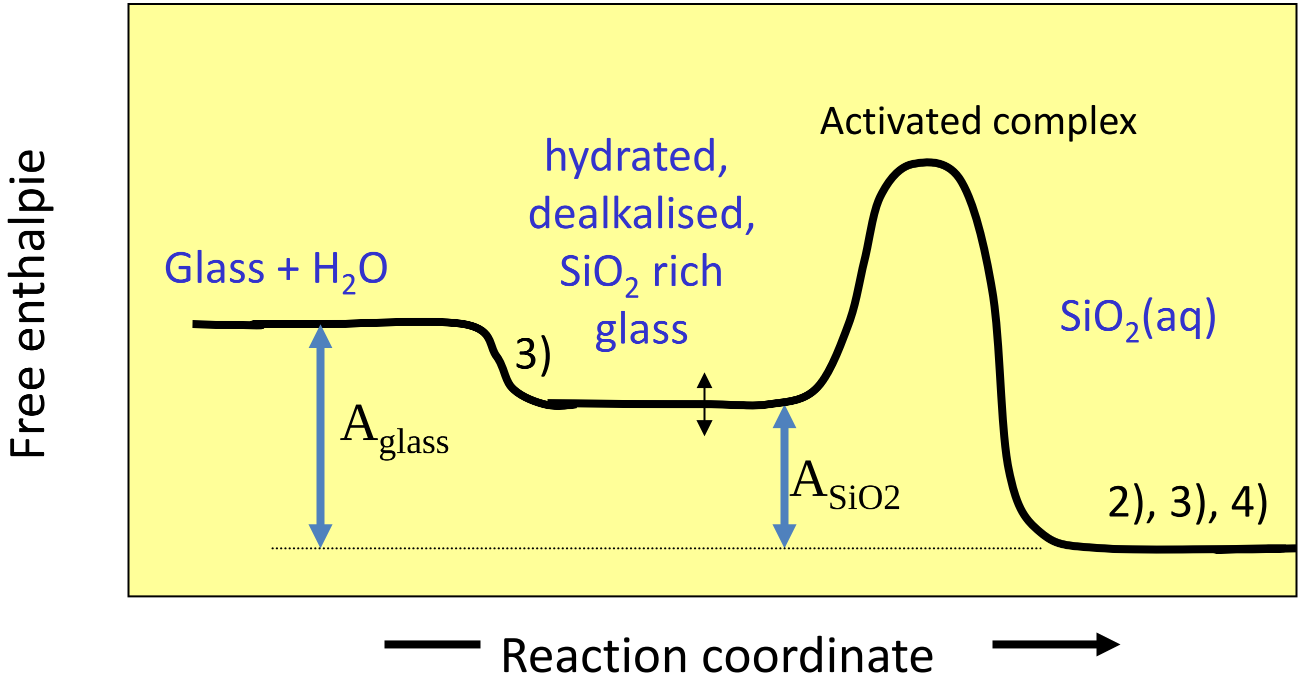
pH, T, glass, V Flow, iron, clay

pH, T, glass

alkaline conditions

Glass dissolution model : irreversible thermodynamics Affinity of glass matrix corrosion coupled to diffusion

- Hypothesis: local equilibrium for surface reactions
- no equilibrium between glass and solution, $A_{glass}>0$



Additional processes considered in GM2003:

1) Mass transfer resistance for Si in gel
2) Adsorption of Si in gel
3) Diffusion H_2O
4) Variation pH

First order rate law

$$r = \vec{r}_1 \cdot \left(1 - \exp\left(\frac{A_{SiO2}}{RT}\right)\right) + r_2(t) = \vec{r}_1 \cdot \left(1 - \frac{C_{Si(aq)}}{C_{Si,sat}}\right) + \boxed{r_2(t)}$$

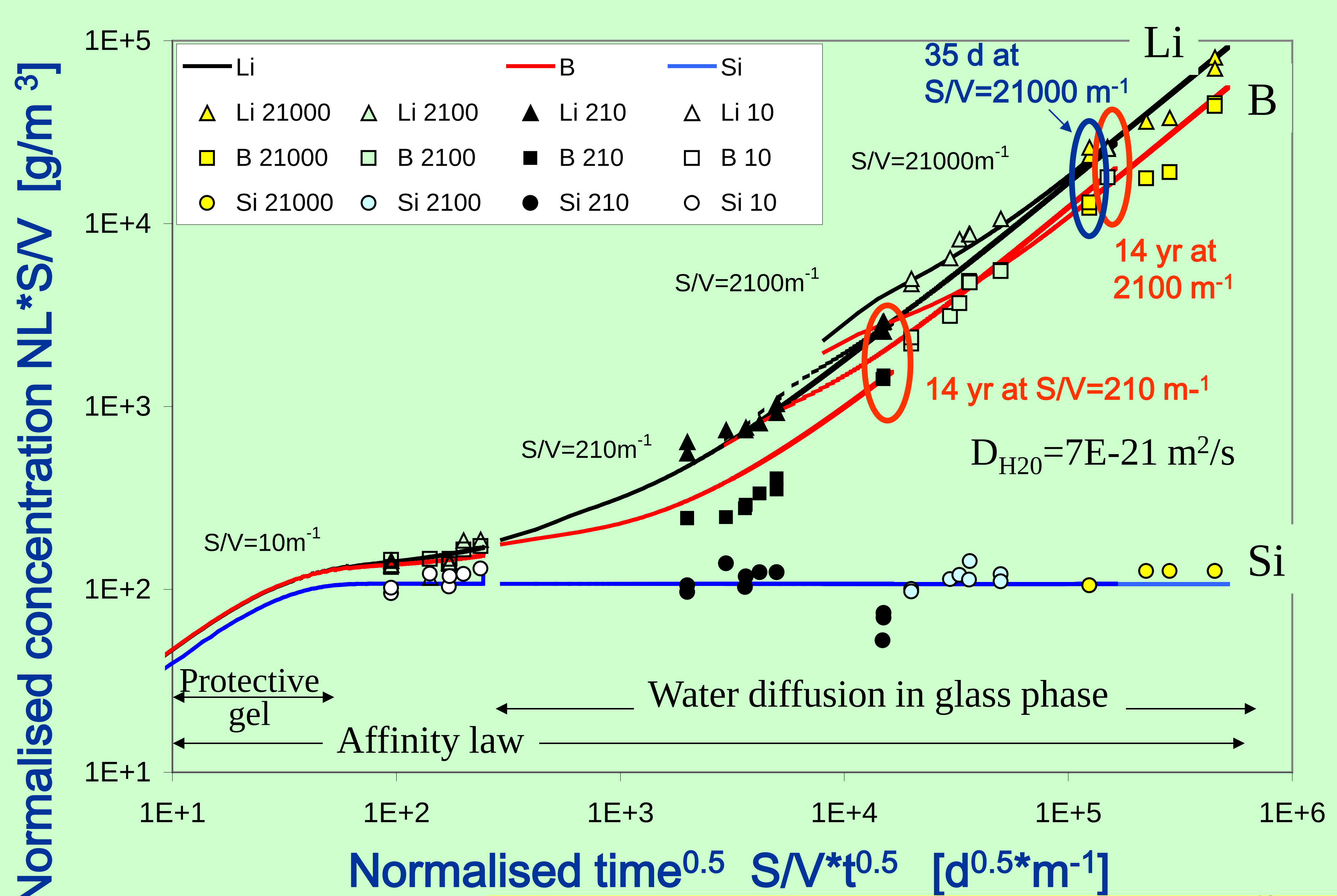
Reaction continues at A=0

r_2 about 10^{-3} to 10^{-4} r_1

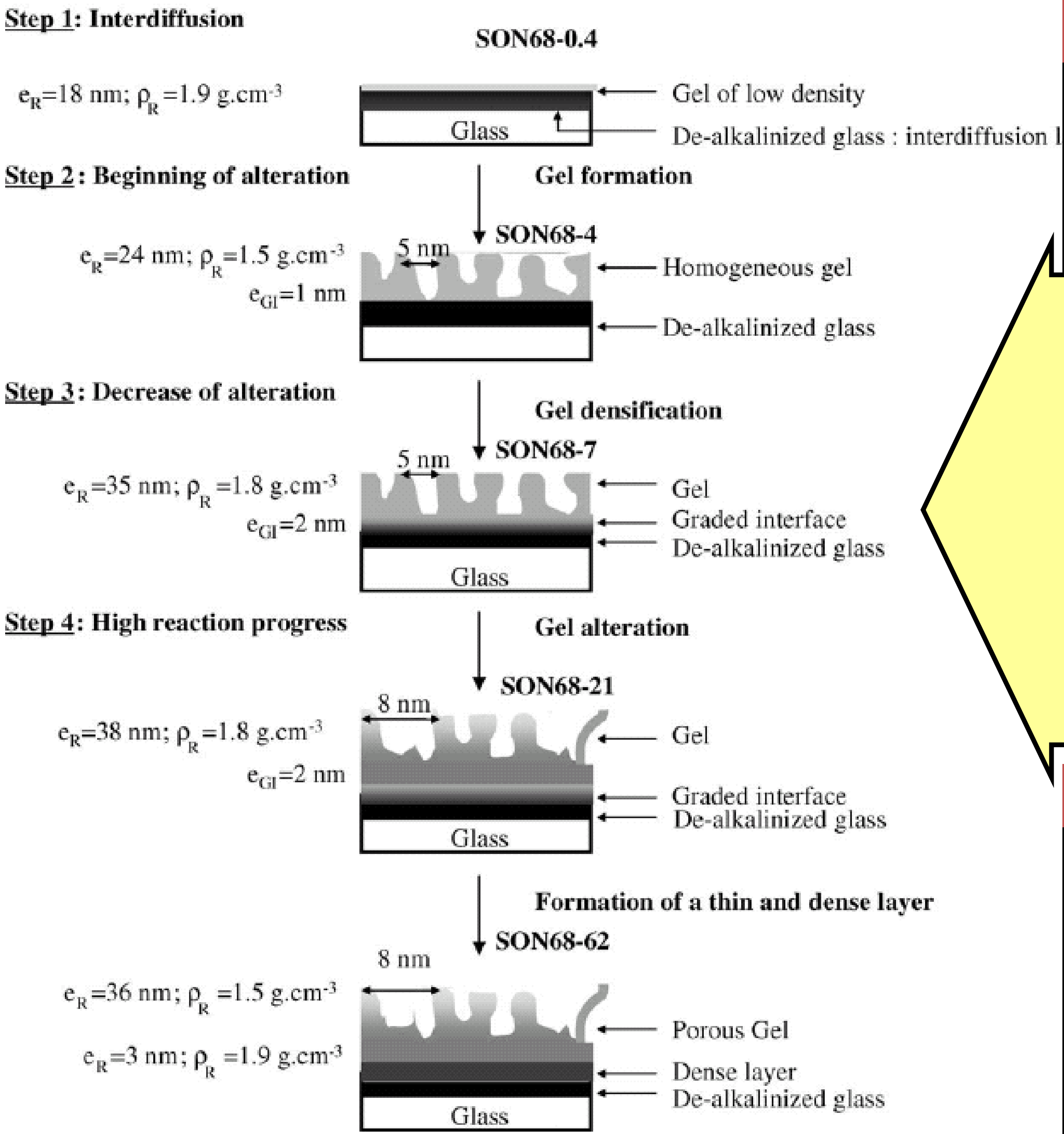
Temperature dependency according to Arrhenius law with EA about 70 kJ/mol

Similarly described in: Report ANL-EBS-MD-00016

Example S/V effect: Acceleration of glass dissolution by using high experimental S/V



Data from Lutze et al 1988-1992, Grambow et al. 1991-2004



2004 PhD thesis

. D. Rebiscoul:

Alteration in pure water:

X-ray reflectometry:

Layer densities :g/cm^3

dealkalised layer 1.9

initial gel: 1.5

densified gel: 1.8

dense layer 1.9

Protective layer= dense layer

2004 PhD thesis

. K. Ferrand:

Alteration in Si-saturated water:

no gel but only

dealkalised layer 2.25

Modeling of glass corrosion by Monte Carlo

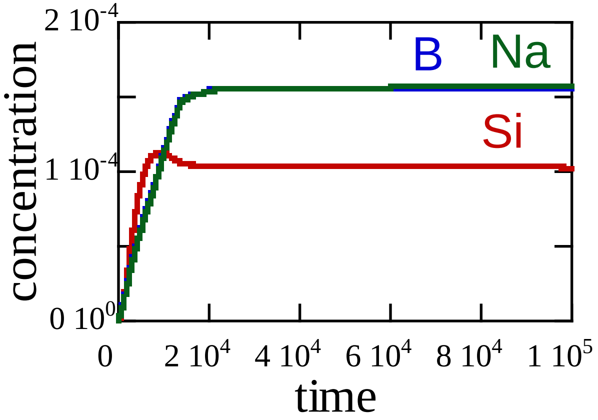
Glass 70Si – 15Na – 15B

S / V = 2000 m^{-1}

Detachment propabilities

{w_d} = 10^{-2}, 10^{-3}, 10^{-4}

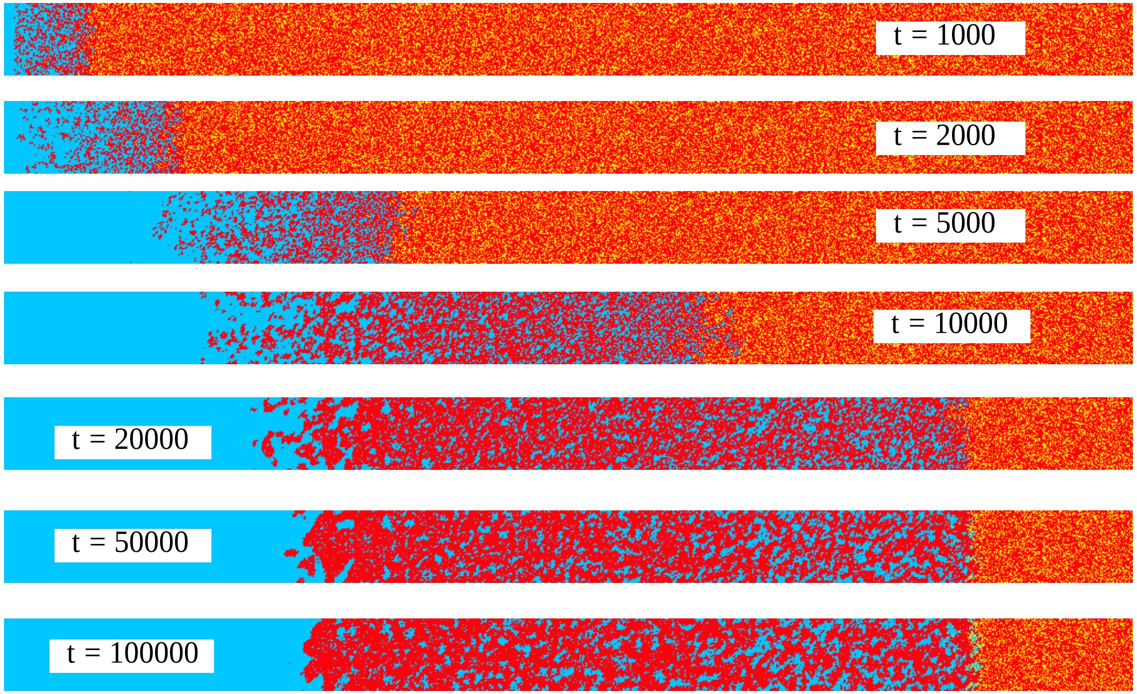
w_c = 10



Ecole Polytechnique, Devreux

Dynamic percolation

Formation of a « protective » layer by dissolution/recondensation



However , gel properties alone cannot explain rate drop without gel:
It is the dissolving phase ,which is stabilized by recondensation of silanol groups, not a secondary phase. This validates the affinity concept

Key role of reacting interface

- The gel constitues the interface to the solution, but it is a reaction product, not a dissolving phase
- The pristine glass phase is modified by hydration water diffusion and alkali exchange prior to dissolution. Hence the composition of the reacting surface is different than that of the glass
- The reacting interface is the hydrated surface layer, sometimes also called passivating reaction layer (PRI) or the interfacial diffusion barrier (IDB). In the latter case the IDB exists only close to saturation

GM2001-2003 models

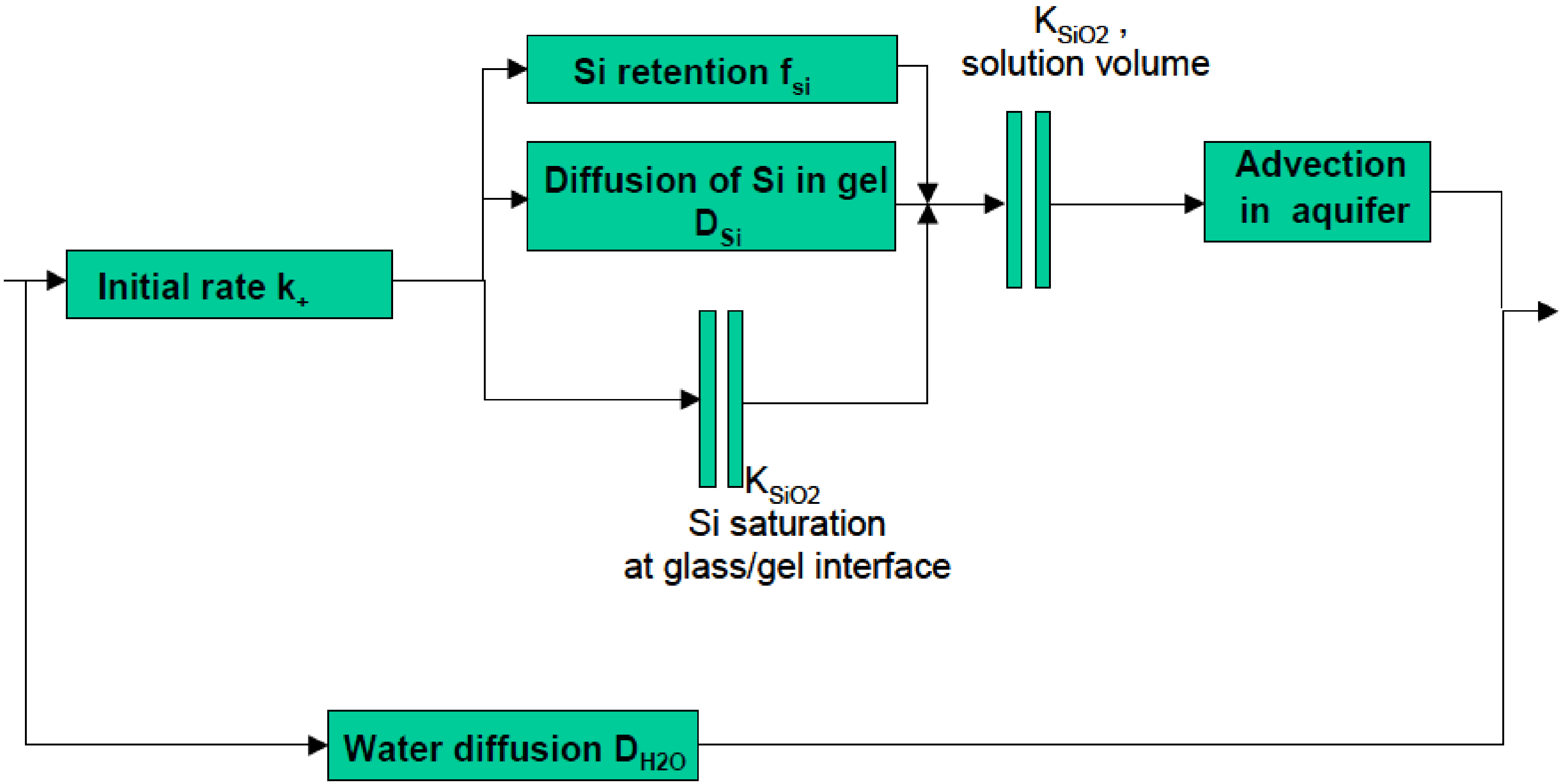
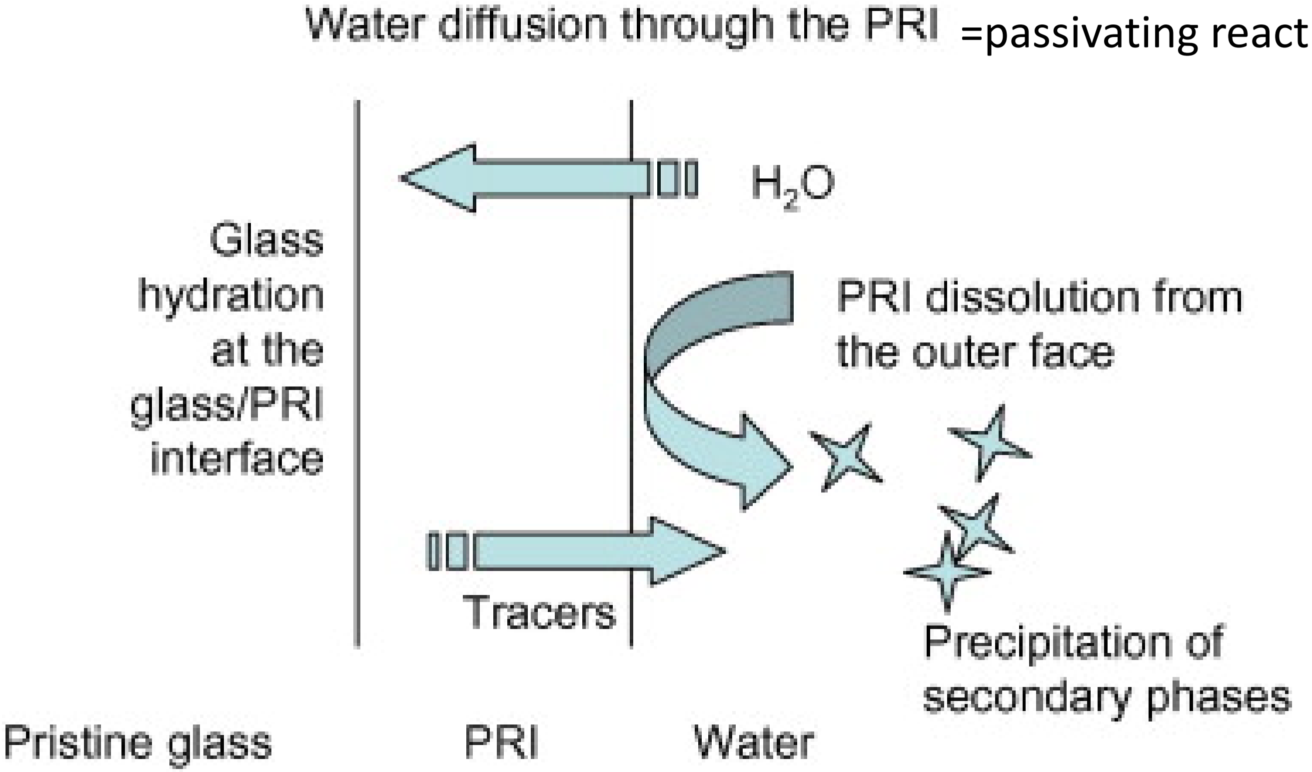


Figure 19: GM2001 model: Scheme of interrelationship of rate controls in the dissolution process of glass, expressed in terms of resistors (for rates) and capacitors (for saturation)

GRAAL model (Frugier et al.)



=passivating reaction interface

Mathematically rather similar to GM2003 model

A fresh look at glass dissolution modeling

- Detailed analyses of previous models (GRAAL, GM2003…..)
- Diffusion and affinity not contradicting, controlling different reactions taking place concurrently
  - water diffusion controlling the reactions that occur rapidly, such as ion-exchange and reactive diffusion, thus controlling the release rate of glass modifiers (like B and alkalis);
  - chemical affinity controlling the distribution of Si among different alteration phases, where rupture and reformation of network (glass, IDB or precipitation minerals).
- The two mechanisms not only control different types of reaction, but also affect each other.
  - For example, rupture and reformation of covalent bonds Si-O-M affects water diffusion, since it can build up a diffusion barrier.
- The model divides glass dissolution behavior into four categories based on Si concentrations (first order control, secondary phase control of r_{fin}, r_{fin} control by diffusion in IDB; complex behavior)
  - Threshold Si concentration necessary to from IDB
  - Threshold Si concentration to form secondary phases
  - Saturation concentration of Si (affinity law)

T. Ma et al. / Journal of Nuclear Materials 486 (2017) 70-85

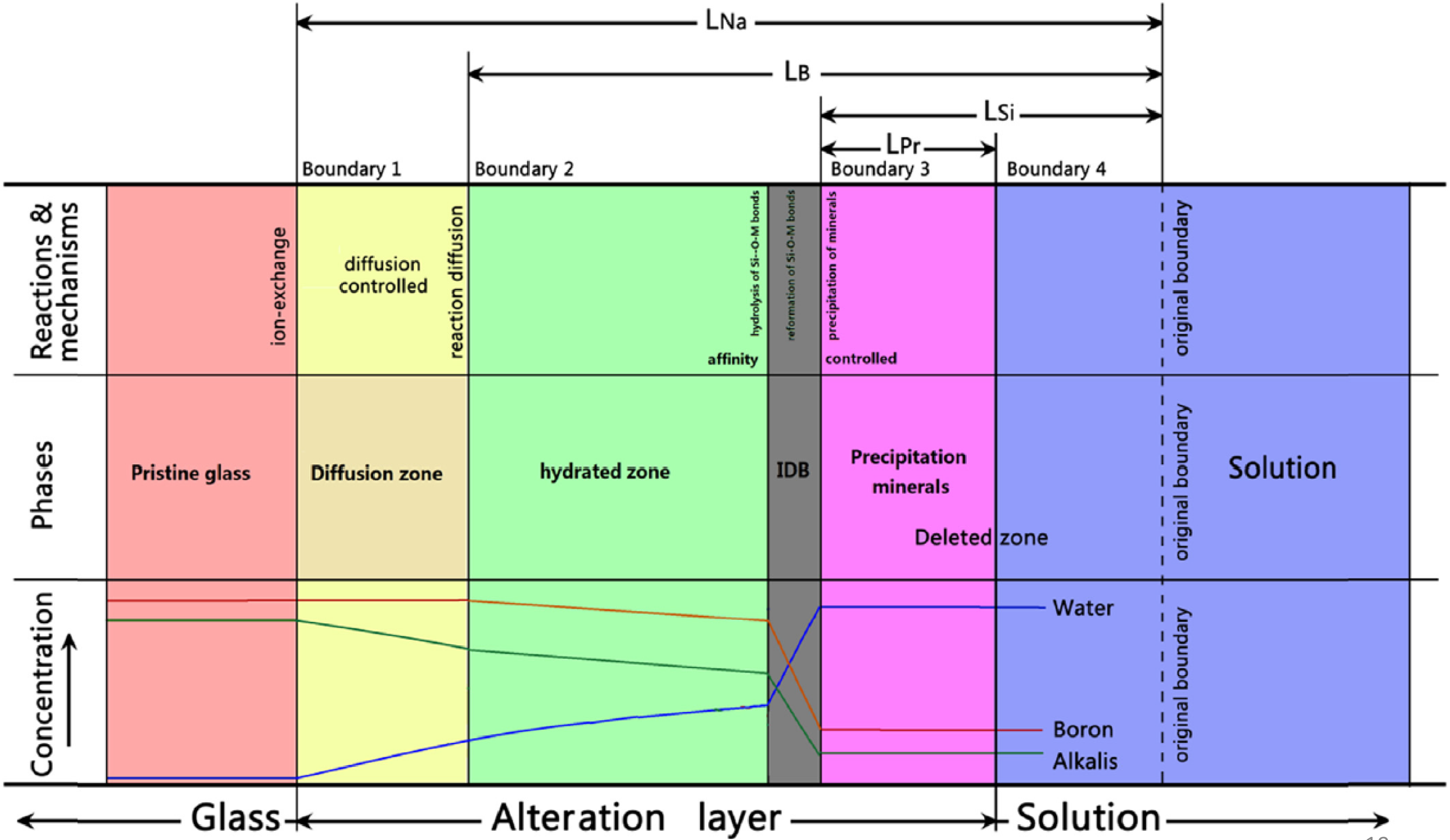


Fig. 2. Simplified presentation of assumptions and mechanisms taken account into this model.

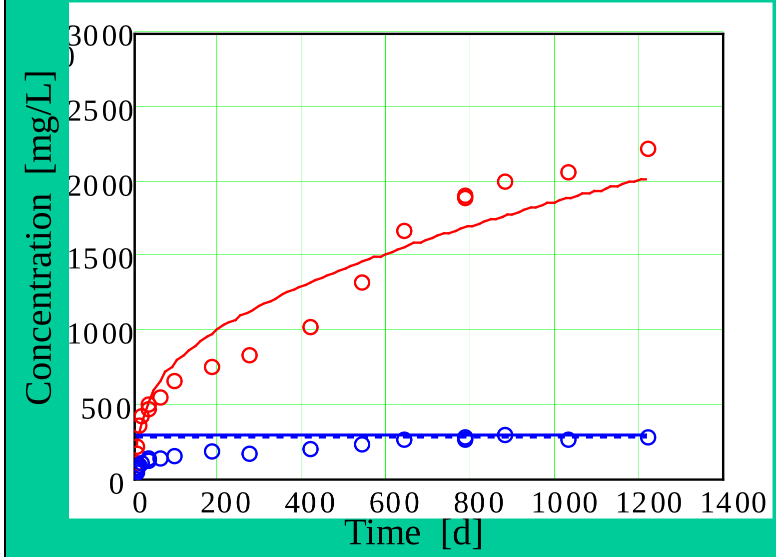
Risk of overinterpretation of data

- Glamor project has shown that same data can be described with different model leading to non-unique desriptions
- The same parameter may have different significance in different models
- How to treat model uncertainty?
- WMO chose typically a model without treating model uncertainty
- Parameter uncertainty and model uncertainty are interdependent

Challenge : data interpretation

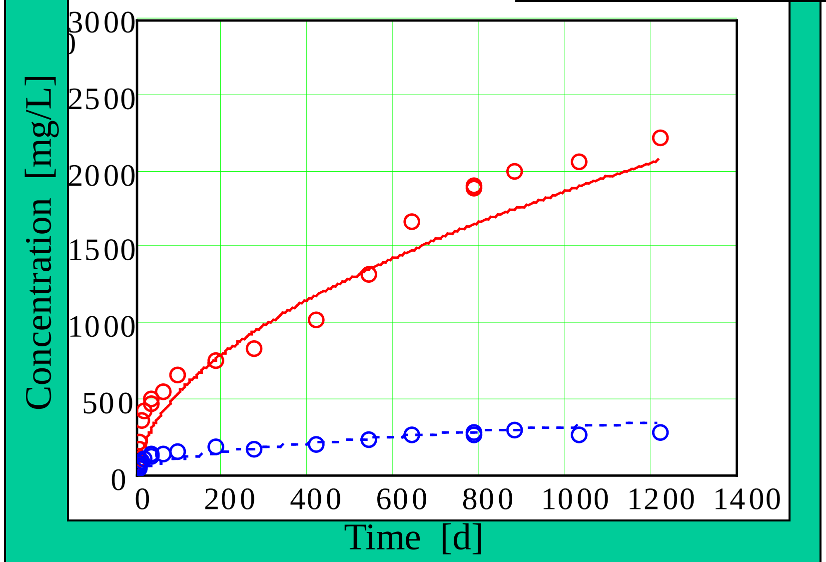
Example	
Glass	R7T7
Test	A1 (CEA)
S/V Static	200000 m^{-1}
	DI water
T	90°C

GM2001 interpretation



k_+	0.7	g/(m^{2}d)
C*	294	mg/L
D_{H20}	$3.5\cdot10^{-23}$	m^2/s
D_{Si}	$3.1\cdot10^{-13}$	m^2/s
f_{Si}	0.98	

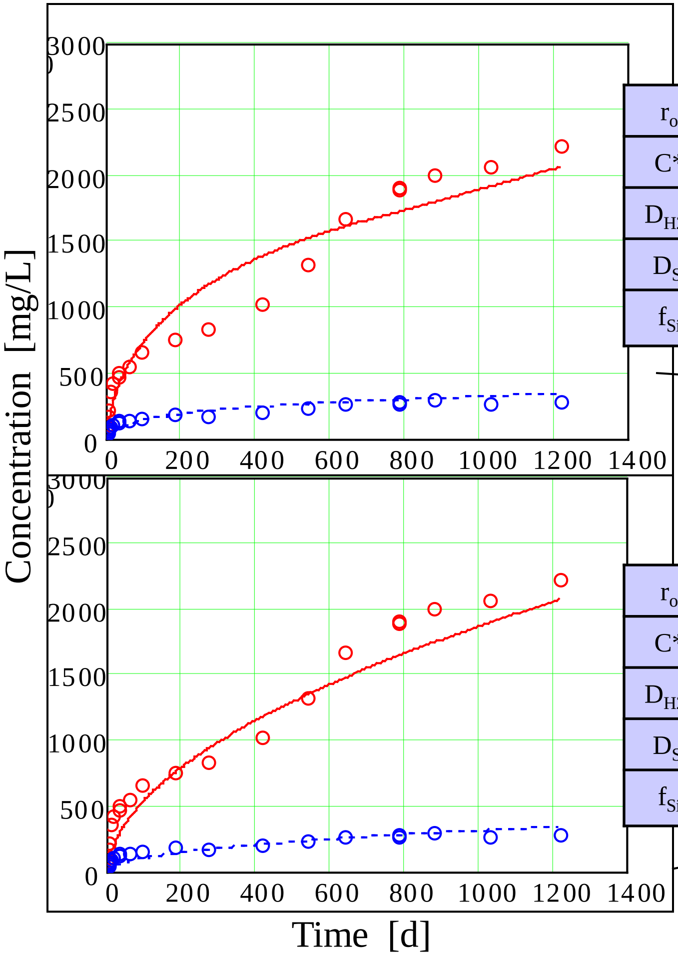
r(t) interpretation



r_o	0.7	g/(m^{2}d)
C*	1170	mg/L
D_{H20}	0	m^2/s
D_{Si}	$1.2\cdot10^{-21}$	m^2/s
f_{Si}	0.97	

Challenge 2 : Identification of interdependencies of parameters

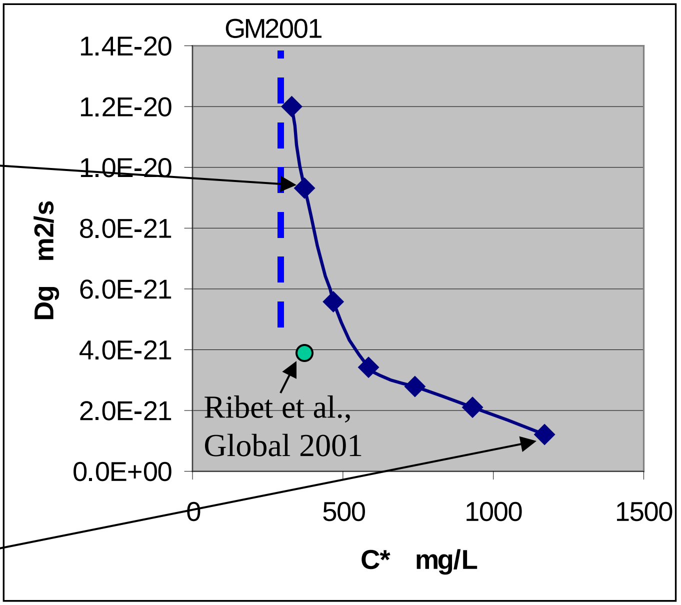
Example : r(t) /A1



r_o	0.7	$g/(m^2d)$
C*	370	mg/L
D_{H20}	0	m^2/s
D_{Si}	$9.3\cdot10^{-21}$	m^2/s
f_{Si}	0.97	

r_o	0.7	$g/(m^2d)$
C*	1170	mg/L
D_{H20}	0	m^2/s
D_{Si}	$1.2\cdot10^{-21}$	m^2/s
f_{Si}	0.97	

Dependency of Si diffusion coefficient on choice of C*



Question 1b

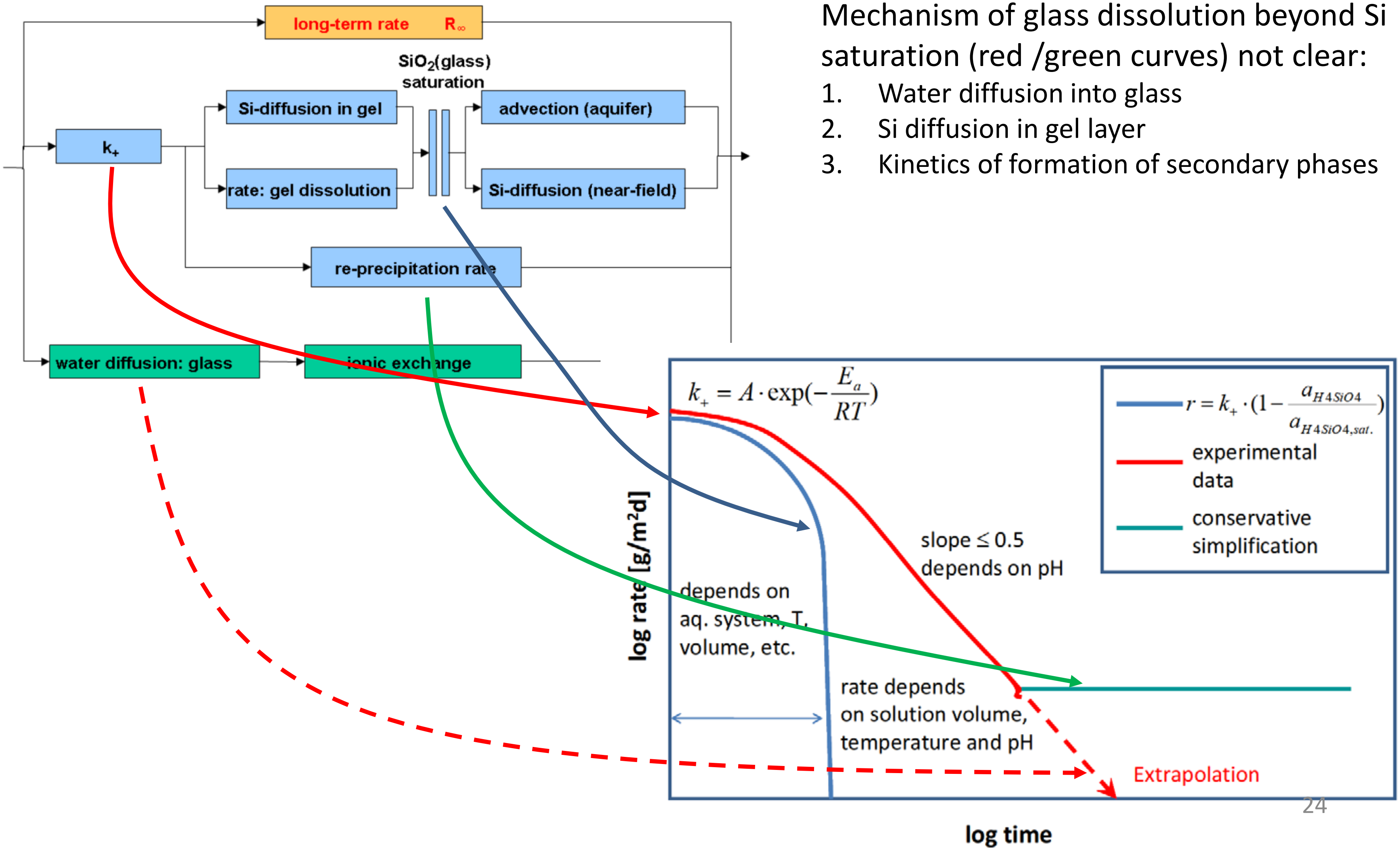
- how do different countries take account of glass corrosion and radionuclide release in repository performance assessments?

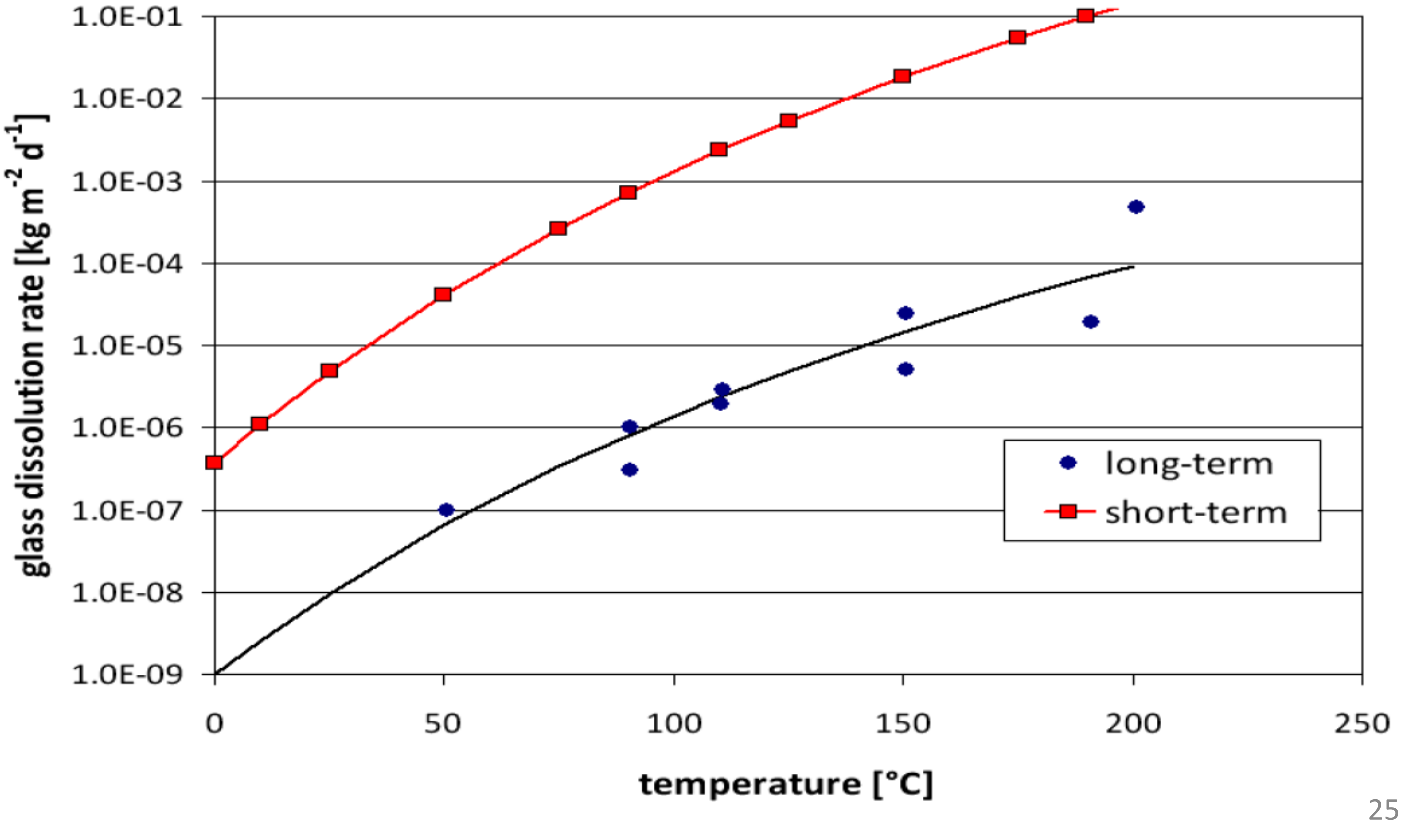
Germany, KIT

Radionuclide Source Term for HLW Glass, Spent Nuclear Fuel, and Compacted Hulls and End Pieces (CSD-C Waste)
by Bernhard Kienzler, Marcus Altmaier, Christiane Bube, Volker Metz

Mechanism of glass dissolution beyond Si saturation (red /green curves) not clear:

1. Water diffusion into glass
2. Si diffusion in gel layer
3. Kinetics of formation of secondary phases

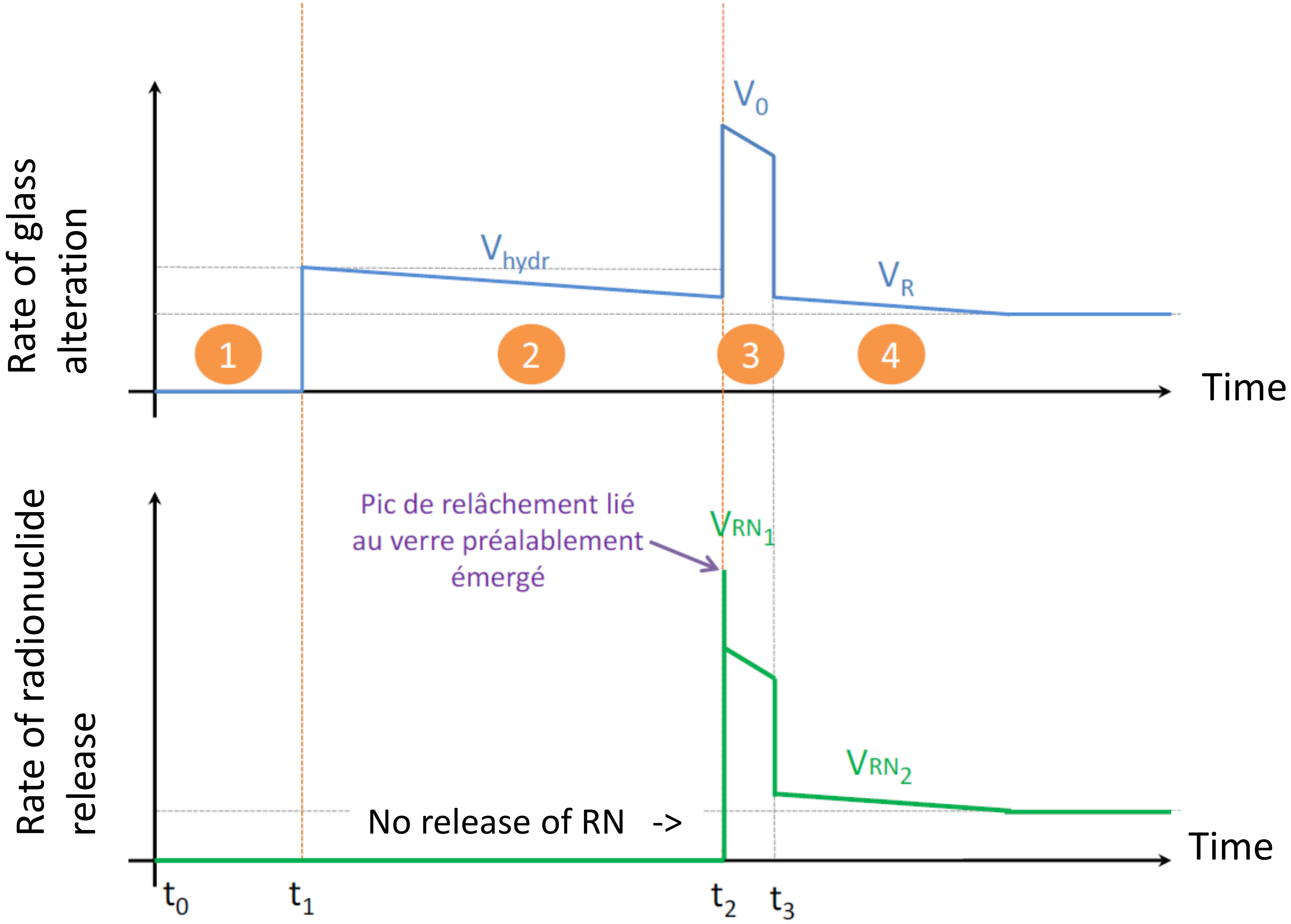



1.0E-01
1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
glass dissolution rate [kg m^{-2} d^{-1}]
0
50
100
150
200
250
temperature [°C]
long-term
short-term

UK: RWM/NDA

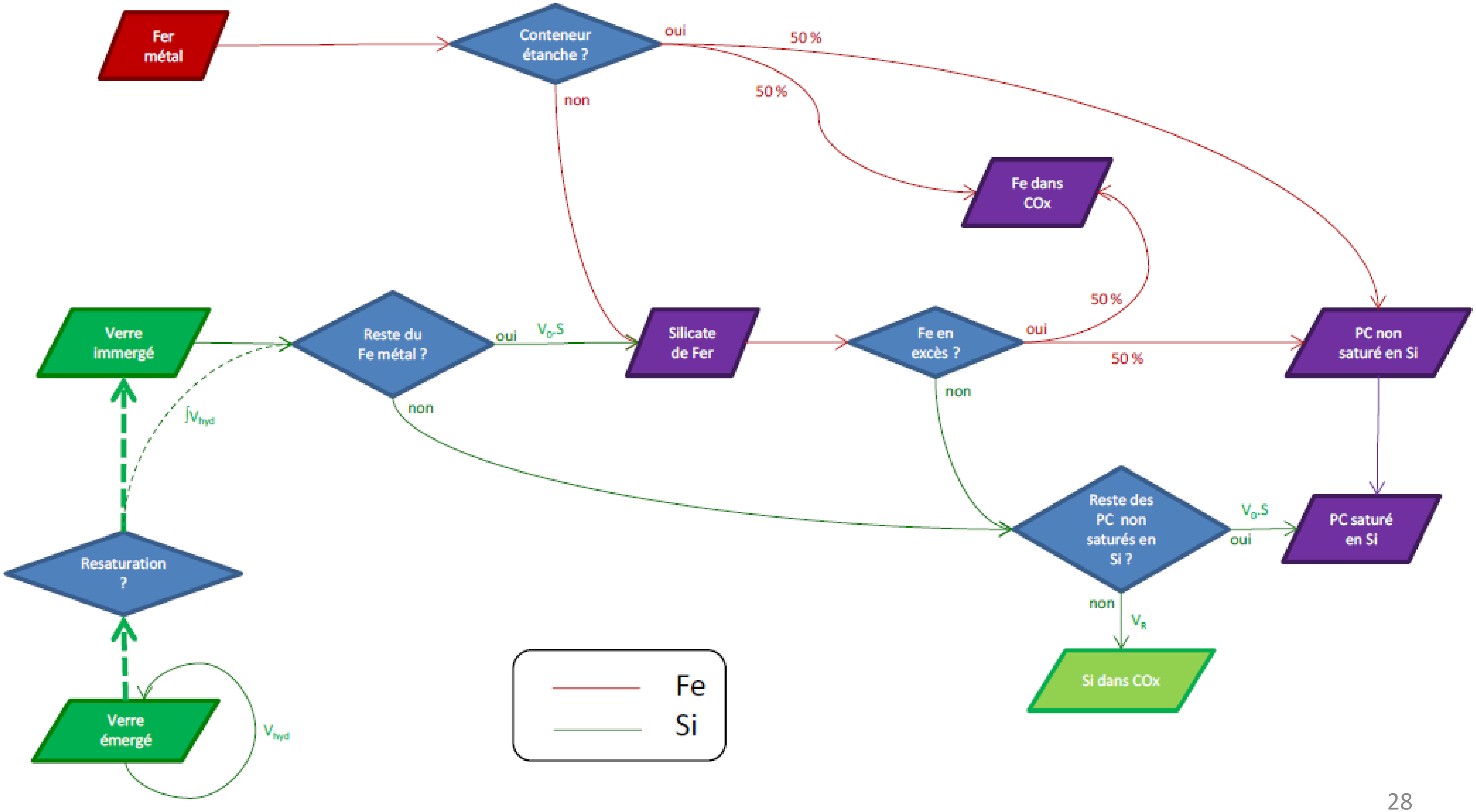
- 2800 tons of glass are considered (NDA/RWMD/031)
  - “There is a sufficiently good understanding of glass dissolution mechanisms to allow the dissolution rate over long timescales to be predicted”
- The dissolution rate used in the safety assessment models is a fractional rate (units of 1/s): LogTri(3×10^{-7}, 7×10^{-6}, 5×10^{-5})
  - They are not dissolution rates for the wasteforms as defined by experimentalists
  - They are derived parameters that include information about the particular wasteform, disposal concept and scenarios/assumptions being modelled.
  - Ignoring that dissolution rate and the surface area are likely to evolve with time
    - Experimentally, at constant environmental conditions, dissolution rates decrease. Thus this assumption might be conservative
    - The hypothesis is that after container breach, environmental conditions (temperature…) change only little.
  - Dissolution rates for HLW glass are largely based on work of the French and Belgian programs and, to a lesser extent, from UK HLW compositions.
  - Dissolution rates for UK HLW (magnesium-rich) are higher than dissolution rates of some HLW compositions (calcium-rich) produced in France. A long-term study (12 years) by PSI comparing the long term dissolution behaviour of 25 wt% Magnox glass from the UK with French R7T7 glass found that the residual rate was an order of magnitude higher for the Magnox glass
- For a co-located ILW/HLW facility the impact of an alkaline plume on glass stability may in future have to be taken into account
- Cracking factor is important but release rates from crack surfaces are lower

France


Rate of glass alteration
V0
Vhydr
VR
1
2
3
4
Time
Rate of radionuclide release
Pic de relâchement lié au verre préalablement émergé
VRN1
VRN2
No release of RN ->
Time
t0
t1
t2
t3

France: impact of environment

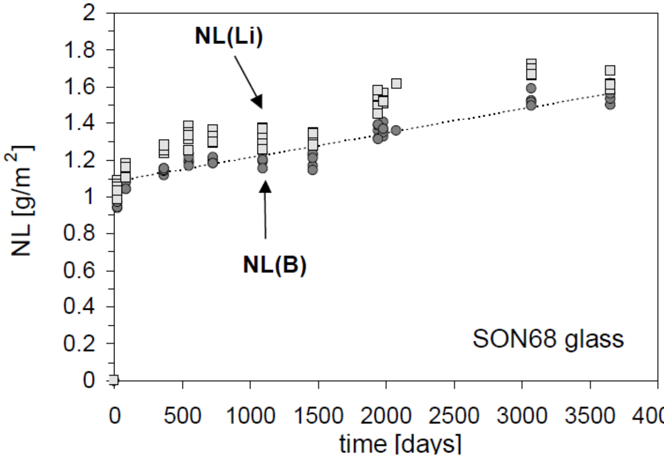
- GRAAL model describes performance but is not capable to treat impact of environment

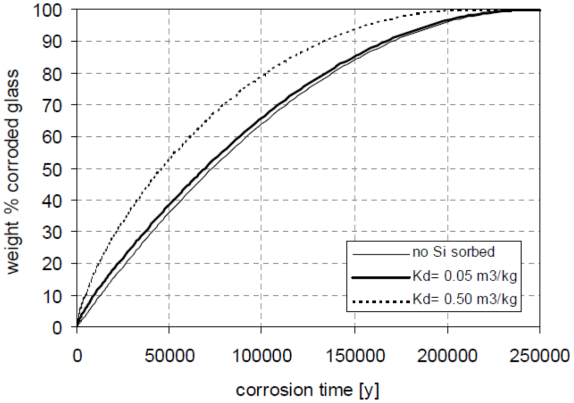


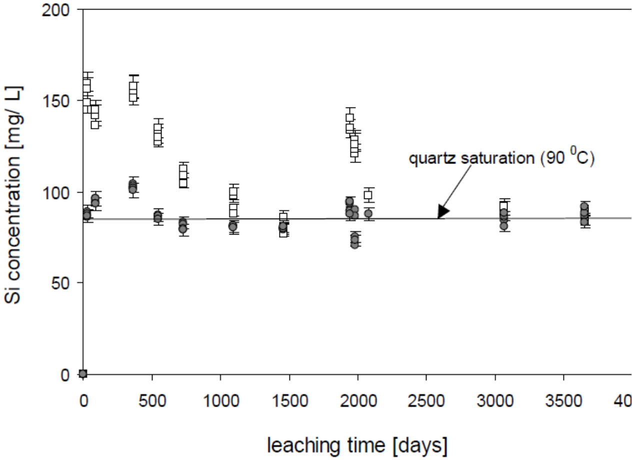
Switzerland: Nagra/PSI

NAGRA NTB 02-21:

- Constant long term dissolution rates in clay environment, based on experimental data (PSI):
  - 1.5 mg·m^{-2}d^{-1} for UK glasses and 0.2 mg·m^{-2}d^{-1} for french glasses from data > 500 d, increase by factor 100 without effect on dose, hence glass is not a critical barrier
  - Largest uncertainty: specific surface area
  - Sorption of Si on clay is only of transient character







- Temperature reduction for the long-term rates not considered
  - in spite of the large temperature difference between laboratory (90^{o}C) and HLW repository environment (40^{o}C)
- The cracking factor is equal to 12.5

Belgium before 2000
Containered glass in boom clay environment

D. Mallants et al. J. Nucl. Mat. 298 (2001) 125-135)

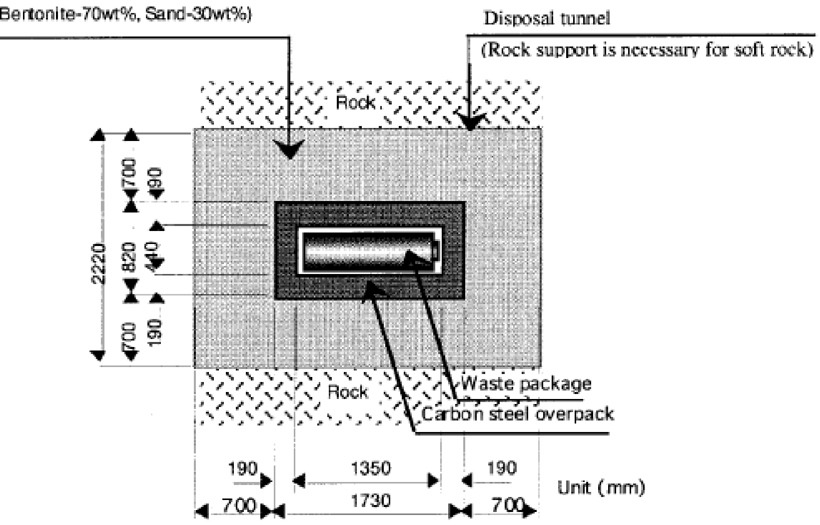
- 4 source term models
  - Fracture factor 5-27, constant dissolution rate, no container
  - Reference rate: 0.002 g/m^{2}d, fracture factor 10, complete dissolution: 72000 yr
  - Worst case: dissolution in 20000 yr
  - Best case: 2.1^{E}7 yr, simulated conservatively by 1 million yr
  - Instant release : no glass is present
- The sensitivity analysis shows, that the glass has a limited contribution to overall performance, since clay is a very effective barrier.
- Glass contributes also only little to fixation of sparingly soluble radionuclides
- **Higher contribution of glass only if lifetime exceeds one million years**
- The conclusion of this study was the abandon of glass as an important barrier and the creation of the supercontainer concept , consisting of a glass in a concret environment,
  - leading to high glass dissolution rate
  - higher long term stability of the container

Belgium: SCK/CEN glass stability in concrete environment

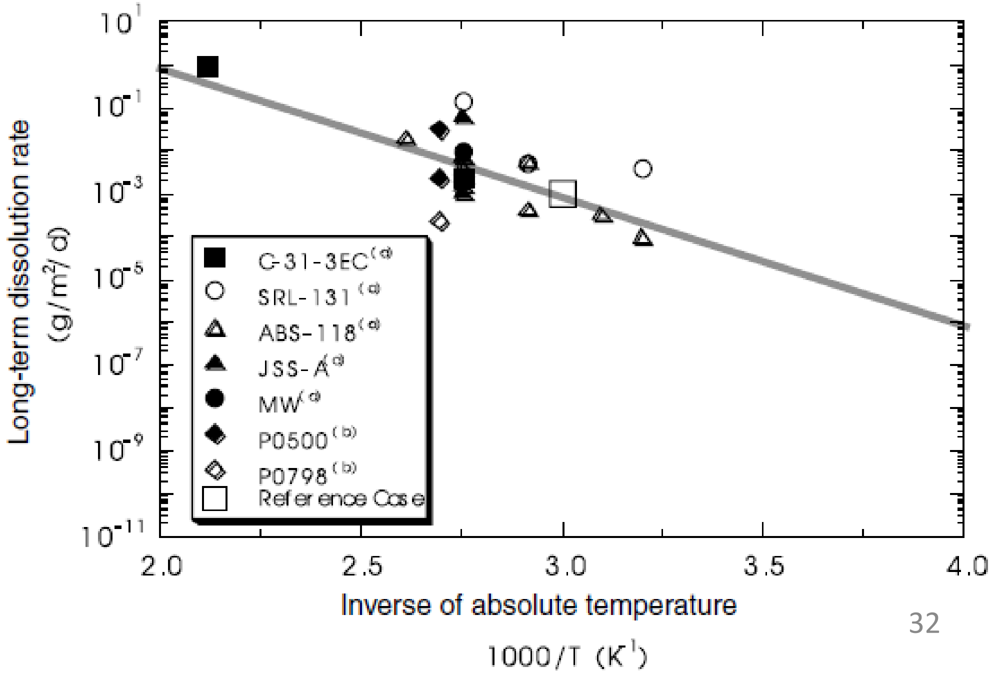
- Impact of cement alteration (fresh=pH13.5, altered= pH11.5)
  - pH 13.5: long term rates between 3 and 6 mg/m2d
  - pH11.5: long tem rates between 0.02 and 1 mg/m2 d
  - Concentration of Al is crucial in affinity controlled reduction of alteration rates mixed Si/AL phases
- Surface area cracking factor 5-40 (SCK•CEN-ER-155, 2011)
  - Cause: mechanical constraints caused by temperature gradients during cooling
  - Radioactive glass should be less fractured than inactive glass, due to smaller gradients
  - Low impact of He bubble generation due to radiation
  - Water vapor hydration and stress-corrosion-cracking can increase surface area by factor 2-3
  - Surface area decrease due to corrosion
- Alteration of cracks surfaces
  - In neutral to slightly alkaline conditions, the volume of the altered glass (glass + alteration layer) is close to the volume of the initial glass („isovolumetric alteration‟).
  - In hyperalkaline conditions only little gel layer is formed, cracks can widen with time. However, alteration products may close fractures
  - Cement accelerates glass alteration, but the effect is much lower in the cracks, because of the slow transport between the internal glass surface and the near field. Smaller pH in cracks
  - Crack-orientation may also be important

Japan: NUMO H12 and follow up

- Generic approach, since no site has been selected
  - Glass surrounded by bentonite
  - The cracking factor was considered constant as a function of time and taken equal to 5. In a conservative approach, it was fixed at 10 [Inagaki 1994].
  - Dissolution rate constant over time at 1 mg/m²d for 60°C
  - (variation: pH dependency)



Tunnel disposal type (hard rock/soft rock)



USA

- In 1998, the cracking factor induced by the stresses due to the cooling was estimated lower than 15 for a DWPF container [DEO report 1998]. A cracking factor of 600 was used for 1% of the containers, to account for any cracking due to the handling. Later, taking into account the dimensions and the characteristics of different waste packages (DWPF, WVDP and Hanford), a cracking factor equal to 20 was considered in a conservative estimation

Glass as key parameters to characterise the behaviour of the EBS acccording to

“Engineered Barrier Systems and the Safety of Deep Geological Repositories”, OECD 2003

Glass as key uncertainty in design of EBS?

- Belgium: no
- France: no
- Japan: no
- Germany: no
- Switzerland: no
- US: no
- UK: no

Glass key parameter for EBS?

- Belgium: no
- France: yes
- Japan: yes
- Germany: no
- Switzerland: yes
- US: general waste package rate
- UK: no

Question 2

- What are the remaining technical gaps or uncertainties in understanding and modeling of long-term glass performance in repository environments and how important is glass performance to the overall safety case for different repository designs?

European strategic research agenda (Joprad, 4/2017)

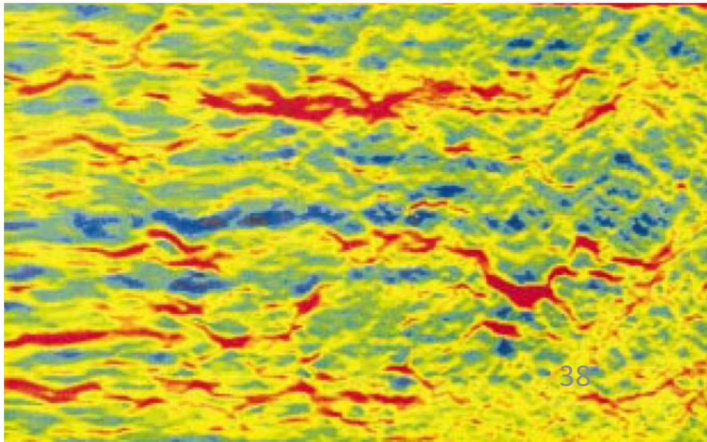
- Vitrified waste (ILW and HLW)
  - Impact of fracturing, hydration under unsaturated conditions, interaction with surrounding materials (carbon steel, corrosion products, concrete (including low-pH concretes), clay, etc.),
  - resumption of alteration,
  - influence of irradiation on residual alteration rate,
  - mechanism governing residual rate,
  - influence of composition, congruency between glass alteration and radionuclide release
- Improve understanding of coupled interactions between reactive transport models and the corrosion of glass and near-field materials (e.g. steel)

Necessary improvements of GM2003 model

- Model does not include a detailed structural, morphological, functional or thermodynamical model of the surface layer including the gel and diffusion layers
  - Data of GLASTAB project show, that gel can be simulated as a solid solution of oxyhydrates, oxides, clays etc.
  - The description of adsorption of Si in the gel is too simple
  - Evolution of « Passivating » properties (diffusion of Si) are not taken into account as function of structural evolution
  - Sorption of radionuclides is not taken into account

Morphology evolution and overall vs. local dissolution rates of fractured glass

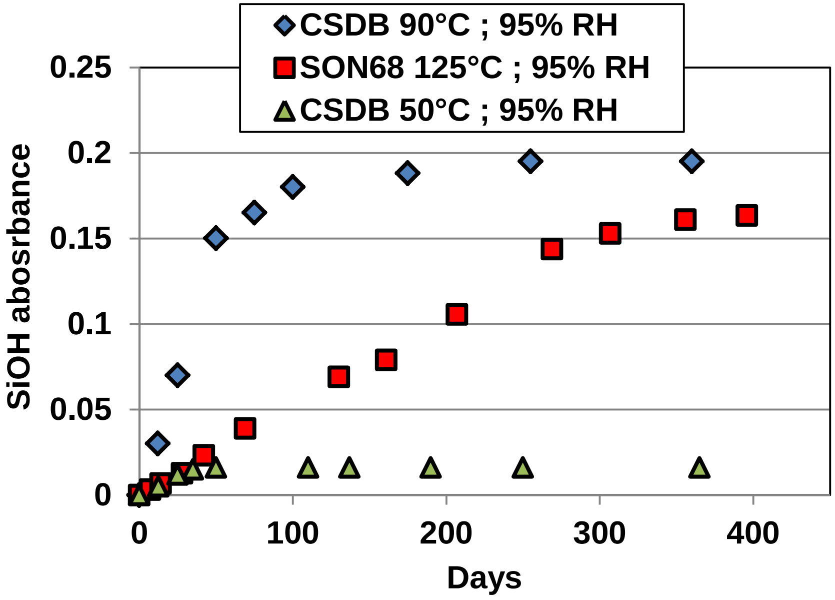
- Dissolution of the surfaces of glass fractures can cause significant alteration of the fracture void space (aperture) and fracture permeability (k). An important parameter is the local Peclet number and its evolution
  - A 110% increase in aperture due to dissolution resulted in estimated permeability increases of 440% and 640% for the Pe = 54 and Pe = 216, respectively (Detwiler et al. 2003)
  - Both surface reaction rates and transport of reactants within the fracture can limit local dissolution. At high Pe, dissolution channels; at low Pe diffusion controlled growth of disconnected cavities
- Lattice Bolzmann calculations suggest for porous rock a strong coupling between transport and morphology (Verberg et al. 2002)
  - further research is necessary to understand the complex coupling between chemical kinetics, flow, surface morphology, and confining pressure.



GLASS HYDRATION – HYDRATION RATE DECREASE

The growth of the SiOH peak at 3595 cm^{-1} for the CSDB intermediate-level and SON68 high-level nuclear waste glasses and ISG glasses hydrated at different temperatures and relative humidities.
(*modified from Bouakkaz, 2014 ; Aït Chaou et al., 2015*).

*The strong decrease of hydration rate is not yet understood. A joint PhD CEA-SUBATECH, started in October 2016, is tackling this issue.

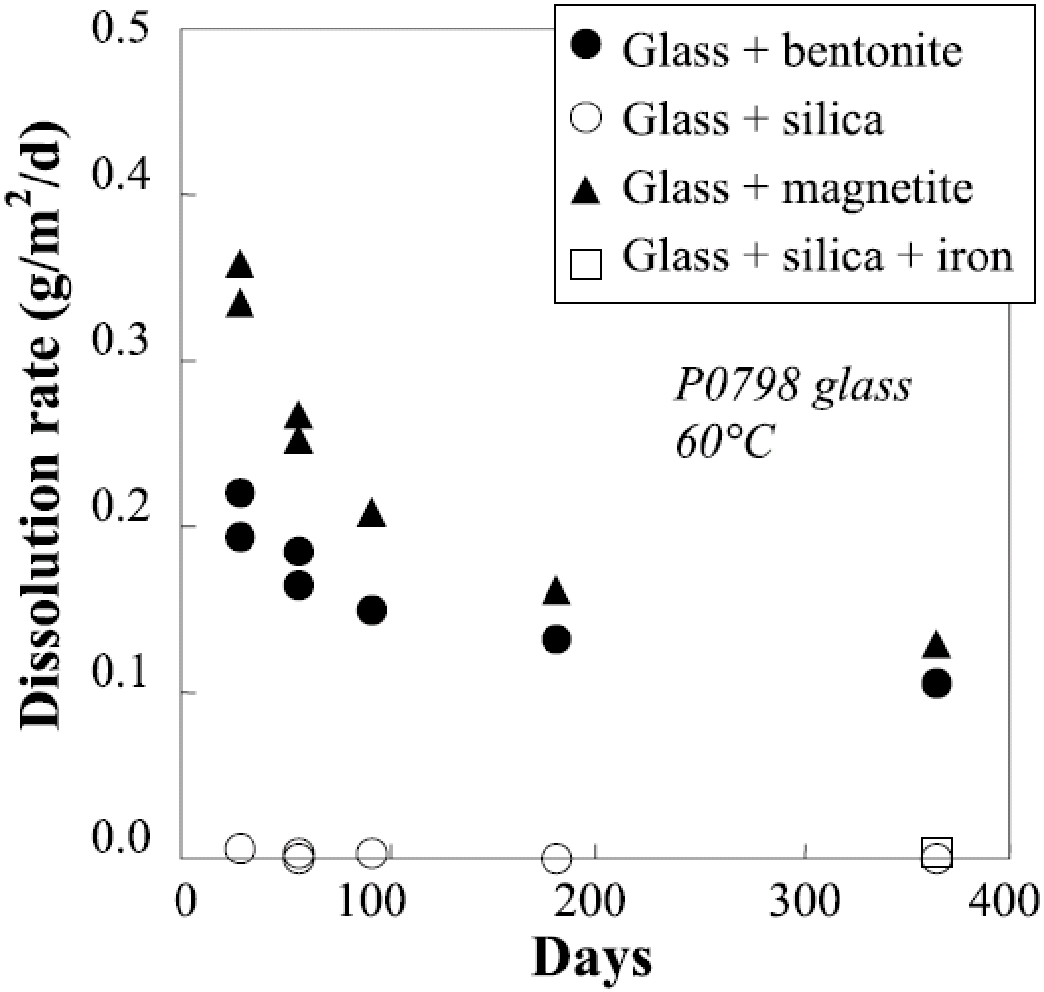


Need to have an overall mechanistic view on worldwide data generated since 35 yr

- Nuclear waste glasses are someof the best studied obejects worldwide
- Tendency of young researchers to produce new data without integrating them in the large body of existing data
- If parameter uncertainty and model uncertainty are interlinked, model validation can only be based on the whole set of data

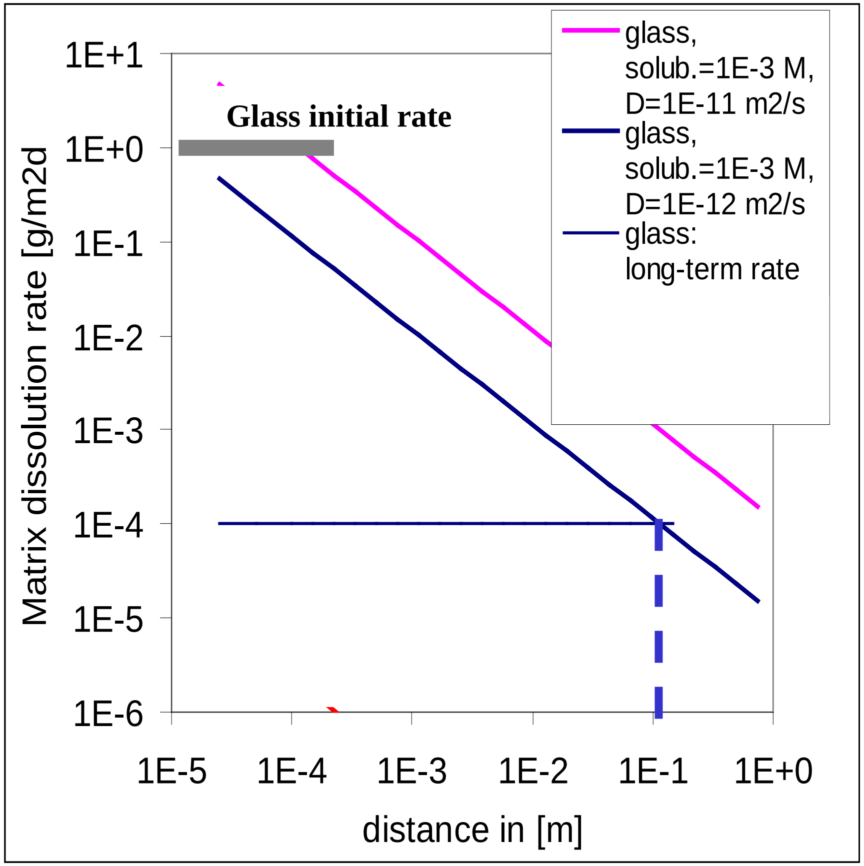
Quantification: pumping effect of near field materials: increasing matrix dissolution rates

S. Mitsui, R. Aoki / Journal of Nuclear Materials 298 (2001) 184–191

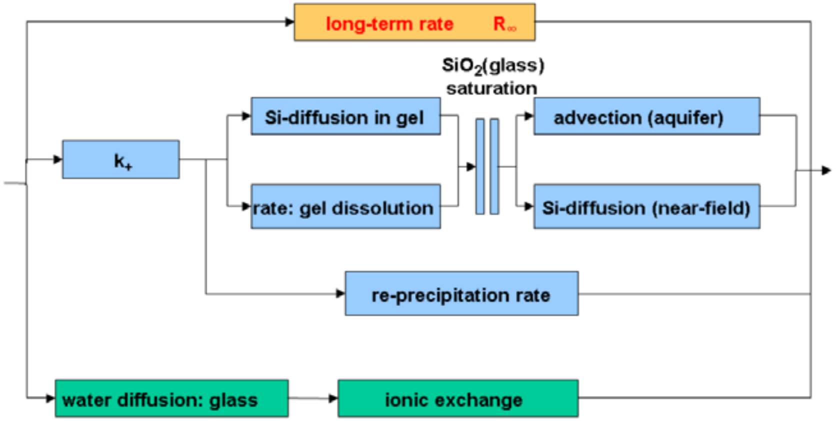


Clearer rationalisation of near field influence sphere

- « Pumping » effect: increased dissolution rate of glass and spent fuel due to coupling of affinity driven dissolution and near field sorption



Surface sites beyond influence sphere are ignored because transport to them is slower than the matrix dissolution rate



Other research subjects

- Release of critical anions from glass: in clay environment: Cl36, I129, Se79
  - Inventories often not known exactly
  - Release sometimes much lower than that of cations (MoO4…)
  - Only few data exists
- 3D Modeling of fractured glass in stainless steel container and metallic overpack
  - impact of clay rock/bentonite and iron corrosion rates much less than in case of direct contact
  - Modeling of unsatured and partially saturated conditions
- A future challenge
  - Computational molecular modelling of glass dissolution
    - Problem of time and space scales…