

ベルギー原子力研究センター (SCK/CEN) との共同研究会議

— α 放射性核種含有ガラス固化体を用いた原位置試験
(CORALUSプロジェクト) に関する会議等への参加報告 —

(会議報告)

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核燃料サイクル開発機構
東海事業所

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— α 放射性核種含有ガラス固化体を用いた原位置試験 (CORALUS プロジェクト) に関する会議等への参加報告— (会議報告)

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要 旨

ベルギー原子力研究センター (SCK/CEN) との共同研究会議に参加し、「 α 放射性核種含有ガラス固化体を用いた原位置試験 (CORALUS プロジェクト)」の試験結果及び進捗状況を確認すると共に、サイクル機構が実施した核種移行モデリング評価結果について討議した。また今回は、CORALUS プロジェクトと関係する廃棄物ガラスの安定性に関する会議 (GLASTAB プロジェクト) にもオブザーバー参加し、関連機関の研究の動向を把握した。会議は、フランス南部のアビニョンで 2003 年 10 月 29、30 日に実施された。

併せて、近郊にある CEA マルクール研究所を訪問し、高レベル廃棄物ガラスの長期安定性を評価する施設、実規模大のガラス固化体の静的・動的浸出試験装置、ATALANTE 1 施設を見学した。ATALANTE 1 では、ガラス固化体、セラミックス固化体、ガラスセラミックス固化体の溶融・固化処理装置、照射燃料も含めた各種固化体の特性を評価する装置がセル内に設置されている状況を見学した。同じく近郊にある SEPR 材料研究所を訪問し、ガラス溶融炉用耐火物の特性を比較検討した。

CORALUS プロジェクトについては、試料の取り出しに向けて今回の会議でのコメントや情報を踏まえ、必要に応じ再解析を実施する予定である。今後ガラス浸出メカニズムに関する世界の最新情報をレビューした報告書を入手し、サイクル機構の研究計画に反映させる予定である。

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Report on Collaboration Research Meeting with Belgian Nuclear Research Center
(SCK/CEN)

-CORALUS:An integrated in situ corrosion test on alpha active HLW glass-
(Meeting Document)

Kazuhiro Kawamura*¹, Kenichi Ueno*²

Abstract

Collaboration Research Meeting with Belgian Nuclear Research Center(SCK/CEN)
-CORALUS:An integrated in situ corrosion test on alpha active HLW glass- was held on
October 29 and 30th, 2003 at Avignon, France. Scientific achievements obtained in the last
year were presented and results on modelling of nuclide migration were discussed. The
meeting of the GLASTAB project related to the CORALUS project was held at the same
period and we attended as observers. Durability of the waste glass was discussed between
researchers of collaborated institutes.

In addition to the meetings, Kawamura visited the CEA Marcoule Research Center and
looked around the laboratories about several kinds of tests such as the long-term,
laboratory scale and real scale, static and flow type leaching tests and then visited
ATALANTE1. At the facility characterization of some kinds of matrix such as glass,
ceramics, glass-ceramics, irradiated fuel can be done by the melters and analyzers installed
in the cells. Additionary, Kawamura visited the SEPR material Research Center and
discussed about the character difference of refractory products for glass furnace.

For the CORALUS project, it is necessary to get data in situ tests and to compare with the
modelling results. If the additional simulation is necessary, new information in the
reviewed reports on glass corrosion mechanism will be reflected and test program of JNC
will be revised.

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1. はじめに

本プロジェクトはベルギーMol の HADES 地下研究施設（粘土質原位置試験場）において放射性ガラス（放射性元素のドープガラス）とベントナイトを埋設し、放射性ガラスの溶解や核種の移行挙動等を調査するものである。サイクル機構は、①放射性元素を用いた原位置試験は、日本では不可能であること、②ホットの原位置試験結果を用いて、第2次取りまとめで用いた核種移行に関わるモデルやデータベースの妥当性を確認できること、③今後の安全基準策定や処分事業推進の上で意義があること、から本プロジェクトに参加した。サイクル機構の実施項目は、以下の通りである。

①ベントナイトー地下水相互作用のモデル化により、圧縮ベントナイト中の間隙水化学を推定、②①の結果に基づき、ガラスの溶解速度、放射性元素の溶解度、分配係数、拡散係数を導出（サイクル機構の放射性元素の熱力学データベース等を用いたモデル化により導出）、③②の結果に基づき、ガラス固化体から放出される α 放射性核種の圧縮ベントナイト中のプロファイルを核種移行解析により導出、④③の結果と原位置試験結果とを比較し、核種移行モデルやデータベースの妥当性を検討し、安全評価の信頼性向上のための課題を抽出。現段階は、原位置試験の遅れから原位置試験結果が出ていないため、③の段階である。

2. 会議等参加報告

2.1 行動記録

年. 月. 日	曜	訪問先・会議名等	記事
15. 10. 27	月	移動日	成田→パリ、Hotel Malte Opera
15. 10. 28	火	移動、SEPR 材料研究所訪問	パリ→アビニョン、Mercure Pont D'Avignon
15. 10. 29	水	GLASTAB 会議	アビニョン、ホテルは同上
15. 10. 30	木	GLASTAB 会議、CORALUS 会議	同上
15. 10. 31	金	CEA マルクール研究所見学、移動	アビニョン→パリ、パリ事務所 Hotel Malte Opera
15. 11. 1	土	移動	パリ発
15. 11. 2	日	移動	成田着

2.2 CORALUS プロジェクト

2.2.1 SCK/CEN 報告

(1) 主に EU からの助成(700k ユーロ)を受けてベルギーMOL 地下研究所において継続実施されている原位置試験 CORALUS プロジェクトについて SCK/CEN の Valcke 氏がこれまでの進捗と今後の計画を述べた (5.1 資料参照)。従来の計画より実験の開始及び試料の取出しが、約1年遅れており、肝心の解析データと比較できるようなデータは取られていなかった。また 2004 年から開始の CORALUS II プロジェクトで試料の取り出し、

評価を実施するという計画に変更されており、日本は次期プロジェクトへの参加は、資金難等の理由により、見合わせる方針であるが、核種移行モデリング結果との比較をすべく、情報交換は続けていくべきである。事前に Valcke 氏からモデリング結果に関する質問を得ていたので会議終了後、約 2 時間ほどかけて回答し、互いに再確認する事項を明確にした。

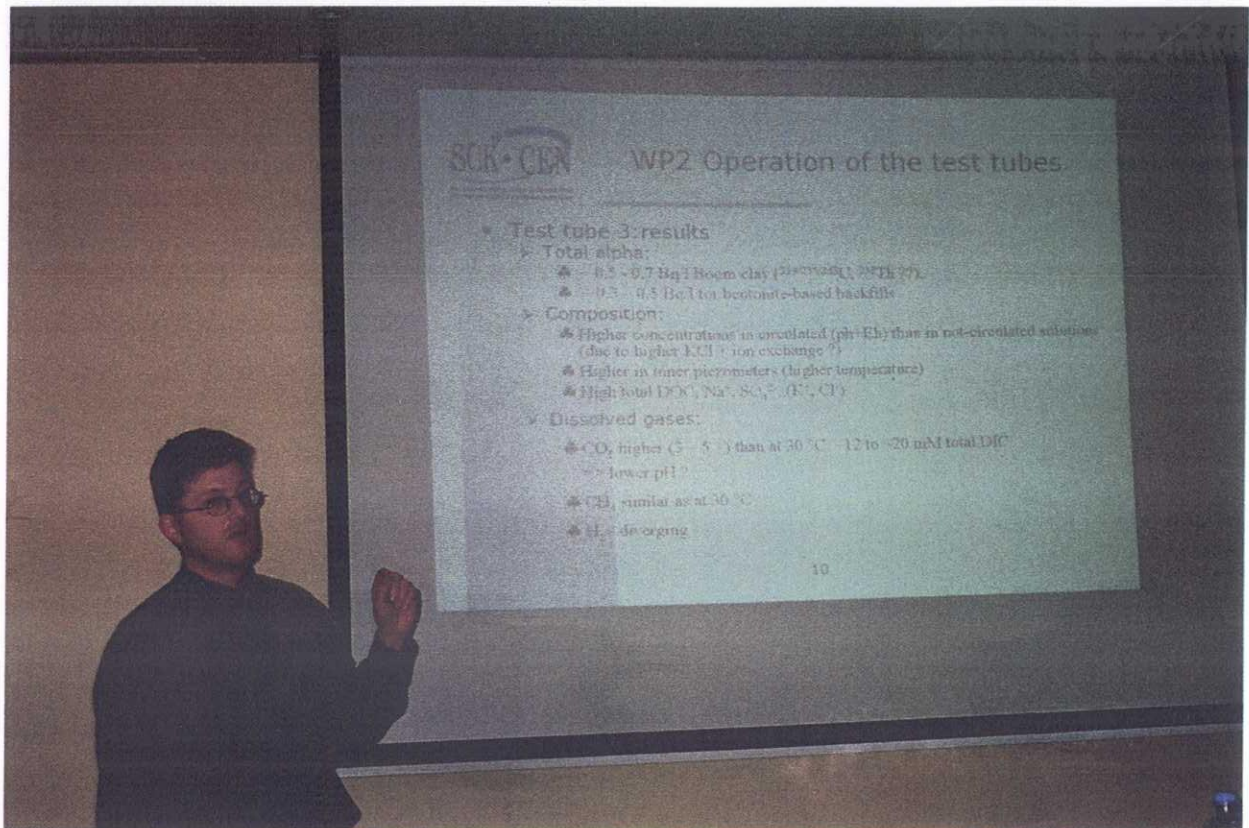
SCK/CEN 側もブーム粘土環境での核種移行評価には関心があるので、今後、CORALUS II で得られる情報も含め、金銭的な契約が無くても情報がもらえるように今後調整が必要である。CORALUS 計画では、コバルト 60 を挿入した条件で Np, Am, Pu, U, Th を入れたガラス試料をベントナイト中に設置し、30、90℃で 2 から 4.5 年地下研究所の原位置で試験できる貴重な試験であるため、是非今後も関係を保持すべきである。別途、JNC が実施した CORALUS プロジェクトのシミュレーション結果を入れた CD を渡すと共に、瑞浪、幌延の地下研究施設の計画に関する情報を提供した。

SCK/CEN の Valcke 氏の報告と併せて GRS 及び CEA マルクールにて実施している室内試験結果も報告された。

(2) 会議参加者及び状況

本会議は EU の放射性廃棄物に関する研究予算を受けて実施されている研究課題であり、今回 3 つのプロジェクト (CORALUS、GLASTAB、GLAMOR) を一緒に開催した。GLAMOR プロジェクトについては、オブザーバの参加は認められなかった。会議にはアメリカの McGrail、Strachan、ベルギーの Valcke、Van Iseghem、フランスの Grambow (ドイツ人であるが、現在フランスの大学教授)、Gin、Minet (CEA)、スイス (PSI)、ドイツ (GRS) など約 20 人の研究者が参加し (参加者名詳細は、参考資料 5.2 参照のこと)、非常に細かい点までつっこんだ議論がなされた。

会場ではポスター展示で、日本からの現状報告、建設が始まった瑞浪、幌延の状況、東海の果たす役割や CORALUS プロジェクトのシミュレーション結果、熱力学データベース、吸着データベース、論文等を紹介した。地下研の計画には関心が多かった。



SCK/CEN の Valcke 氏の発表状況



会議状況 (その1)



会議状況（その2）



会議状況（その3）

2.2.2 サイクル機構が実施した核種移行モデリング評価結果に対する質疑応答 モデル解析に関する質問及び回答、再確認事項を以下に示す。

Valcke 氏からの質問(Q)、コメント(CS)に対するサイクル機構の回答(AJ)、コメント(CJ)

(CS1)解析結果を確認したが、サイクル機構の精緻な解析手法に興味を持っている。また我々の主な関心は有機物の重要性についてである。特にブーム粘土 (module A) について関連していると考えている。有機物については、コロイドと同じように、immobile organic と mobile organic (RN-organic matter complexes) への核種の収着反応が生じると考えている。これらの反応はブーム粘土中で重要な核種移行の挙動と考えているが、これらの反応について得られているデータはわずかである。

(CJ1)サイクル機構でも有機物に関する基礎的な試験は、実施している。今後、幌延の地下研究施設でも重要なテーマとして取り上げていくことになる。CORALUS の計画が1年程度遅れているので試験計画の改訂版を送付願いたい。

→会議後送付された CORALUS 試験の現状

	設置	運転開始	運転終了	期間(年)
Tube°2 (⁶⁰ Co 無, 30 °C)	2000.04.10	2001.02.21	2004.03.31	3.1
Tube°3 (⁶⁰ Co 有, 90 °C)	2001.04.25	2002.12.05	2004.02.28	1.3
Tube°4 (⁶⁰ Co 有, 90 °C)	2001.10.25	2003.04.15	2009.04.15	6.0
Tube°5 (⁶⁰ Co 無, 30 °C)	2003.11.06	2004.09.01	2014.08.31	10

(Q2) ガラス溶解モデルについて：ガラス溶解初期に関し、(OHP の) model 2 にあるベントナイト間隙水中の Si 濃度を考慮した調和溶解により計算を行っているのか。ガラス溶解長期としてどのモデルを採用しているのか。また、初期から長期へはいつ変更しているのか。

(A2) ガラス溶解モデルはベントナイト間隙水中での Si 濃度変化を考慮した

$$R = A \times K_+ (1 - C/^*C)$$

による調和溶解モデルにより計算している。溶解速度 K_+ および Si のベントナイトへの K_d を変化させて計算を行っている。

$K_+ = 0.017 / K_d \text{ of Si } = 0.01 \text{ mol/l}$: case 1, 3, 5, 6 and 7

$K_+ = 0.017 / K_d \text{ of Si } = 0.5 \text{ mol/l}$: case 2

$K_+ = 1.1 / K_d \text{ of Si } = 0.01$: case 4

(Q3) 間隙水化学について：イオン交換反応および表面錯体反応の定数は Kunigel V1 の平均値を使っているのか、あるいは、その他のデータ（組成が明らかな粘土のデータ、例えばスメクタイトのデータなど）を用いているのか。

(A3) イオン交換反応および表面錯体反応の定数は Kunigel V1 のデータを用いている。

(Q4) 間隙水化学のモデル化について：モジュール A に関し、ブーム粘土のイオン交換および表面錯体反応はどのデータを用いたのか。また表面錯体反応に関する有機物の影響は考慮したのか。ブーム粘土の収着容量に関する化学、データは重要である。

(A4) イオン交換および表面錯体反応のデータは Kunigel V1 のデータを用いている。

また有機物の影響は考慮していない。有機物、表面錯体反応等の解析に必要なデータが何かを別途連絡する。→会議後、ブーム粘土に関する取得データを問い合わせた。

(Q5) 脱ガスを考慮した解析について：なぜ炭酸ガスの脱ガスを考慮しているのか。

(A5) 間隙水抽出時に圧力が低下している。そのため $\text{CO}_2(\text{g})$ の脱ガスの可能性が考えられ、その影響によるバリエーションを考慮した。

(Q6) 間隙水組成モデル計算の結果について：表に記述されている C は無機炭素のトータル濃度かそれとも (重) 炭酸濃度なのか (表中では例えば $1.4\text{e-}2$ と表記されている)。S の化学種は何か。

(A6) 表に記載されている C は全炭酸/メタン濃度、表に記載されている S は全硫酸/硫化物濃度。間隙水中での S は主に硫化物イオン (HS^-) である。

(CS6) C については、各 pH に対する C を含むイオンの形から考えると、メタンではなく、 HCO_3^- となっているのではないか。(pH が大きくなるにつれ、 H_2CO_3 , HCO_3^- , CO_3^{2-} になる) また S についても各 pH に対するイオンの形から考えると、 SO_4^{2-} ではないか。(pH が大きくなるにつれ、 H_2S , HS^- , S^{2-} になる)

(CJ6) 再確認する。

→会議後再確認し、以下のように返答した。

PHREEQC と JNC-TDB で得られた炭素と硫黄の主な化学種は、

- (1) モジュール A (calcite と pyrite で平衡) HCO_3^- , HS^-
- (2) モジュール B (calcite と gypsum で平衡) HCO_3^- , SO_4^{2-}
- (3) モジュール C (calcite と gypsum で平衡) HCO_3^- , SO_4^{2-}

(Q7) 溶解度制限固相について： $\text{NpO}_2(\text{am})$ や $\text{PuO}_2(\text{am})$ は、それぞれ $\text{Np}(\text{OH})_4(\text{am})$ および $\text{Pu}(\text{OH})_4(\text{am})$ のことか。溶解度計算は TDB を JNC-TDB、計算コードについては PHREEQC を用いたのか。

(A7) $\text{NpO}_2(\text{am})$ や $\text{PuO}_2(\text{am})$ は、表記上 $\text{Np}(\text{OH})_4(\text{am})$ および $\text{Pu}(\text{OH})_4(\text{am})$ と書く、同じものである。溶解度計算は TDB を JNC-TDB、計算コードについては PHREEQC を用いた。

(Q8) Am と Cs の収着メカニステックモデルについて(1)：Cs の Kd は小さいように思われる。予想では $1\text{m}^3/\text{kg}$ 程度である。メカニステックモデルにはイライトの Frayed Edge Sites における特異収着を考慮しているのか。

(A8) 今回のモデルはイライトへの吸着は考慮していない。しかし、イライトの含有率を考慮して、frayed edge, FES および type II site (Poinssot et al., 1999) の考慮により Cs の Kd を求めることは可能。要求事項表を再確認する。

→会議後、ブーム粘土に関する取得データを問い合わせた。

(Q9) Am と Cs の収着メカニステックモデルについて(2)：比表面積の $29\text{m}^2/\text{g}$ はブーム粘土の値か。

(A9) Kunigel V1 の値である。

(Q10) ケース 1, 5 および 6 の Np の 2.5 年のプロファイルについて：Case 5 においてなぜ沈殿を考慮していないのか（収着しやすいためか、しかし、高い Kd のため、溶解度制限には達することはないと言えるのか）。

(A10) 沈殿の影響は考慮している。Case 5 については Np の Kd の値が大きく、リザーバの Np 濃度が溶解度に達していない状態となっている。

(Q11) ケース 1, 5, 6 および 7 の Am の 2.5 年のプロファイルについて：ケース 5 について、2 つの Kd の違い（高いものと低いものは 5 倍、Np ならば 50 倍）および、Am 溶解度はやや Np よりも低い。高い収着分配係数と溶解度で計算を行っているのはこのためか。また、なぜ Am の溶解度が支配的になっているのかが理解できない（OHP に” solubility dominates” と書いてある理由について）。むしろ、収着が支配的なのでは（仮に、ケース 5 と 1 を比較した場合、（5 は 1 に比べて 5 倍 Kd が高い）濃度プロファイルは 5 が 1 に比べて非常に短くなる）。7 と 1 の比較については（ケース 1 に比べてやはり低い Kd であるが）、濃度プロファイルは相当長い。一方、10 倍低い溶解度（ケース 6 に対する 1）は濃度プロファイルに対して小さな影響しかない。

(A11) OHP の Results : Solubility dominates はガラス表面からの核種の溶出について支配的な反応を記述している。Am の 2.5 年における case 1, 5, 6 および 7 についてはガラスの調和溶解より溶解度により放出量が決定されており、これは、Reservoir（ガラス表面）の濃度から減少した後、プロファイルが表れていることから推定している。

(Q12) ケース 1, 2, 3 および 4、1, 5 および 6 における Pu の 2.5 年について：収着支配だと考える（OHP には Glass dominates, solubility dominates と書いている）、例えば、5 と 1 を比較すると（Kd で 10 倍）、ガラスの溶解速度および Pu 溶解度はわずかな影響しか与えていない（ガラス溶解速度は 50 倍以上ケース 4 より高い、しかし、濃度プロファイルに劇的な変化はない。溶解度については、1 に比べて 6 は 100 倍低い値であるが濃度プロファイルの減少は、やはり、わずかである）。個人的には module A におけるブーム粘土で Pu 溶解度が $\sim 1e-6$ は高すぎるように感じる、 $1e-7$ 程度ではないか。

(A12) (A11) と同じように reservoir（ガラス表面）の濃度(A)とプロファイルが始まる濃度(B)との差から判断している。 $A > B$ の場合 Solubility dominates, $A < B$ の場合 Glass dissolution rate dominates としている。また Pu(III) が支配化学種となるため、溶解度が上昇する

(Q13) Am-doped glass の Cs 計算ケース 2.5 年における 1, 2 および 4、1, 6 および 6：Kd の値も含めて、（JNC の計算結果と比べて）まったく異なる結果を予測している。例えば Cs の Kd は $1m^3/kg$ 程度であると考えている。また、ブーム粘土の透過実験(percolation experiments)において、Cs の移行が速くないことを確認している（Cs は固相に収着する、おそらくイライトへの特異吸着のため、上述参照）。

(A13) Cs はイライトへの収着を考慮していないので Kd が低くなっている可能性がある。イライトへの収着モデルを考慮することは可能。ブーム粘土の透過実験から出てくる Kd をお教え願いたい。一方、JNC でも Kunigel V1 の値を確認する。

→会議後、Kunigel V1 がイライトを含有していないことを確認し、ブーム粘土に関する取得データを問い合わせた。

(Q14) 間隙水化学：粘土鉱物についての表面特性値が必要であると、と示されているが、必要であれば試料を送付するので、これらのデータを JNC にて測定していただきたい。またベントナイト間隙の外(outside the system)で測定された間隙水組成は地球化学モデルにより補正する必要があると、とあるが、その意味が分からない。

(A14) サイクル機構にてブーム粘土や Fo-Ca 粘土の表面特性を測定することはしない。また粘土の空隙水で通常のバッチタイプの溶液化学が適用できるかどうか疑問を持っている。

(Q15) ガラス溶解：変質層における拡散の考慮が必要とあるが、解析結果の通り、ガラスの溶解は Np, Pu および Am (Cs についてもさえも) ほとんど影響を及ぼすことはない。このため、変質層における拡散は考慮する必要はないと考える。また難溶性元素の非調和溶解について、溶解および沈殿が重要であり、非調和溶解はモデル計算の結果には大きな影響を与えないと考える。

(A15) 本モデル化ではガラスの溶解速度はあまり効かないが、変質層における核種の拡散は評価の信頼性を高める上で重要であると考えている。

(Q16) 溶解度：実際の溶解度を知るには拡散試験での溶解度測定が必要である、とあるが、どのようにして、収着や沈殿が生じている拡散実験において溶解度を測定するのか。モデル化された間隙水組成 (the modeled interstitial solution) の溶液において溶解度を決定するのは良い方法ではない。あるいは、ベントナイトと接触している状態での溶解度という意味か、言い換えれば、溶解および収着の結果における溶解度ということか。

(A16) 微細なベントナイト間隙中での溶解度は通常の溶液系と異なる。正確な間隙水や溶解度の測定は困難である。ベントナイト空隙中での核種の溶解度を推定する方法として、Mol サイドで “effective solubility” を採用していると聞いているので、今後このことは議論したい。

(CS16) 了解した。

(Q17) 収着：溶解度と同じ質問である、90℃における収着実験（昨年送信している）を参照のこと。Pu の収着メカニステックモデルについては同意した。

(A17) Case 4 の解析におけるガラス溶解速度は以前メールで送ってもらった Dr. Karel Lemmens の値を用いている。

2.3 GLASTAB プロジェクト

同時に開催された別の会議 GLASTAB は、EU 主催のガラス固化体長期健全性に関する研究会であり、EU の原子力分野研究助成金 (FP5、4 年間で 1300k ユーロ) の助成を受けて開催され、今年は 4 年の研究期間の最終年であるので、これまで各研究所、大学 (CEA, SCK/CEN, PSI, FZK 等) で行われてきた研究のとりまとめが行われ、廃棄物ガラス

が水と接触し水和、変質したゲル層の状況、核種移行、長期にわたる結晶化などについて、かなり詳細な議論が交わされた(5.1 資料参照)。基礎的な元素挙動研究としては、変質層を、SEM、TEM などの表面分析装置で分析する方法以外に、モンテカルロ法、分子動力学(MD)法によるモデリングなど、まだ不完全であるが興味深い解析手法に関する発表もあった。来年3月頃には報告書を完成させる予定とのことである。研究全体としては、外部環境(共存物などの有無)によって状態が変化する変質層の形成メカニズムや浸出挙動などに関してはそれなりに知見が蓄積されてきたが、処分で想定される時間スケールの長期挙動を予測するモデル化には至っていないのが現状である。

3. 会議関連研究施設の見学

3.1 CEA マルクール研究所の見学

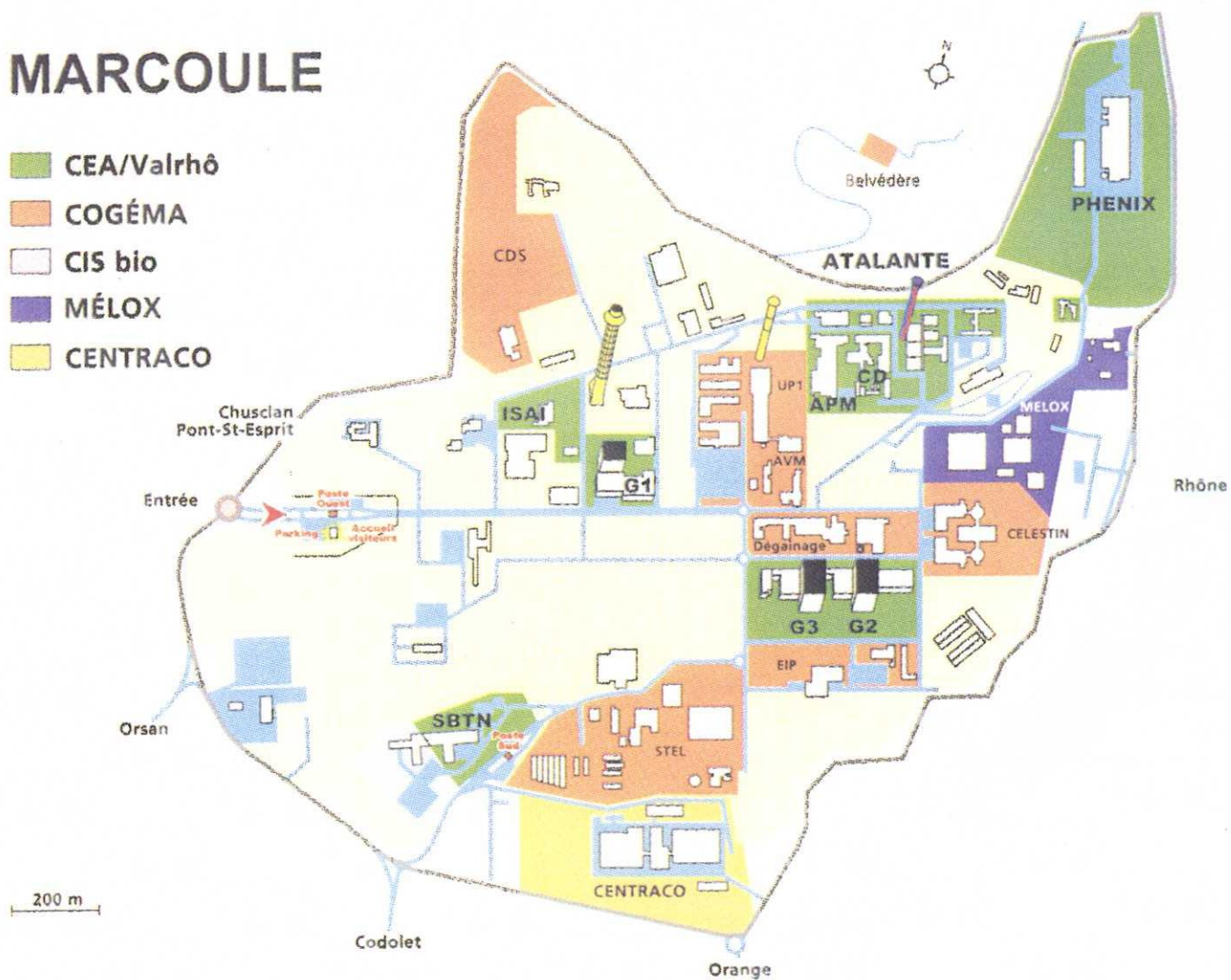
(1) CEA マルクール研究所の見学では、研究所内の地図に APM と書かれた建屋へ行った。この建屋は、研究試験部分とモックアップ試験部分とを併合した作りになっており、コールド実験室ではガラスの長期浸出挙動試験として20年近く継続している試験、120℃で加速試験しているものがあり、ステンレス製のソックスレー装置が多数並んでいた。雰囲気制御グローブボックスもあったが、あまり大規模に実験している様子は無かった。発表であった MD モデリングに関する研究の紹介、地中海に沈んでいた古代の人工ガラスをそのまま海水中に入れて置いてある展示物、黒曜石などナチュラルアナログ研究に関する展示物があった。また新規固化体の例としてヨウ素のアパタイト固化、ジルコノライト固化したものなどの小片が置かれていたが、活発に開発を進めている様子ではないように感じた。隣の別建屋で実規模大の試験体として表面に1cm程度の穴がたくさん開いた容器に鑄込まれたガラス固化体を静的、動的な水環境下で数年間保持している浸出試験状況が紹介された。実規模大で鑄込んだガラスは実際と同様にガラスの割れが入っており、試験体表面及び内部の割れ面での浸出状態の違い、実験室試験との違いを評価する。

(2) ATALANTE では、ATALANTE 1 の高レベル放射性廃棄物研究施設である DHA の C18, C19 セルを中心に見学した。廃棄物固化体作製、特性評価施設は、ガラス、ガラスセラミックス、セラミックス、燃料などを対象として特性評価できる小さなセル群からなっており、できるだけセル内を汚さないようにし、試料間のコンタミ防止、機器のメンテナンスを容易にできるようにしている。非常に使い易そうな施設構成になっており、ガラス等の熔融固化装置として1700℃程度まで上げられる炉、通常の AVH 式の仮焼・小型熔融炉があった。コールドクルーシブルは使っていないとのことであったが、ATALANTE 2 にはあるかもしれない。今回 ATALANTE 2 は、見学できなかったが、各種の分離処理試験ができ、分析設備を ATALANTE と独立して持っている。分離したマイナーアクチニドなどを今回見学した固化処理・特性評価のためのセルに持ってこられるような改造をしているとのことであった。特性評価装置としては、SEM, EPMA, γ 分布測定(各種方向、回転可能)、熱分析、熱拡散測定、浸出率測定、XRD など各種測定装置があった。

(3) 今回訪問希望施設にコールドクルーシブル研究開発施設をいれておいたが、意図的かどうかかわからないが、見学できなかった。コールド実験室のある建屋と実規模ガラス固化体の浸出試験装置が設置されている建屋に、それぞれ、遠目ではあるが、

MARCOULE

- CEA/Valrhô
- COGÉMA
- CIS bio
- MÉLOX
- CENTRACO



Atalante



HISTORIQUE

Le projet ATALANTE a été engagé par le CEA dès le début des années 80 dans le but de regrouper sur un même site un ensemble de moyens de recherche nécessaires à l'aval du cycle nucléaire :
retraitement des combustibles irradiés et traitement-conditionnement des déchets de haute activité. Installation conçue de façon modulaire et évolutive afin de répartir l'effort d'investissement, l'ensemble du projet ATALANTE est conduit en deux étapes :

ATALANTE 1

Ouverture du chantier : 1985
Maîtrise d'œuvre : NOVATOME/SRTI
Mise en service actif : de 1992 à 2000

ATALANTE 2

Ouverture du chantier : 1995
Maîtrise d'œuvre : SGN
Mise en service actif : de 2000 à 2002

CARACTÉRISTIQUES TECHNIQUES GÉNÉRALES

Afin de fonctionner dans le respect des règles définies par l'autorité de sûreté, cette Installation Nucléaire de Base (INB 148) conçue pour la mise en œuvre de quantités significatives de matières radioactives, est sectorisée pour limiter le risque incendie et améliorer le confinement. Elle est dotée d'importants dispositifs de contrôle pour la radioprotection ainsi que d'une ventilation pour le confinement dynamique.

PROTECTION INCENDIE

13 secteurs de feu et de confinement
34 secteurs de feu
900 points de détection et d'alarme incendie
61 extinctions automatiques
400 points d'alarme technique

VENTILATION

210 000 m³/h d'air extrait
302 ensembles de filtration
1 cheminée de 42m de hauteur

RADIOPROTECTION

230 voies de mesures continues.
70 voies de mesure "tout ou rien" reliées au traitement centralisé de radioprotection (TCR).
Plus de 100 voies d'appel reliées au service de protection contre les rayonnements (SPR).
170 contrôleurs de contamination mains, pieds, vêtements

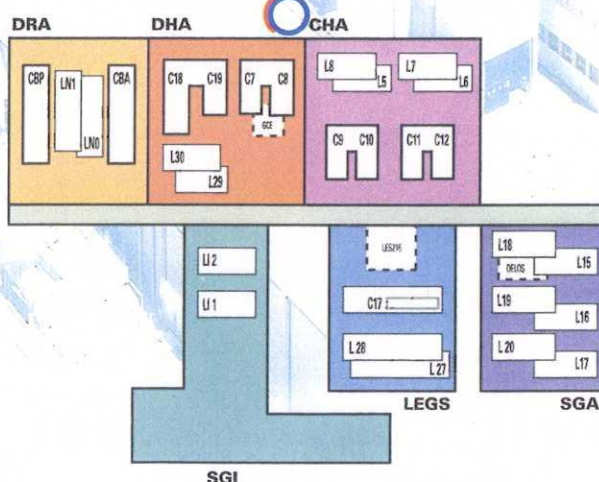
DISTRIBUTION ÉLECTRIQUE

4,8 MW de puissance installée
2 groupes électrogènes de secours de 800 KVA
2 onduleurs de 80 KVA

CHA : Chimie de Haute Activité
2 halls de chaînes blindées : C9-C10 et C11-C12
4 laboratoires : L5, L6, L7 et L8

LEGS : Laboratoire Equipé en Géométrie Sûre
1 hall avec chaîne de B&G et caissons blindés C17
2 laboratoires : L27, L28
1 hall avec caisson blindé
Microscope électronique à balayage : LES216

DRA : Développement Retraitement et Analyses
2 chaînes blindées CBA et CBP (grande hauteur)
2 laboratoires LN0 et LN



DHA : Déchets de Haute Activité
2 halls de chaînes blindées C7-C8, C18-C19
2 laboratoires : L29 et L30
2 cellules blindées GCE (Gestion centralisée des effluents)

SGA : Services Généraux Actifs
7 laboratoires : L15, L16, L17, L18, L19, L20
Unité de destruction des effluents organiques (Delos)

SGI : Services Généraux Inactifs
1 laboratoire de chimie en inactif : LI 1
1 laboratoire de modélisation : LI 2

○ Cheminée d'Atalante

ATALANTE
cea

Centre de la vallée du Rhône - BP 171 - 30207 Bagnols-sur-Cèze Cedex

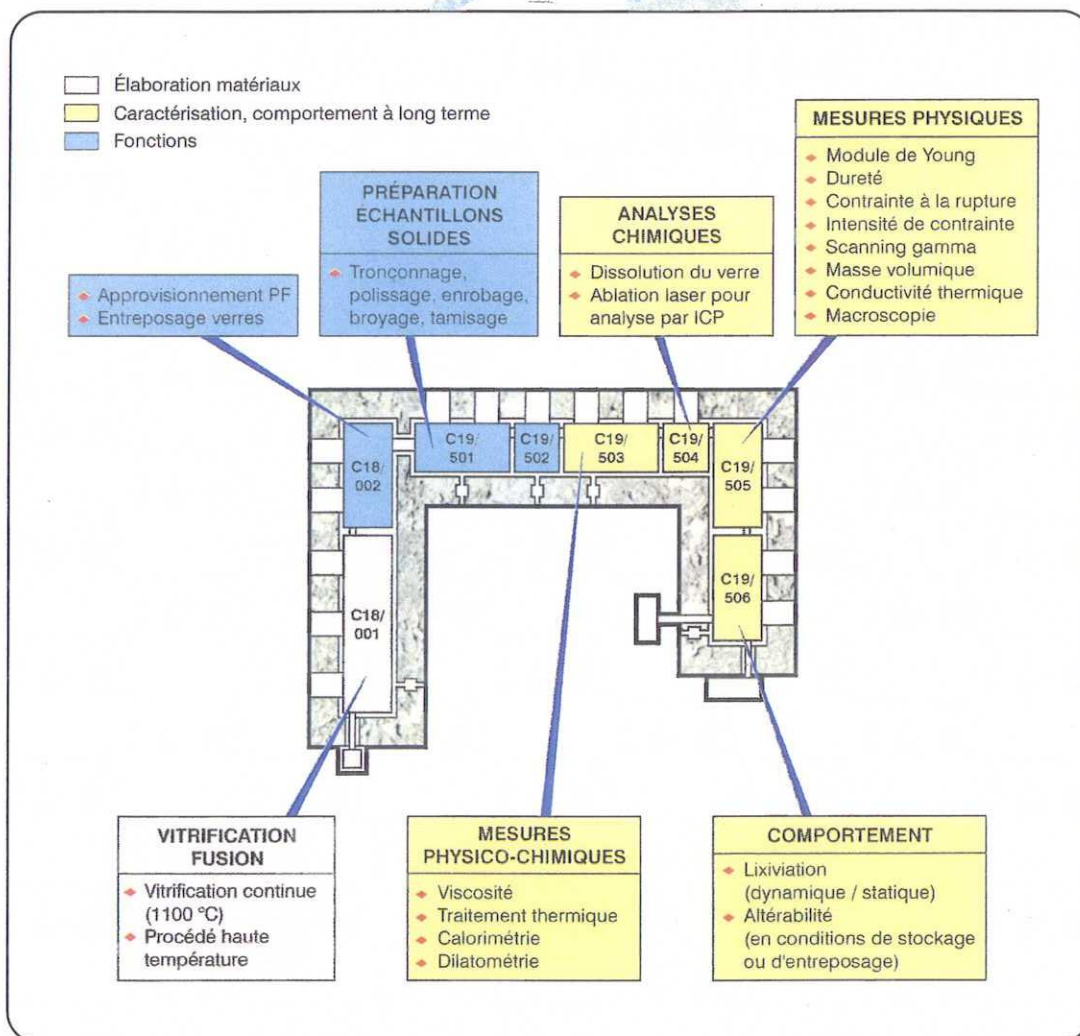


C18 - C19
L29 - L30

R&D

TRAITEMENT & CONDITIONNEMENT DES DÉCHETS DE HAUTE ACTIVITÉ

CHAÎNE BLINDÉE C18 - C19 : PRINCIPAUX ÉQUIPEMENTS





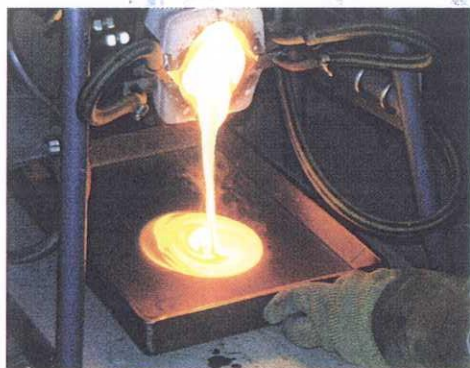
C18 - C19
L29 - L30

R&D

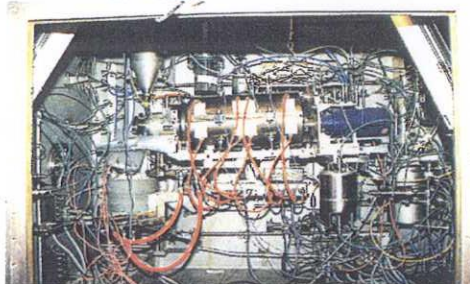
TRAITEMENT & CONDITIONNEMENT DES DÉCHETS DE HAUTE ACTIVITÉ

OBJECTIFS

- Développement (en alpha, beta, gamma et neutrons) de procédés thermiques dans le cadre des études de conditionnement des déchets de haute activité (produits de fission/actinides mineurs ou radioéléments à vie longue) par incorporation dans des matrices vitreuses ou vitrocéramiques.
- Études du comportement à long terme des colis de déchets de haute activité : verres, nouvelles matrices, combustibles irradiés.



• Coulée de verre en laboratoire inactif



• Ensemble calcination-vitrification (Chaîne C18)



• Structure microscopique d'un verre HA

MOYENS

→ C18-C19

Ensemble de 8 caissons blindés disposés en U, équipés d'appareils permettant :

- l'élaboration des matériaux (calcinateur, four de fusion, traitement de gaz).
- la préparation d'échantillons (tronçonnage, polissage, enrobage, broyage, tamisage).
- la caractérisation physique et physico-chimique (viscosité, calorimétrie, dilatométrie).
- l'étude de l'altérabilité à l'eau (lixiviation statique et dynamique, altérabilité en conditions de stockage).

Laboratoire L29

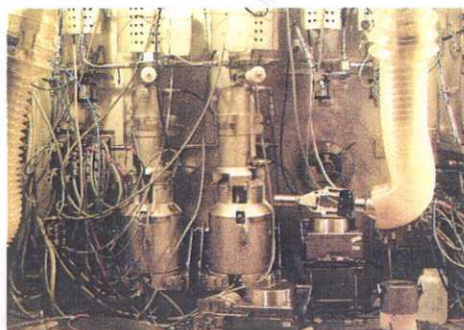
- Microscope électronique à balayage (MEB), microsonde de Castaing, diffraction X, à l'intérieur de boîtes à gants blindées permettant la caractérisation d'échantillons solides.

Laboratoire L30

- Spectromètre de masse et torche à plasma couplés, implantés en boîtes à gants pour la caractérisation d'échantillons liquides.

CARACTÉRISTIQUES C18 -C19

- Protection biologique 950 mm de béton lourd (800 mm pour C18).
- Maîtrise de la sûreté-criticité par une géométrie adaptée.



• Pots de lixiviation (Chaîne C19)

それらしきモックアップ規模又は実規模大の装置があるのがわかった。それぞれの建屋は、ATALANTE の隣（研究所の地図に APM, CD と書かれたエリア）に位置している。



CEA マルクール研究所正門

3.2 SEPR 材料研究所での製品紹介と耐火物の特性比較

SEPR 材料研究所は、フランスの SGN 傘下の会社であり、ドイツの高レベル放射性廃棄物ガラス溶融炉の耐火物材料も供給した実績がある。色々な業種での納品実績を持ち、国際的な工場運営販売活動を行っている。研究開発施設としては、訪問した施設と米国にある施設の 2 箇所とのことであるが、Le Pontet にある工場、Cavaillon にある研究施設内は、安全上、機密保持上見せてもらえなかった。説明図（パソコン画面）で順に解説してはくれたが、大型の耐火物を作る熱処理条件など多くのノウハウ情報については、教えてもらえなかった。TVF、K 施設で使用しているモノフラックス社製のものと同等品の ER2161 電鍍レンガについては、還元雰囲気で作られる K3 に対して、酸化雰囲気で作られる ER2161 の方が熱衝撃に強く割れにくい特徴を持っている。電気的な特性でも同等であり、K3 の割れによるガラスの漏れなどの現象が生じた場合には、代替材料として適切な材料であることを確認した。白金族元素との反応性などは不明であるのでサンプル材料を送付してもらうことにした。品質保証上の事項に関しても世界中の工場でも均一になるよう原材料、工程など変更が無いように細かく情報を把握し、確認しているとのことである。



Le Pontet にある SEPR の工場



Cavailon にある SEPR 材料研究所

EFI ELECTROFUSED INDUSTRY

EFI is a department of SEPR company (Saint-Gobain Industrial Ceramics Group). The mission of this department is to introduce to the broadest users the benefits of the fused cast products and their large diversity of applications..

Fused cast ceramics are used as protecting linings and specially designed for industrial equipment to resist to severe physico-chemical aggression at high or low temperatures.

It is a chemically controlled mixture of metallic oxides, melted in an electric furnace at high temperature up to 2400 °C (4350 °F) and cast into moulds.

SEPR Le Pontet (France) is the largest manufacturer of fused cast ceramics in the world.

Five other manufacturing sites contribute to the diversity and complementarity of the ceramics manufactured by the Group: Refradige in Italy, Corhart in the USA, SEPR in Australia, SEPR in China and Grindwell Norton in India.

The world-wide presence of the Group and its factories, the experience of the EFI department of more than 30 years in the specific industrial markets, the quality and motivation of its teams allow to answer to your needs and bring in each case an adapted solution and technical support.

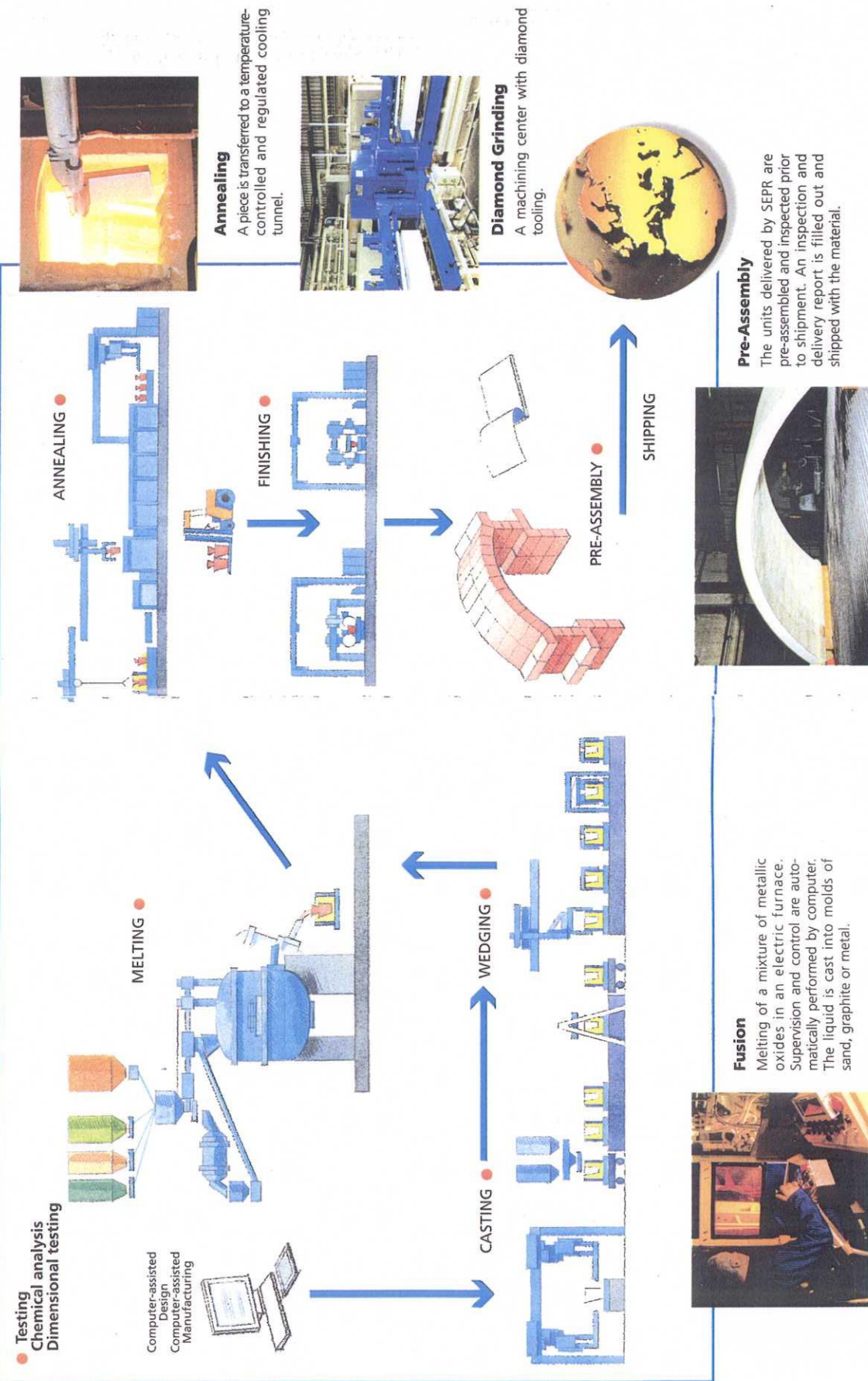
Besides, the R&D centre is always testing new solutions to develop new materials.

Innovation is a SEPR tradition.



Le Pontet manufacturing plant in France certified ISO 9002.

Typical manufacturing cycle



2

3

4. おわりに

ヨーロッパ特にフランスでは、廃棄物ガラス固化・処分関連でも若手研究者が育っているのに対し、他国では、昔から研究してきた人が会議に出席してきており、会議では Grambow 氏のような古手研究者が、若手研究者に不明点を指摘し、教育しているような場となっていた。このような国際的な専門家会議には、研究者数が限られているが、若手研究者がどんどん出席し、議論によって鍛えられる場が多くあると良いと思った。

フランスの技術開発の特徴は、高レベル廃棄物処理技術では AVM 法から AVH 法、コードクルーシブル法と継続的に技術開発を続けていること、また廃棄物ガラスの浸出試験でも長期試験を実施し続け、新固化体研究も始めているなど、長期的な視野にたった研究、技術開発、人材育成をしていることであると思った。サイクル機構でも JNFL、NUMO 等のユーザー、メーカーといった産業界、大学等の研究機関と連携した技術基盤創り、人材育成を図る必要があると思った。

今回の会議は、ホスト機関が CEA であった。交通の便が悪いマルクール研究所ではなく、TGV 駅、飛行場が近くにあるアビニョンのホテルで開催され、会議期間中の昼食、夕食はホスト機関が費用を持ち、会議参加者は、早朝から晩まで会議に集中できた。日本で同様な会議が開催される場合は、このような配慮も必要であるかと思った。また会議前の段取り、見学対応の連絡も電子メールを使って素早く処理された。また会議期間中に発表者の OHP が配布されたり、会議後に II-1 に添付した CEA 作成の議事録が送付されるなど、手際良く会議全体が進行された。議事録には、必ずしも会議中に話し合われた内容ではないことも記載されているので (JNC への対応など)、十分確認し、今後の対応を決定する必要がある。

CORALUS プロジェクトについては、試料の取り出しに向けて今回の会議でのコメントや情報を踏まえ、必要に応じ再解析を実施する予定である。今後ガラス浸出メカニズムに関する世界の最新情報をレビューした報告書を入手し、サイクル機構の研究計画に反映させる予定である。

5.1 CEA 作成の議事録

5. 参考資料

5.1 CEA 作成の議事録（河村訳文と原文）

概要

この会議は、GLASTAB と CORALUS-II プロジェクトの合同会議であり、GLASTAB プロジェクトとしては最後の会議である。会議は、2003 年 10 月 29 と 30 日にフランスのアビニョンで開催され、続いて GLAMOR プロジェクトの技術会議が開催された。GLASTAB 部分は、最終報告書に統合される主要な結論を引き出すため、プロジェクトの骨格に沿ってすべての技術的な結果を包含するように進められた。最終報告書作成に係わる最後の要求事項も議論された。CORALUS-II 会議の部分は、前年に得られた科学的な達成事項の発表に当てられた。次の 6 ヶ月間の契約における仕事をまとめるために、管理上の問題点も議論された。

すべての討議事項は、詳細に科学報告書としてまとめられる予定である。発表された OHP のコピーは、会議中に配布された。

GLASTAB

プロジェクトの骨格となる結果の概要

前回の会議で議論されたように、最終報告書の 5 章に対応した 5 つのセッションが開催された。各セッションの議題は、関連した章の著述と対応して各担当者により準備された。

ゲルの特性と観察 (J.L.Crovisier)

次の題目が会議で発表され、議論された：

- ・ 玄武岩質ガラスの変質層の研究
- ・ 核廃棄物ガラスの変質層の研究
- ・ 層を通しての拡散（玄武岩質ガラス、核廃棄物ガラス）
- ・ 原位置での照射
- ・ ゲルの安定性

これらすべての研究から得られた結論が会議で議論された：

- ・ ゲルの性質（組織、組成、拡散特性）は、外部環境に大きく依存し、時間により変化する；GLASTAB プロジェクトでは、異なる種類のゲルをより正確に記述することとした。
- ・ 二次的な析出物の形成は考慮しなければならない；
- ・ ゲル層が防御的か、否かの疑問は明らかだが、拡散過程が、重要な役割をすることが確認された；
- ・ 関連用語を定義することは重要である。（最終報告書の最初の技術的な章に用語集が記される）

変質挙動とゲル形成のモデリング (B.Grambow)

Bernd Grambow は、各種現象の理解を改善するため、GLASTAB プロジェクトの骨格内で用いられたものと異なるモデル化のアプローチを紹介した：

- ・ 文献紹介：最終報告書用に準備され、まとめられる；
- ・ モンテカルロモデリング：いくつかのメカニズムの定性的説明に有効である；

- ・ ゲル形成の熱力学的モデリング：論文が書かれた；
- ・ ゲル内での空孔の進展と物質移動のモデリング：見込みのあるアプローチであると思われるが、KIRMAT コードの使用はプロジェクトの始めに予想したよりも困難であることがわかった；
- ・ 動力学反応系の総合モデリング：GLASTAB では、初期の純水中でガラスが変質する時に観察される重要な変質率の低下を記述するいくつかの方法を提供してきた。GLAMOR プロジェクトでは、それに関しさらに詳細な情報を提供するだろう。

主要な結論は次のモデリングの課題に関連して記述される：

- ・ いくつかの現象に一般的な同一性が見られる：Si 移動、Si 保持、反応の遅延、時間によるゲルの濃密化；
- ・ 本質的なパラメータの代わりにモデルでフィッティングパラメータを用いるようにしたというようないくつかの不確定さが残る。
- ・ 私たちは、ゲルの空効率、組織、鉱物相の溶解/析出動力学に関するより詳細な情報がさらに必要である；
- ・ 残った取り組みは、長期浸出率のモデリングに関することである。：いくつかのモデリングの選択は可能であるが、この割合は、まだモデル化されていない。

ニアフィールド環境におけるガラスの変質 (K. Lemmens)

本会議で最終報告書でこの章を RN (放射性核種) に関連した部分と合わせることに決定した。ニアフィールド環境におけるガラスの変質は (第 4 章の代わりに) 第 3 章になる。この課題は、3 つの主要な部分に分けられる：

1. ニアフィールド材料の研究
2. 統合した実験
3. ガラス/粘土相互反応の地球化学的モデリングとモンテカルロモデリング

主要な目的は：

1. プロセスを明確にすること
2. パラメータを明確にすること
3. 値/不確実性を決定すること
4. 残りの問題を明確にすること

GLASTAB プロジェクトの枠でなされた実験とモデリングから次の結論が導かれる：

- ・ 新しいブーム粘土と FoCa7 粘土は、ガラス溶解率を増加させる、
- ・ 粘土が Si で飽和している場合は、粘土の存在により非常に低い溶解率を得うる。
- ・ 残った Si を固定する機構 (析出) が起きうる粘土の短期吸着容量に到達した時、つまり溶解率が強力に減少するのを止めない時にガラスの溶解が止まらない。
- ・ 濃縮された粘土中のガラスの溶解は、基本的に水中や希釈された粘土懸濁液中でのガラスの溶解とは異なる。
- ・ GLASTAB プロジェクトは、FoCa 粘土での詳細な移行パラメータ値を提供した。
- ・ 放射性核種が関連する限り、酸化還元効果がニアフィールドで放射性核種濃度を決定するのに非常に重要であり、もし環境が還元状態であるならば、粘土の型はあまり重要ではない。

残りの問題は、高 Si 濃度にもかかわらず高い溶解率である矛盾、ゲル溶解動力学、関連したベントナイト量とその最終溶解率への影響、全体として考慮される廃棄物処分時

の Si 添加効果に関することである。

放射性核種の収着と共析 (M. Del Nero に代わり R. Barillon)

GLASTAB プロジェクトとして実施された研究は、3つの主要なトピックスに分けられる。

1. ランタニド、アクチニドの吸着/析出プロセスに関する基本的な知見を得ること
2. ガラス変質層でのランタニド、アクチニドの収着を定量化すること
3. 炭酸塩環境で浸出したゲル中でのストロンチウム、ランタニド、アクチニドの放出/取り込みの研究

GLASTAB プロジェクトとして実施された研究は、ゲル/溶液系におけるストロンチウム、ランタニド、アクチニドの元素挙動を支配するプロセスに価値ある洞察を与えた。

一方、基礎的な知見も得られた：

- ・ 析出プロセスに関して：長期間に“酸性媒体”中で HLW が溶解した後に、最大元素濃度は、溶解度の低い水酸化物、 $\text{Th}(\text{OH})_4$, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$ と多少溶解度を持つ炭酸塩 AmOHCO_3 (Y, La, REE と類似である) と MgCO_3 の形成によって制限される。
- ・ 吸着プロセスに関して：3価の元素は、強い AlOH 表面サイトへの非常に高い親和力を持っている。また3価のランタニド、アクチニドの吸着は水相の炭酸塩複合体化と競合する。 $\text{Np}(\text{V})$ は、 AlOH の表面サイトに対して3価元素よりも親和力が低い。そして $\text{AlOH}(\text{FeOH})$ 表面サイトの濃度は、ゲルの組成に依存しない。ゲル組成がいかになっているにもかかわらずアルカリ性の pH 下では $\text{Np}(\text{V})$ が最小限取り込まれることは、確かである。

他に、複雑なゲル/溶液系における収着過程の同定/定量に関し顕著な進展があった：ゲル構造は吸着をコントロールする（非常に高い親和性を持つサイトが少ない。 SiOH サイトが支配し、高い親和性の FeOH , AlOH サイトが少ない）中性に近い pH で吸着は、たったトレース濃度レベル程度で、効果的な遅延過程がある。すなわち短時間でガラス溶解からの元素放出率が低くなるかどうかである。アルカリ性の媒体では、元素の遅延が、移動し易く強い炭酸塩液複合体 ($\text{Np}(\text{V})$ と HREE に対する) によって占められる。酸性の媒体では、3価の元素がイオン交換によって永続する荷電サイトを占める。

- ・ 複雑なガラス/ゲル/溶液系での3価元素の（吸）収着の研究では、中性に近い pH で Am と Eu に対してゲルへの強い（吸）収着効果があることを示した。ガラスの溶解によって放たれた3価のランタニドでも同様な効果あり、液相の炭酸塩の存在効果を減少させた。液相の炭酸塩との複合体化とゲルへの収着との競合は、水中のガラスの浸出における3価元素の保持状態をコントロールする。 MgCl_2 塩水中では、ゲル上でのイオン交換が、3価元素の低い保持状態をコントロールする。

最終的な結論は次のようになる。

- ・ 長期におけるアクチニドとランタニドの挙動は、少し溶解性である水酸化物 ThO_4 , $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ と多少溶解性の炭酸塩 AmOHCO_3 (Y, La, REE も同様) の析出によりコントロールされる。短期においては、形成されたゲル上の元素吸着が、強いサイトとゲル構造（少量で高い親和力のあるサイト）に対する元素の親和力によってコントロールされる。
- ・ 吸着は中性に近い pH のみで、低い元素濃度で、高いゲル/溶液表面比率であるかどうかの場合に、LREE, Am^{3+} にとって有効な二次的遅延過程となるであろう。（非常に高いゲル/溶液表面比率であっても、吸着の予想を確実にするには、試験するべきであ

る。・・・将来の仕事)

- ・ 吸着は、液相で動き易い炭酸塩複合体が支配する（溶解度制限相：炭酸塩）アルカリ性媒体下で Np(V) と HREE 共に有効な遅延機構ではないし、イオン交換が支配する酸性の pH で Am^{3+} と Ln^{3+} に対しても有効な遅延機構ではない。
- ・ ガラス/形成中のゲル/溶液の複合系での実験は、元素の挙動と顕著な収着機構が物理化学的条件に依存する：ガラスの溶解により放出された 3 価元素が中性に近い pH でゲル上に（吸着）収着によって取り入れられる。アルカリの pH 下では、吸着と（溶解度制限相は、おそらく炭酸塩である）保持量の減少を導く溶液の炭酸塩複合体化との競合がある。 MgCl_2 塩水中では、顕著な収着機構がイオン交換（低い効率）である。

性能評価計算：長期ガラス固化体挙動(I. Ribet)

このセッションで発表された結果は、第一にガラスと中間的なまわりの環境だけが考慮される（運用上のモデリング）システムで、第二に全体（性能評価）に関して処分概念で、ガラス性能を概観して GLASTAB プロジェクトの枠で得られたすべての知識を統合しようとするものである。最終的な結論を以下に示す。

- ・ ガラスの性能は、まわりの環境の反応性による（短、中期間）そして長期では関連したメカニズムが同定できないために浸出率による。有効な表面に関する課題は、GLASTAB プロジェクトの枠に位置づけられなかった。
- ・ 性能評価に関する限り、ガラス浸出率の感度解析は、ニアフィールドのバリア系内で、ガラス浸出率が Nagra の参照値 $7 \times 10^{-5} \text{kgm}^{-2}\text{a}^{-1}$ ($1.9 \times 10^{-4} \text{gm}^{-2}\text{j}^{-1}$) あたりの顕著な値から始まる。セシウムの保持能力はセシウムの移行で選択された主要な現象（溶解度制限か収着か）に依存する。
- ・ ガラスが良い閉じ込め性を持ったマトリックスかどうかという質問に対しては、考慮される放射性核種の性質によることと環境の材料の性質によるということである。処分概念はガラス性能に最小の影響を与える。

締め切りと管理発行物

GLASTAB の結果に関する伝達

3つのプロジェクト (GLASTAB, CORALUS, GLAMOR) の発表は、EC によって Euradwaste' 04 会議（ルクセンブルグで 2004 年 3 月開催）の枠で要求されている。I. Ribet が論文を書き、それを 3つのプロジェクトの関係者に提出する。（締め切り：12 月 15 日）

GLASTAB の結果の発表は、EC によって要求されている一般的なパンフレット Geological Disposal of Radioactive Waste としてまとめられる。（締め切り：12 月 1 日）I. Ribet が論文を書き、それを GLASTAB の関係者に提出する。

一般的な公開書類 (GLASTAB プロジェクトの work-package WP6-3) に関しては、GLASTAB の結果を廃棄物、処分、放射能などのたくさんの一般的な知識を説明せずに発表することは不可能であることが明らかである。この情報は、すでにいくつかのウェブサイトにも存在する。EC へは、この書類の執筆を次の事項を合わせて置き換えることを提案する：

1. パンフレット Geological Disposal of Radioactive Waste の論文
2. 課題に関係するウェブサイトのリスト

Mr. McMenamin 氏はこの提案を承諾した。

最終報告書

各技術的な章の長さは、約 10 ページでなければならない。これは強制ではないので、もし必要なら（各章の調整役により）長くなっても良い。

管理報告書は、技術報告書とは別にしなければならない。

締め切り

- ・ コスト報告書：12 月末
- ・ 技術的实施計画：1 月末
- ・ 最終報告書：
 - 技術的な章のドラフト：12 月 15 日
 - 関係者に提出される編集したドラフト報告書：1 月 25 日
 - 関係者による査読：2 月末
 - 最終版：3 月末

この最終報告書の配布遅延は、前回の会議で議論され、EC に提出され、10 月 31 日以降でプロジェクトに費用がかからないという条件で承諾された。EC に代わって Mr. McMenamin 氏はこの締め切りは必須であることを主張した。遅延は許されない。

CORALUS-II

昨年成果の発表

E. Valcke 氏は、CORALUS プロジェクトの全容を短く紹介した後、昨年以来の原位置試験で得られた進捗を報告した：WP1 では、No3 と No4 試験管の設置、WP2 では No2 試験管の運転、WP3 は再取出しと解体（準備中）、WP4 は放射性ガラス試料の輸送（準備中）、そして WP5 はガラスと粘土の分析（準備中）。ピエゾメータ溶液の総 α 放射能はいつもベントナイトを基にした材料に対する検出限界値以下（ $<0.3\text{--}0.5\text{Bq/l}$ ）である。そして乾燥したブーム粘土の検出限界値（ $0.5\text{--}0.7\text{Bq/l}$ ；多分ほとんどは、自然に存在する U-と Th-同位体によるものである）あたりでもある。イオン組成は、2 ヶ月の pH と酸化還元電位の測定によって非常に影響を受けている。（高 KCl とイオン交換、他の高濃度の陽イオン；定常的に再生させる平衡溶液の添加効果、こうして拡散限界を減少させている）陽イオンと陰イオンの濃度、総 DOC 量も $90^\circ\text{C} + ^{60}\text{Co}$ 試験管中でかなり高い。試験管の pH と酸化還元電位、3 つのピエゾメータ溶液（ $90^\circ\text{C} + ^{60}\text{Co}$ ）は、 30°C （1 つ又はより多くの pH ユニットの pH 値が低い、酸化還元値がより低い負となっている）で取得された値からかなり異なっている。 CO_2 は最も重要な溶解ガスである。溶解した CO_2 （総無機炭素）ガス含有量は、ブーム粘土で平衡になっている予想値 $10\text{--}15\text{mM}$ より低い。試験管 2 では、 CH_4 濃度の増加と同時に CO_2 濃度の減少するのは、メタノジェニックバクテリアの存在によると思われる。

P. Jollivet は、ガラスの溶解（WP7、 30°C で 1 年と 2 年、 90°C で 1 年と 1.6 年）の実験室試験系の結果を報告した。実験室での反応容器を開けたところ、すべてのガラス試料が、壊れていた。それは、不十分な平板の支持と高い膨潤圧によるものである。物質の減量は直接測れなかったが、SIMS の分布からと付着粘土中のいくつかのキーとなる元素（B, Zr, ...?）濃度分布から導かれるだろう。この様な分析を行うには多くの注意が払われなければいけないことが特記される。異なるガラス試料の SEM 写真が示され、ゲル層に対応する厚みが、Lixiver2 でなされた予測と比較された。ベントナイト + 砂 + グラ

ファイトの埋め戻し材料の実験結果がモデリングの予測とかなり異なっていたため、追加のガラス変質実験が始められた。また埋め戻し材料に対する Si の収着（係数）をきめるためのパーコレーション試験も始められた。

管理発行物と技術的発行物

クラスター会議の間に、CORALUS プロジェクトの関係者がいくつかの管理発行物に關し議論した。

- ・ いくつかの締め切りが再確認された：ブリュッセルの EC 本部へ 2003 年の 11 月 30 日までに年報を提出しなければいけないこと。11 月 15 日までにコスト報告書がコーディネータのところに届けられなければならないことである。
- ・ コーディネータは CORALUS プロジェクトについて来たる Euradwaste2004 会議で（ポスター発表）発表することを要求されている。関係者の承認の後に、10 月 15 日までに EC へアブストラクトが送付された。E.Valcke と P.Van Iseghem が共著で 3 つの EC が出資したガラスに関するプロジェクト（Glastab, Coralus, Glamor）の結果を報告する論文を書く。
- ・ CORALUS プロジェクトの延長（2005 年 3 月 31 日まで）があり、このプロジェクトには 3 つの関係者のみが参加するという事実がある。EC の科学役員が承認しているのは、次の技術会合が 4 年の研究の 2 年目（すなわち、場所までは決められていないが、2004 年の 10 月か 11 月）に開かれることである。さらなるプロジェクトの実行に対して、コーディネータは CEA 又は GRS へ直接確認し、もし適切ならば第 3 の関係者に知らせる。
- ・ 統合プロジェクト NF-PRO (EC の第 6 回構成計画 (Euratom)) では、CORALUS 試験管 2 と 3 で得られた結果の詳細な解釈のみが予定される。さらに試験管 4 の運転と解体は、NF-PRO 統合プロジェクトに含まれていない。従って CORALUS への EC の投資は、2005 年 3 月 31 日で止まる。コーディネータは、この日付以降に EC の共同投資が得られるかどうか確認する。（以下を参照）
- ・ 現時点で、CORALUS-II 以降について 3 つの関係者の共同研究の同意はない。ベルギーにおける研究計画内で、試験管 4 の再取り出しと解体が 2008 年-2009 年の期間に予定されている。（もしピエゾメータ溶液の汚染がなければ、より早く試験管を再取り出しせざるおえない）この判断の利点は、約 6 年の変質後のガラス試料を研究できるということである。逆に、これは、運転コストをより高くすることを意味する。（特に利用コスト）来年の内に、関係者は異なる選択肢についてさらなる共同に対して考えなければならない。（二者間ベースか、他の出資方法、・・・）
- ・ SCK は 11 月の始めに第 5 の試験管を設置し、10 年間、30℃、⁶⁰Co が無い条件で運転する。この試験管は、高放射性の Pu と Am を含んだガラス試料を含んでいないが、非放射性的のものとわずかに放射性的の Np を含んだ SON68 ガラス試料を含んでいる。これらのガラス試料は、正式の共同合意のサインなしで CEA Valrho により提供された。CEA は後のガラス試料と粘土材料の分析に参加しようとしている。現時点でピエゾメータ溶液に溶解したガスが分析されるかどうかは、まだ明らかではない。
- ・ 関係者が思い起こさなくてはいけないのは、CORALUS に参加するためにサイクル機構が加えて 50000 ユーロ払った分の利用に関して判断されなければいけないことである。この合計は CORALUS-II プロジェクトのより高いコストを克服するために助けに

なり、歓迎されるものである。1年の延長、又はいくつかの追加的な分析をしなければならぬためである。コーディネータは、数ヶ月の内に提案を作るだろう。

GLASTAB – CORALUS – GLAMOR – meeting: October 29-31
Agenda

October, 29th : GLASTAB

08h30 – 10h30 Characterising the gels (J.L. Crovisier)

- Introduction + SEM-STEM characterisation of natural gels (J.L. Crovisier) 15 mn
- SEM-STEM on gels formed during long term experiments with nuclear glass (E. Curti, J.L. Crovisier) 25 mn
- Measure of diffusion coefficients in natural gels (P. Berne) 20 mn
- Measure of diffusion coefficients in nuclear glass (K. Ferrand) 25 mn
- In situ irradiation (+ gel stability- biblio ?) (A. Abdelouas) 10 mn
- Gel stability (S. Gin) 10 mn
- Discussion 15 mn

10h30 – 11h00 Break

11h00 – 13h00 Modelling of alteration kinetics and gel formation (B. Grambow)

13h00 – 14h30 Lunch

14h30 – 16h15 Glass alteration under near-field conditions (K. Lemmens)

- Introduction : Kle 10 min
- Study of near field materials (WP4-4, WP4-5): Kle 15 min + 5 min discussion
- Dissolution kinetics in integral conditions I (WP4-1, WP4-3): CEA 15 min + 5 min discussion
- Dissolution kinetics in integral conditions II (WP4-6, WP5-7): Kle 15 min + 5 min discussion
- RN solubility in the near-field (WP4-7, WP4-8) : VPi 15 min + 5 min discussion
- Scientific conclusions and planning of the final report: Kle 10 min + 5 min discussion

16h15 – 16h45 Break

16h45 – 18h30 Performance calculations: long-term glass package behaviour (I. Ribet)

- Operational modelling: I. Ribet 30 min + 20 min discussion
- PA : B. Schwyn 20 minutes + 15 minutes discussion
- Conclusions and planning of the final report: 20 min

19h40 Dinner

October, 30th : GLASTAB (am) / CORALUS (pm)

08h30 – 10h30 RN sorption and coprecipitation (Remi Barillon)

10h30 – 11h00 Break

11h00 – 13h00 General conclusions, final organisation

-Planning and final report: I. Ribet 20 min

-General discussion on GLASTAB conclusions and outlook: 1h40

13h00 – 14h30 Lunch

14h30 – 16h30 CORALUS

16h30 – 17h00 Break

17h00 – 18h30 CORALUS

19h40 Dinner

October, 31st : GLAMOR

08h30 – 10h30 GLAMOR

10h30 – 11h00 Break

11h00 – 13h00 GLAMOR

13h00 – 14h30 Lunch

14h30 – 16h30 GLAMOR

Direction de l'énergie nucléaire
Département d'ingénierie et d'étude des confinements
Service d'étude des systèmes de confinement
Laboratoire d'études du comportement à long terme

CEA/DEN/VRH/DIEC/SESC/LCLT
DO 93 24/11/03



diffusé le : 24/11/03

COMPTE RENDU DE REUNION



OBJET : Cluster meeting GLASTAB – CORALUS-II

REDACTEUR : Isabelle RIBET

LIEU : Avignon – France

VISA :

DATE : October 29-30, 2003

Diffusion :

Les participants :

Mc MENAMIN Thomas
RIBET Isabelle
GIN Stéphane
MINET Yves
JOLLIVET Patrick
DENELEE Dimitri
LAMARE Véronique
VAN ISEGHEM PIERRE
LEMMENS Karel
VALCKE Elie
PIRLET Véra
CROVISIER Jean-Louis
BARILLON Rémi
LUCKSCHEITER Berthold
SCHWYN Bernhard
GRAMBOW Bernd
ABDELOUAS ABDESSALAM
KARINE FERRAND
CURTI Enzo
VAN HUMBEECK
McGRAIL Pete
STRACHAN Dennis
WICKS George

KAWAMURA Kazuhiro
UENO Kenichi

European Commission
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CEA – DIEC/SESC/LCLT
CEA – DDIN/HAVAL
SCK•CEN
SCK•CEN
SCK•CEN
SCK•CEN
CNRS/CGS
IN2P3
FZK
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JNC

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Saclay – France
Mol – Belgium
Mol – Belgium
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Mol – Belgium
Strasbourg – France
Strasbourg – France
Karlsruhe – Germany
Wettingen – Switzerland
Nantes – France
Nantes – France
Nantes – France
Villigen – Switzerland
Brussels – Belgium
Richland, Washington – USA
Richland, Washington – USA
Aiken, South-Carolina – USA

Ibaraki-ken – Japan
Paris – France



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Summary

This meeting was both a cluster meeting for the GLASTAB and CORALUS-II project and the final meeting of the GLASTAB project. It took place at Avignon, France, on October, 29 & 30th, 2003 and has been followed by a technical meeting of the GLAMOR project. The GLASTAB part of the meeting was devoted to an overall view of all the technical results acquired in the frame of the project, in order to draw to major conclusions to be integrated into the final report. The last requirements to organize the writing of the final documents were also discussed. The CORALUS-II part of the meeting was devoted to the presentations of scientific achievements obtained during the previous year. The administrative issues were also discussed, in order to organise the work for the next 6-months period of the contract.

All the discussed achievements will be reported in detail in the scientific reports.

A copy of the presented overheads was distributed during the meeting.

GLASTAB

Overall view of the results acquired in the frame of the project

5 sessions were organized, corresponding to the five chapters of the final report, as discussed during the previous meeting. The agenda of each session was prepared by the partner in charge of the coordination of the writing of the relevant chapter.

Gel characterisation and observation (J.L. Crovisier)

The following issues were presented and discussed during the meeting:

- study of alteration layers from basaltic glasses
- study of alteration layers from nuclear glasses
- diffusion through the layer (basaltic and nuclear glasses)
- in-situ irradiation
- gel stability

The conclusions that can be drawn from all these studies were discussed during the meeting:

- the nature (texture, composition, diffusive properties) of the gel depends greatly on external conditions and varies with time ; the GLASTAB project provided a more accurate description of different kinds of gels ;
- the formation of secondary precipitates has to be taken into account ;
- the question if the gel layers are protective or not remains open, but the diffusion processes are identified to play an important role ;
- it is important to define the relevant terminology (a glossary in the first technical chapter of the final report is indicated).



Modelling of alteration kinetics and gel formation (B. Grambow)

Bernd Grambow presented the different modelling approaches that were used in the frame of the GLASTAB project in order to improve the understanding of various phenomena:

- literature review: it is ready and will be summarized in the final report ;
- Monte-Carlo modelling: useful for providing qualitative explanations of several mechanisms ;
- thermodynamic modelling of gel formation: a paper has been written ;
- modelling of porosity evolution and of mass transfer in gel: it seems to be a promising approach but the use of the KIRMAT code proved to be more difficult than expected at the beginning of the project ;
- overall modelling of kinetic reaction scheme: GLASTAB has provided several ways to describe the important rate drop that is observed when glass is altered in initially pure water. The GLAMOR project will provide more detailed information on that subject.

The main conclusions that can be drawn related to the subject of modelling are the following:

- there is a general agreement on several phenomena: Si transport, Si retention, slow-down of the reaction, gel densification over time ;
- some uncertainties remain, that lead to use some fitting parameters in the models instead of intrinsic parameters ;
- we still need more detailed information on gel porosity and texture, and on dissolution / precipitation kinetics of mineral phases ;
- the remaining challenge concerns the modelling of the long-term rate: several modelling options are available, but this rate has not been modelled yet.

Glass alteration under near-field conditions (K. Lemmens)

It has been decided during the meeting to invert the place of this chapter in the final report with the one related to RN. The Glass alteration under near-field conditions becomes the chapter 3 (instead of 4).

This subject was divided into 3 main parts:

1. Study of near-field materials
2. Integral experiments
3. Geochemical and Monte Carlo modelling of glass/clay interactions

The main objectives were:

1. to identify the processes
2. to identify the parameters
3. to determine the values / uncertainties
4. to identify the remaining problems

The conclusions that can be drawn from the experiments and the modelling work performed in the frame of the GLASTAB project are the following:

- fresh Boom clay and FoCa7 clay increase glass dissolution rate,
- very low dissolution rates can be obtained in the presence of clay, when the clay is saturated with Si,



- the glass dissolution does not stop when the short term sorption capacity of the clay is reached: a remaining Si fixation mechanism (precipitation) is likely, that does not prevent a strong decrease of the dissolution rate,
- glass dissolution in concentrated clay is fundamentally different from glass dissolution in water or in diluted clay suspensions,
- the GLASTAB project provided detailed migration parameters values for FoCa clay,
- as far as radionuclides are concerned, it has been shown that the redox effects are very important for determining the RN concentrations in the near-field, and that the type of clay is not so important if the conditions are reducing.

The remaining problems are related to the contradiction between the high dissolution rate despite a high Si concentration, to the gel dissolution kinetics, to the relevant mass of bentonite and its effect on the final rate, and to the effect of Si-additives on the waste disposal considered as a whole.

Radionuclide sorption and coprecipitation (R. Barillon on behalf of M. Del Nero)

The studies performed during the GLASTAB project can be divided into 3 main topics:

1. Gaining basic knowledge on adsorption / precipitation processes of Ln and An
2. Quantifying sorption of Ln and An on glass alteration gels
3. Studying the release / uptake of Sr, Ln and An during gel leaching under carbonated conditions.

The studies performed during the GLASTAB project provided valuable insights into the processes that govern the behaviour of Sr, Ln and An elements in gel / solution systems.

On the one hand, basic knowledge has been gained:

- on the precipitation processes: maximal element concentrations after dissolution of HLW in "acid media" in the long term controlled by formation of poorly soluble hydroxides $\text{Th}(\text{OH})_4$, schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), gibbsite ($\text{Al}(\text{OH})_3$) and of more or less soluble carbonates AmOHCO_3 (homologue for Y, La, REE) and MgCO_3 .
- on the adsorption processes: trivalent elements have very high affinity for strong AlOH surface sites, so adsorption of Ln^{3+} , An^{3+} may compete against aqueous carbonate complexation. $\text{Np}(\text{V})$ has lower affinity than trivalent elements for AlOH surface sites, and the concentration of AlOH (FeOH) surface sites does not depend on the composition of gels, that ensure only minimal uptake of $\text{Np}(\text{V})$ under basic pH, whatever the gel composition.

On the other hand, significant progresses have been made with the identification / quantification of sorption processes in complex gel / solution systems: The gel structure controls adsorption (low amounts of very high affinity sites, low amounts of high affinity FeOH , AlOH sites, SiOH sites predominate). At near-neutral pH, the adsorption is an efficient retardation process only at trace concentration levels i.e. at short term and / or at low release rates of elements from glass dissolution. In basic media, the retention of elements may be dominated by the formation of mobile strong carbonate aqueous complexes (for $\text{Np}(\text{V})$ and HREE). In acidic media, sorption of trivalent elements may be dominated by ion exchange on permanent charged sites.

- The studies on (ad-)sorption of trivalent elements in complex glass / gel / solution systems show that at near-neutral pH, there is a strong effect of (ads-)sorption on gel for Am and Eu, a



similar effect on Ln^{3+} released by glass dissolution, and a decrease of the effect in presence of aqueous carbonates. The competition between aqueous carbonate complexation and adsorption on gel controls the retention of trivalent elements during glass leaching in water. In MgCl_2 brine, ion exchange on gels controls the low retention of trivalent elements

The final conclusions are the following:

- In the long term, the behaviour of An and Ln is controlled by precipitation of poorly soluble hydroxides $\text{Th}(\text{OH})_4$, schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$) and of more or less soluble carbonates AmOHCO_3 (homologue for Y, La, REE). In the "short" term, the adsorption of elements on forming gels is controlled by the element affinity for strong sites and gel structure (low amounts of high affinity sites).
- Adsorption may be efficient secondary retardation process for LREE, Am^{3+} only at near-neutral pH, at low concentrations of elements and / or at high surface gel / solution ratios. (Although at very high gel / solution ratios, the validity of prediction for adsorption has to be tested....Future work).
- Adsorption is not an efficient retardation mechanism, neither for Np(V) and HREE under basic media, where mobile aqueous carbonate complexes may predominate (solubility limiting phases : carbonates), nor for Am^{3+} and Ln^{3+} , under acidic pH, where ion exchange predominates.
- Experiments in complex glass / forming gels / solution systems have confirmed that the behaviour of elements and the predominant sorption mechanism depend on the physico-chemical conditions: trivalent elements released by glass dissolution are incorporated by (ads)orption on gels at near-neutral pH. Under basic pH, there is competition between adsorption and aqueous carbonate complexation leading to a decrease of retention (the solubility limiting phases are possibly carbonates). In MgCl_2 brines, the predominant sorption mechanism is ion exchange (low efficiency).

Performance calculations: long-term glass package behaviour (I. Ribet)

The results presented during this session intends to integrate all the knowledge acquired in the frame of the GLASTAB project into an overall view of glass performance, firstly in systems where only the glass and its immediate surrounding environment is considered (operational modelling) and secondly in disposal concepts taken as a whole (performance assessment).

The final conclusions are the following:

- The glass performance depends on the reactivity of the surrounding environment (short-medium term) and on long-term rate, for which the relevant mechanisms are not identified so far. The issue of the efficient surface was not addressed in the frame of the GLASTAB project.
- As far as PA is concerned, a sensitivity analysis on glass dissolution rate shows that within the near-field barrier system, the glass dissolution rate starts to get significant around the Nagra reference value of $7 \cdot 10^{-5} \text{ kg.m}^{-2}.\text{a}^{-1}$ ($1.9 \cdot 10^{-4} \text{ g.m}^{-2}.\text{j}^{-1}$). The retention capability of caesium depends on the dominant phenomenon chosen for Cs migration (solubility limit or sorption).
- The question if the glass is a good confinement matrix or not depends both on the nature of the considered radionuclide and on the nature of environmental materials. The disposal concept has an impact on the minimal glass performance.



Deadlines and administrative issues

Communication on GLASTAB results

A presentation of the 3 projects (GLASTAB, CORALUS, GLAMOR) has been required by the European Commission in the frame of the Euradwaste'04 conference (March 2004 in Luxembourg). I. Ribet will write the paper and submit it to the partners of the 3 projects (deadline: December, 15th).

A presentation of the GLASTAB results in a general Brochure devoted to Geological Disposal of Radioactive Waste has been required by the European Commission (deadline: December, 1st). I. Ribet will write the paper and submit it to the GLASTAB partners.

Concerning the general document for the public (work-package WP6-3 of the GLASTAB project), it appeared that it was impossible to present the GLASTAB results without explaining a lot of general knowledge on waste, disposal, radioactivity and so on. This information already exists in several websites. It has been proposed to the Commission to replace the writing of this document by the combination of:

1. the paper for the Brochure on Geological Disposal of Radioactive Waste
2. a list of websites related to the subject.

Mr. McMenamin accepted this proposition.

Final Report

The length of each technical chapter has to be around 10 pages. This is not compulsory, the chapters may be longer if necessary (up to each chapter coordinator).

The management report has to be separated from the scientific report.

Deadlines

- cost statements: end of December
- Technological Implementation Plan: end of January
- Final report:
 - draft of technical chapters: December, 15th
 - compiled draft report submitted to partners: January, 25th
 - proof-reading by partners: end of February
 - Final version: end of March.

This delay in the delivery of the final report was discussed during the previous meeting, submitted to and accepted by the Commission, provided that no expenses will be charged on the project after October, 31st. Mr McMenamin, on behalf of the European Commission, insisted on the fact that this deadline is compulsory. No delay will be accepted.



CORALUS-II

Presentations on the achievements of the last year

E. Valcke gave a short introduction to the overall CORALUS project, and then presented the progress obtained with the in situ tests since last year: WP1 installation of test tubes N° 3 and N° 4, and WP2 operation of test tube N° 2, WP3 (preparation of) retrieval and dismantling, WP4 (preparation of) transport of radioactive glass samples, and WP5 (preparation of) analyses on glasses and clays. Total alpha activity of the piezometer solutions is always below detection limit for the bentonite-based materials (< 0.3- 0.5 Bq/l), and around the detection limit for the dried Boom Clay (0.5 – 0.7 Bq/l; most probably due to the presence of naturally present U- and Th- isotopes). The ionic composition is heavily affected by the two-months measurement of the pH and redox potential (high KCl, and, due to ion exchange, also high concentrations of other cations; additional affect of constant refreshing of the equilibrating solution, thus diminishing diffusion limitations). The concentration of cations and anions and the total DOC content is also considerably higher in the test tubes at 90 °C + ⁶⁰Co. pH and redox potentials in the test tube 3 piezometer solutions (90 °C + ⁶⁰Co) differ considerably from the values obtained at 30 °C (pH values one pH unit or more lower, redox potentials less negative). CO₂ is the most important dissolved gas. Dissolved CO₂ (total IC) gas contents are lower than the expected 10 – 15 mM in equilibrium with Boom Clay. In test tube 2, the increase of the CH₄ concentration and the simultaneous decrease of the CO₂ concentration might be due to the presence of methanogenic bacteria.

P. Jollivet presented the results of the laboratory test systems on glass corrosion (WP7, 1 and 2 years at 30 °C, 1 and 1.6 years at 90 °C). The opening of the laboratory reactors revealed that all glass samples were broken due to the combination of insufficiently plane support and high swelling pressure. Mass losses cannot be measured directly, and will have to be derived from the SIMS profiles and the concentration profiles of some key elements (B, Zr,...?) in the contacting clay. It was remarked that much care has to be taken when performing this type of analyses. SEM photographs of the different glass samples were shown, and the corresponding thicknesses of the gel layer were compared with the predictions made with Lixiver 2. Because the experimental results for the bentonite+sand+graphite backfill material differed considerably from the modelling predictions, additional glass alteration experiments were started, as well as a percolation test to determine the Si-sorption (coefficient) for this backfill material.

Administrative and technical issues

During the cluster meeting, the partners of the CORALUS project also discussed on some administrative issues.

- Some deadlines were reminded: the annual report is due at the EC headquarter in Brussels by November 30, 2003. Cost statements should be delivered to the co-ordinator by November 15.
- The co-ordinator was asked to present the CORALUS project at the forthcoming Euradwaste 2004 conference (poster presentation). After approval by the partners, the abstract was sent to the EC by October 15. E. Valcke and P. Van Iseghem will also be co-authors to a paper that reports the results of the three EC-funded projects on glass (Glastab, Coralus, Glamor).
- Given the extension of the CORALUS project (until 31.03.2005) and the fact that only three partners are involved in this project, it was agreed with the EC scientific officer that the next technical meeting will be organised only in the second semester of the fourth working year (*i.e.*



October or November 2004, place yet to be defined). For further execution of the project, the co-ordinator will check directly CEA or GRS, and inform the third partner if appropriate.

- In the integrated project NF-PRO (6th Framework Programme (Euratom) of the EC), only a detailed interpretation of the results obtained for CORALUS test tubes 2 and 3 is foreseen. The further operation and the dismantling of test tube 4 is not included in the NF-PRO integrated project. Consequently, EC funding for CORALUS will stop by 31.03.2005. The co-ordinator will check whether there are possibilities to obtain EC co-funding for the period after this date (see below).
- At present no agreement exists on the post-CORALUS-II collaboration of the three partners. Within the Belgian research programme, the retrieval and dismantling of test tube 4 is foreseen for the period 2008 – 2009 (unless any contamination of the piezometer solutions would necessitate the earlier retrieval of the test tube). An advantage of this decision is that this will enable to study glass samples after about six years of alteration. Conversely, this implies a higher operational cost (especially the exploitation costs). During the next year, the partners should think about the different options for any further collaboration (on a bilateral basis, other ways of funding,...).
- SCK will install in the beginning of November a fifth test tube, to be operated during 10 years at 30 °C, without ⁶⁰Co sources. This test tube does not contain the highly radioactive Pu and Am doped glass samples, but yet includes the non-radioactive and slightly radioactive Np doped SON68 glass samples. These glass samples were provided by CEA Valrhô, without a formal collaboration agreement being signed. CEA intends to participate in the later analyses of glass samples and clay materials. At present, it is not clear yet whether the dissolved gases of the piezometer solutions will be analysed.
- The partners are reminded that a decision will have to be taken on the utilisation of the 50 000 Euro instep fee of JNC to participate in CORALUS. This sum might be welcome to help to overcome the higher cost of the CORALUS-II project, a.o. because of the one-year extension, or to do some additional analyses. The co-ordinator will make a proposal during the coming months.

5.2 CORALUS プロジェクト



CORALUS: an integrated *in situ* corrosion test on α -active HLW glass



SCK·CEN, Mol, Belgium (co-ordinator)



CEA-Valrhô, Bagnols-sur-Cèze, France (glass)



GRS, Braunschweig, Germany (gas analysis)



EC-Contracts FI4W-CT96-0035 (1997-2000)
FI4W-CT2000-00011 (2000-2004)



ONDRAF/NIRAS

N/O Contract CCHO-98/332 (2000-2003)

JNC (Japan)

Collaboration agreement for modelling of results



The objective is to study the performance of the glass SON68 18 17 L1C2A2Z1 in realistic “close-to-real” conditions (1/2)

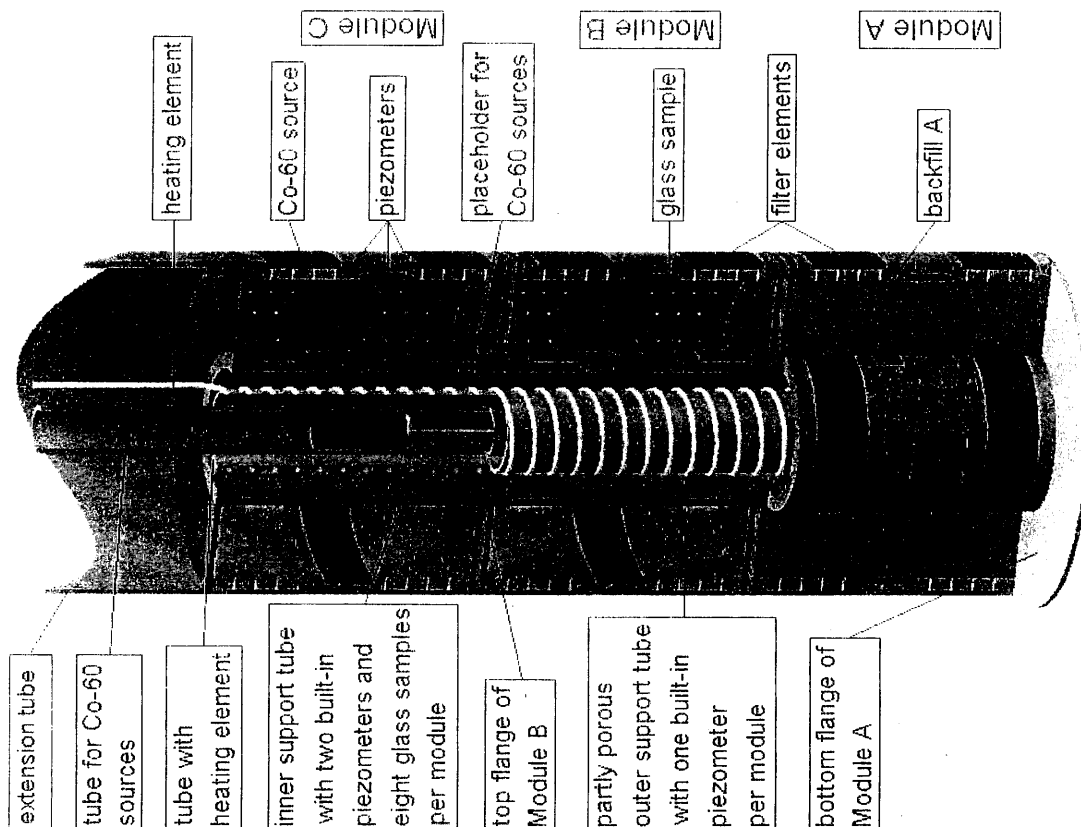
- *dissolution of and RN leaching from the glass*
- *migration of RNs through three backfill materials*
- *combined effect of γ -irradiation and temperature*
- *effect of α -irradiation dose rate*

- α -active SON68 glass (0.85 wt% RNs)
- backfill materials exert swelling pressure of 2 MPa
- presence of α, β, γ -irradiation
- contact with host rock (pH, redox conditions)

The objective is to study the performance of the glass SON 68 18 17 L1C2A2Z1 in realistic “close-to-real” conditions (2/2)

- ➔ Five modular test tubes for integrated *in situ* testing
- ➔ + laboratory experiments:
 - glass corrosion (+ clay alteration)
 - thermal gas generation

Results of the *in situ* test to be compared with results of CORALUS and other lab experiments, and with modelling predictions



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CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE

Five CORALUS test tubes are included in the *in situ* test

Tube	Active or Inactive Glass	Temp. (°C)	Gamma (^{60}Co)	Duration (year)
1	I	90	no	1
2	A+I	30	no	2.5
3	A+I	90	yes	1.5
4	A+I	90	yes	4
5*	A+I	30	no	10

* For NIRAS/ONDRAF only

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE

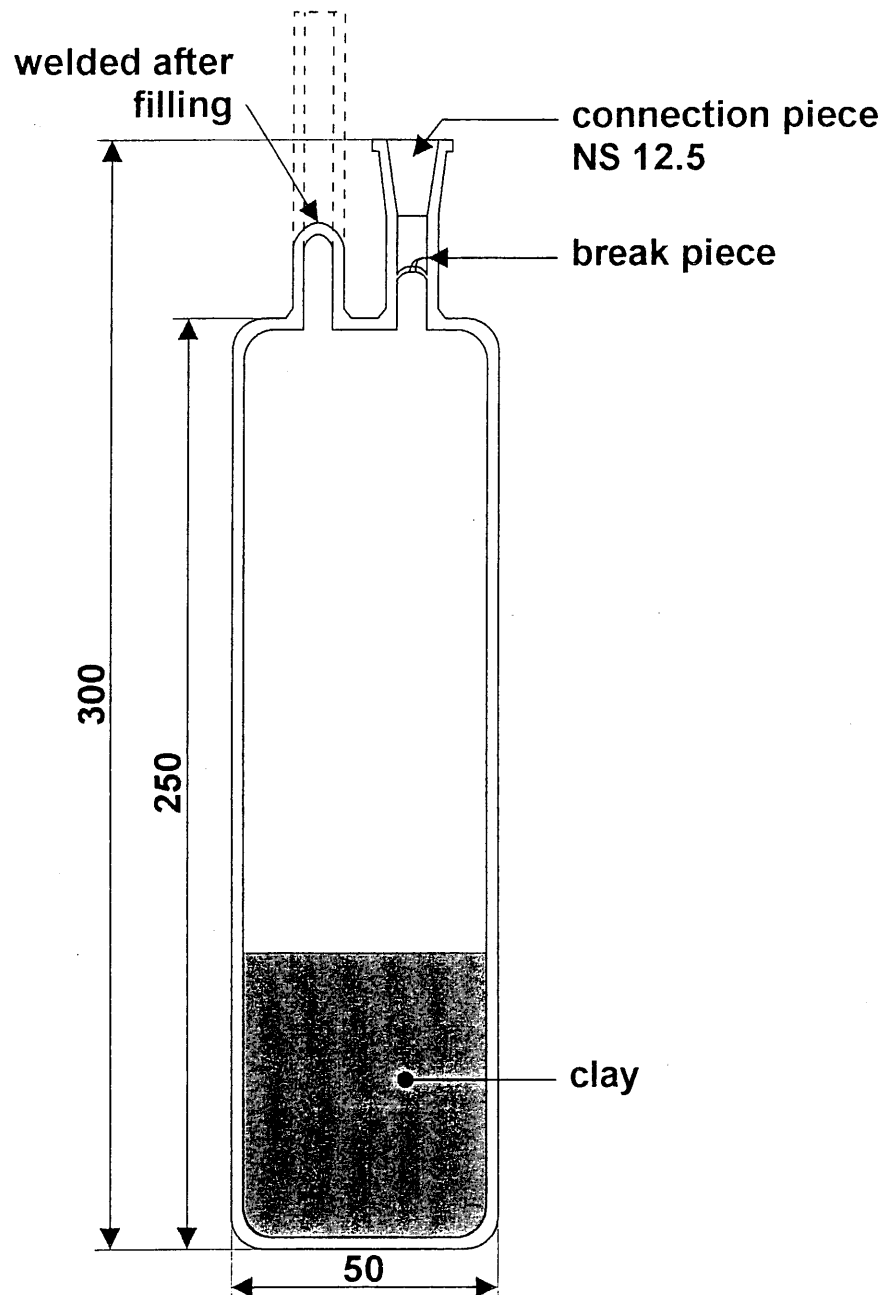
Active glass samples contain 0.85 wt% of actinides

Type of glass	Actinide	Activity/sample (MBq)	Total Activity (MBq)
Np-doped	^{237}Np	1.1	20
Pu-doped	$^{238-242}\text{Pu}$	179	3 220
	^{241}Pu	1 658	29 835
	^{241}Am	61	1 092
Am-doped	^{241}Am	5 095	91 708
	$^{239-240}\text{Pu}$	<205	<3 690

Laboratory Program

Gas generation and release from the different backfill materials as a function of time at a temperature of 90 °C

- preparation of the ampoules
21 ampoules from each of the different backfill material
additional 6 ampoules for blank tests
- exposure periods will vary between 1 and 1000 days
- ampoules for the periods of 30, 100, 300, and 1000 days have already been exposed
- analyses for the periods of 1, 10, 30, and 100 days will be performed Oct. to Dec. 2001
- analyses for the periods of 300 days will be performed Feb. 2002
- analyses for the periods of 1000 days will be performed Nov. 2003



Ampoule for the investigation of the generation and release of gases from the clay as a result of elevated temperature

R7T7 gel stability (WP4.2)

Objective : to assess the durability of the passivating effect of the gel between pH 4 and pH 11

Experiments at imposed pH

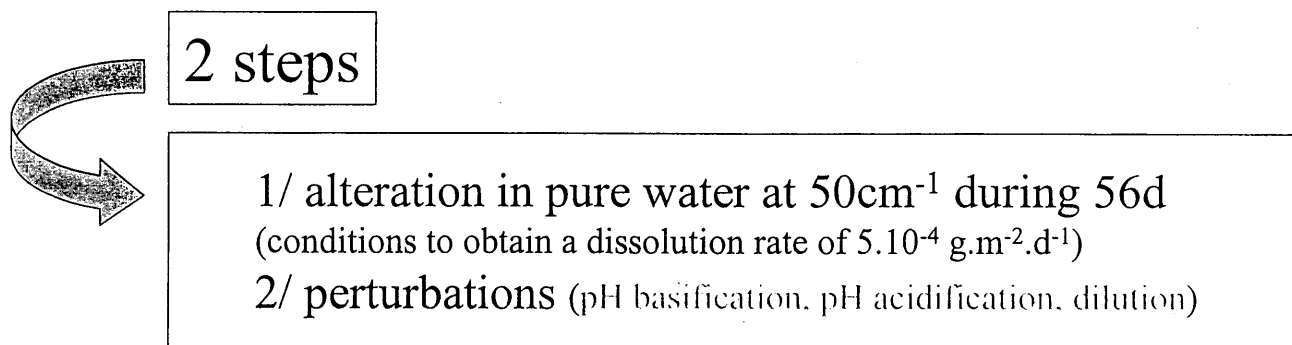
Perturbation of experiments at unrestricted pH

Avignon, October 29 2003

Glastab WP 4.2

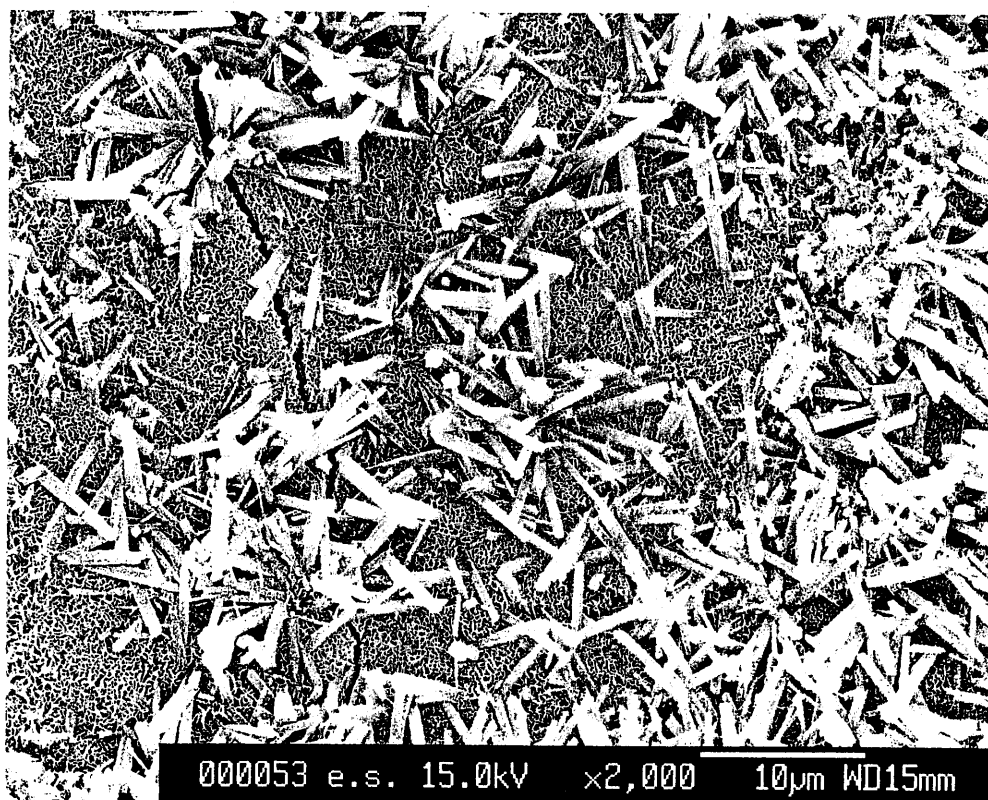
S. Gin

Effect of pH perturbations



Comparison of the glass dissolution kinetics between the reference medium and the perturbed medium

Alteration products at pH 11.5

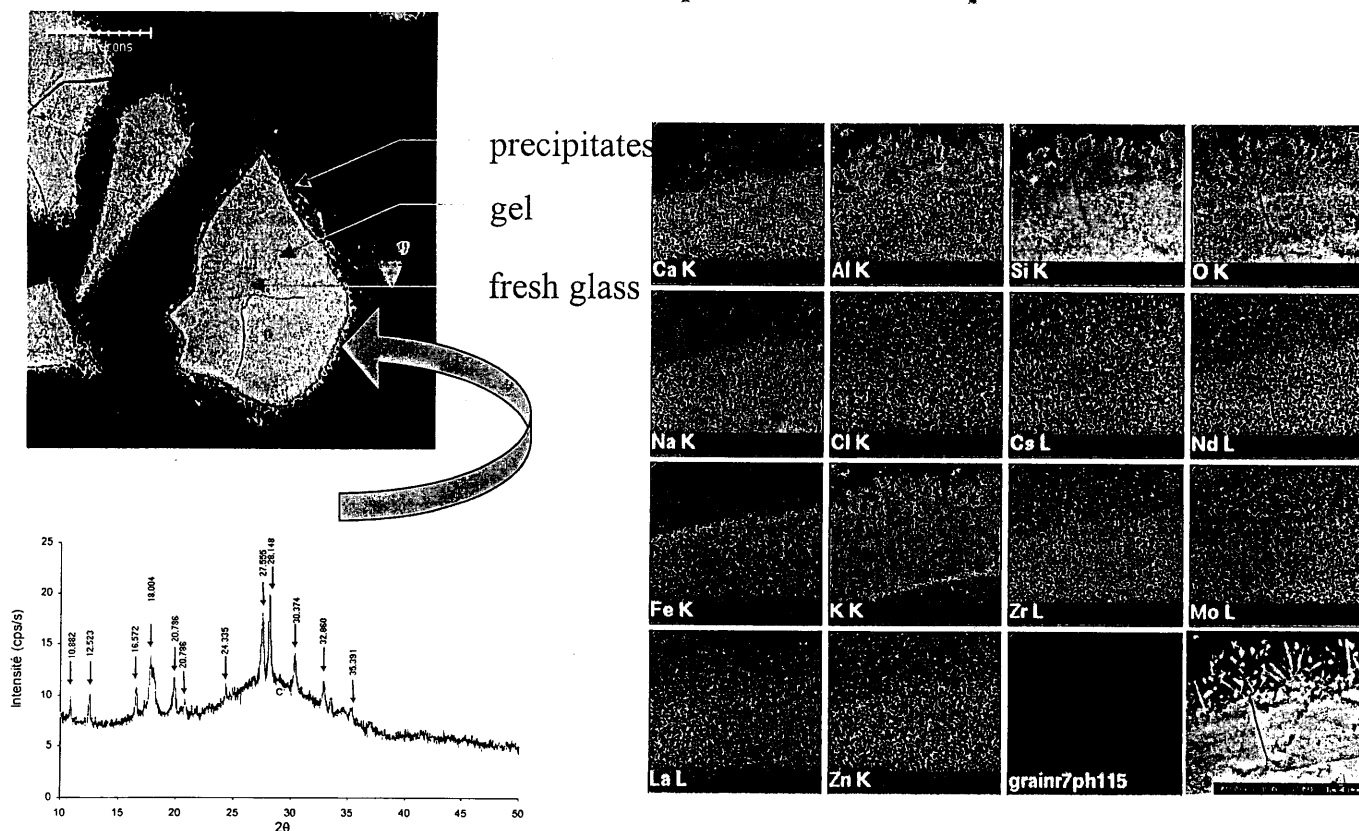


Avignon, October 29 2003

Glastab WP 4.2

S. Gin

Alteration products at pH 11.5

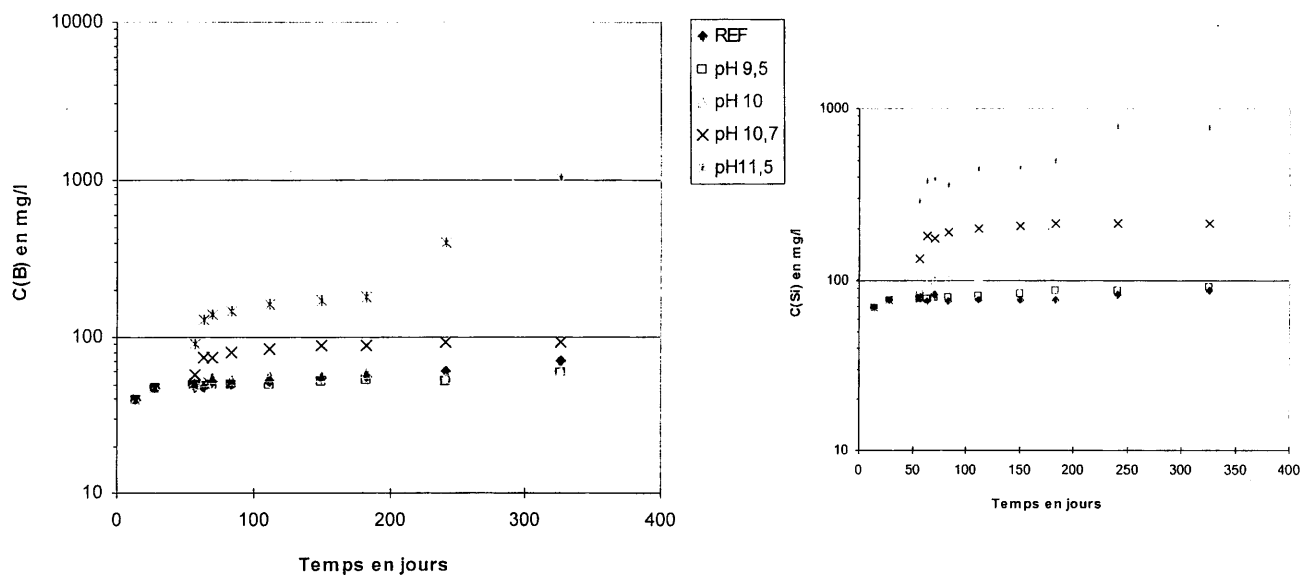


Avignon, October 29 2003

Glastab WP 4.2

S. Gin

Effect of pH increasing

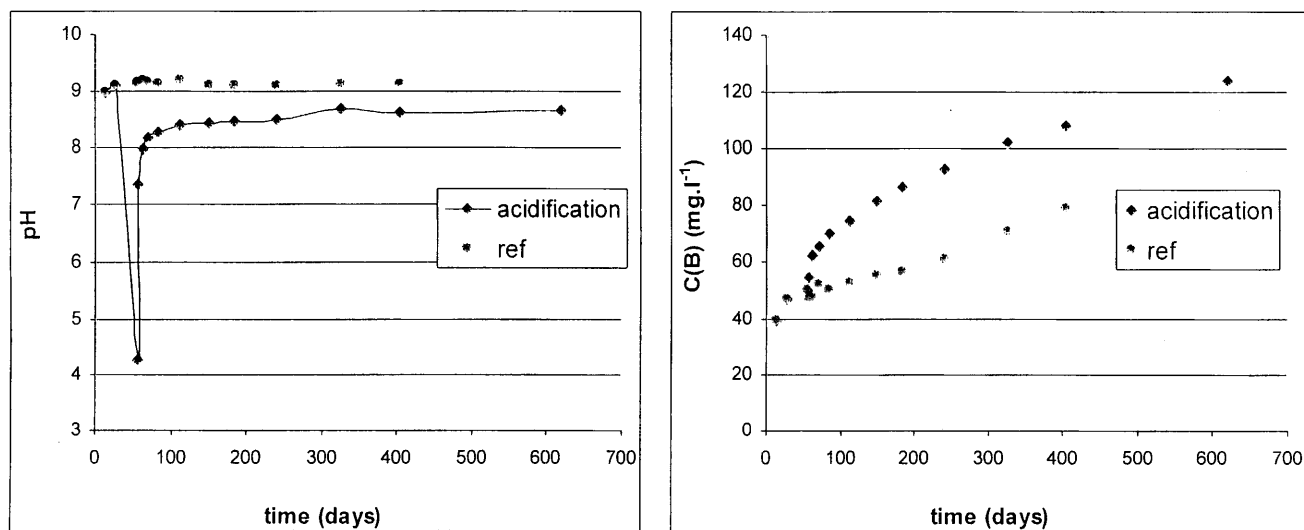


Avignon, October 29 2003

Glastab WP 4.2

S. Gin

Effect of pH acidification

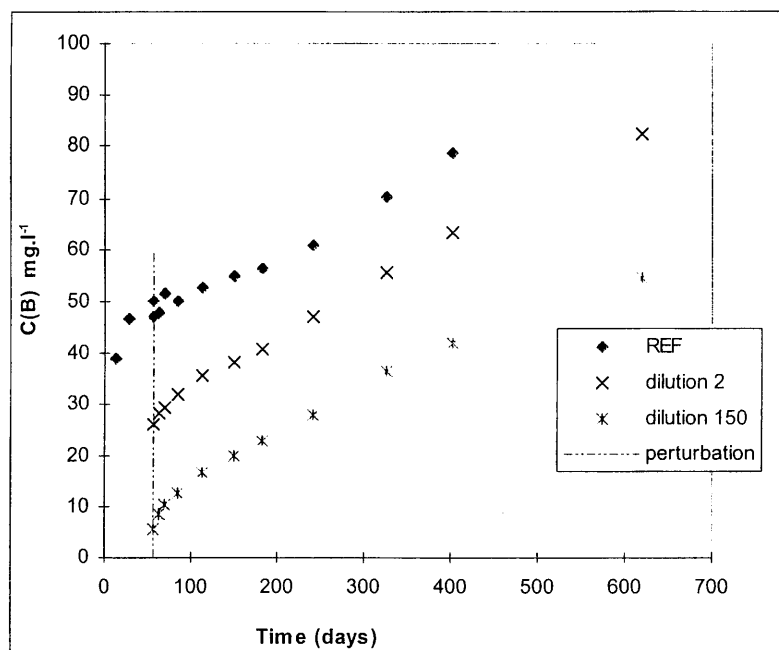


Avignon, October 29 2003

Glastab WP 4.2

S. Gin

Effect of dilution



See also *Gin (2000) MRS Sydney*

Avignon, October 29 2003

Glastab WP 4.2

S. Gin

Conclusions

- Until pH 10 a drop of pH has no consequence on the glass dissolution kinetics. Above pH 10, the results could be interpreted by considering the phenomenon observed previously (experiments at imposed pH).
- A rough decrease of pH leads to an increase of the glass alteration and also to an increase of pH. After 6 months the kinetics become again equal to that measured in pure water.
- The dilutions (x2 and x150) have little consequence on the kinetics of glass dissolution.
- From a chemical point of view, the gel formed on the SON68 glass remains stable and protective below pH 11, even if you change the Si concentration.

Avignon, October 29 2003

Glastab WP 4.2

S. Gin



CORALUS II: Laboratory Glass Corrosion Tests

- **Progress report of laboratory experiments**
- **Comparison between experimental and calculated gel thicknesses**

N. GODON, P. JOLLIVET, G. PARISOT

CEA Marcoule

CORALUS - October 30th 2003

1



CORALUS II: Laboratory Glass Corrosion Tests

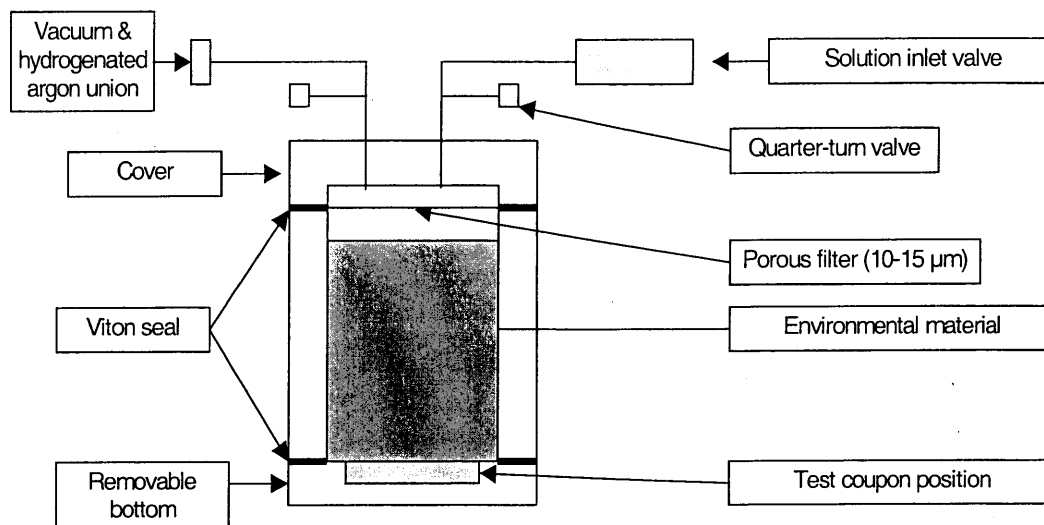
- The european project CORALUS II included laboratory alteration studies of non radioactive R7T7 glass monoliths in contact with environmental materials to allow comparison between laboratory and in situ glass alteration behavior
- The laboratory experiments must be as representative as possible of the in situ experiments
- The laboratory experiments were done in stainless steel reactors and have begun for 2 years
- the same 3 backfill materials than for in situ tests have been used
- Alteration at 30° and 90°C
- 3 durations per temperature: 1 y (30,90°C), 16 m (90°C), 2 y (30°C), x years

CORALUS - October 30th 2003

2



CORALUS II: Schema of a reactor



block material size : $\approx \phi 4 \times 4 \text{ cm}^2$

glass monolith : $\phi 30 \times 3 \text{ mm}^2$

CORALUS - October 30th 2003

3

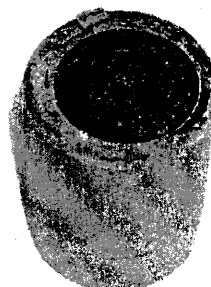
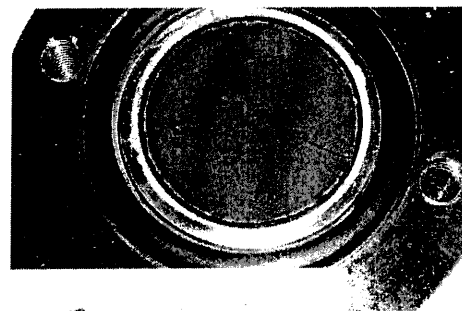
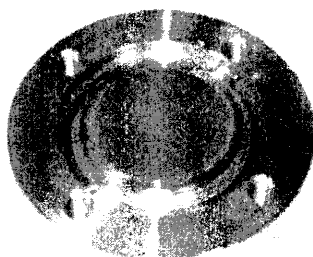


CORALUS II: Module A - Boom clay (1)

30°C - 2 years

Boom clay - bottom side

90°C - 16 months



CORALUS - October 30th 2003

4

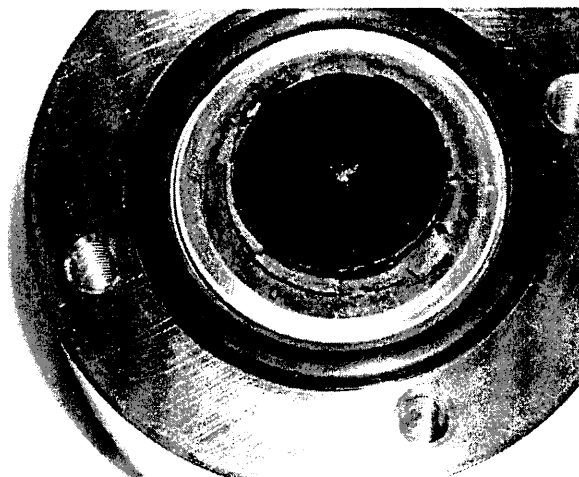
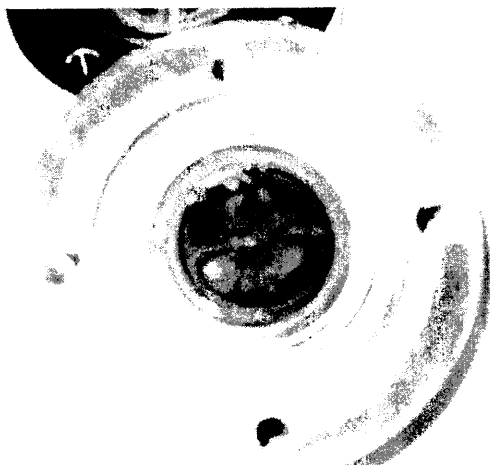


CORALUS II: Module A - Boom clay (2)

Boom clay - bottom side

30°C - 2 years

90°C - 16 months



CORALUS - October 30th 2003

5

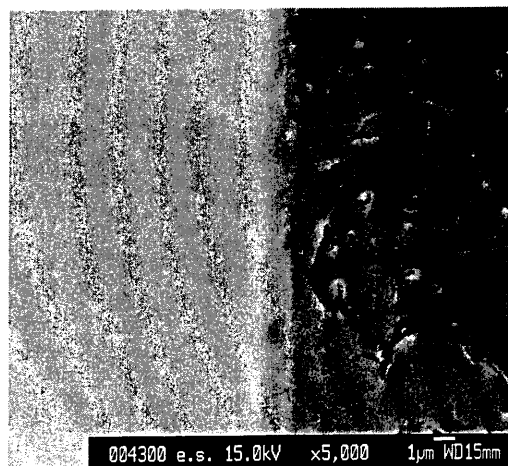
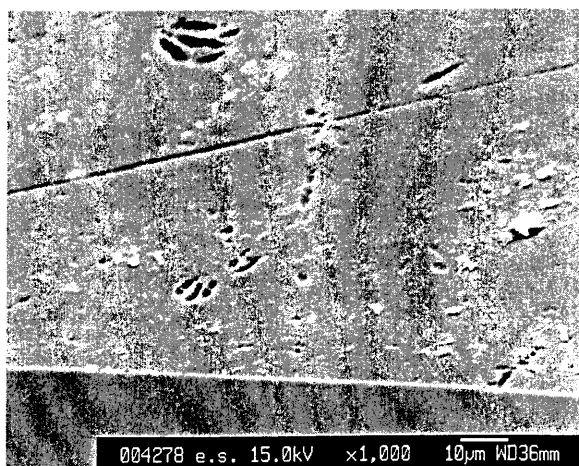


CORALUS II: Module A - Boom clay (3)

30°C - 2 years

semi profile

polished section



altered layer: $1 \pm 0.5 \mu\text{m}$

CORALUS - October 30th 2003

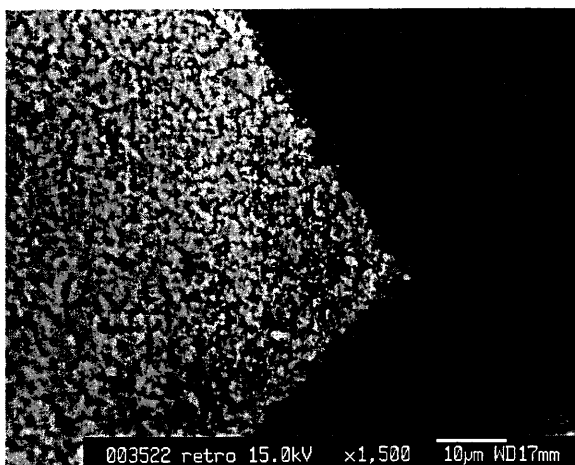
6



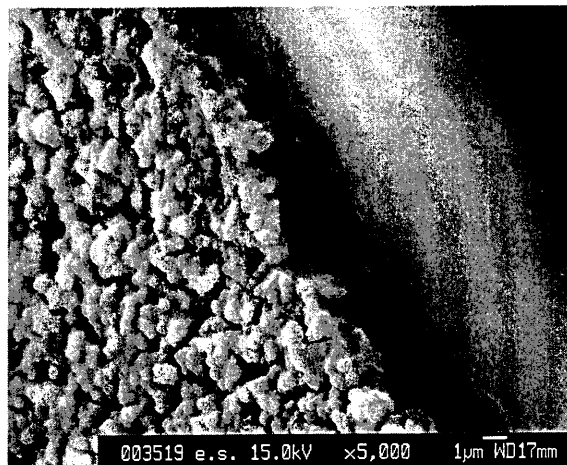
CORALUS II: Module A - Boom clay (4)

90°C - 1 year

semi profile



semi profile



CORALUS - October 30th 2003

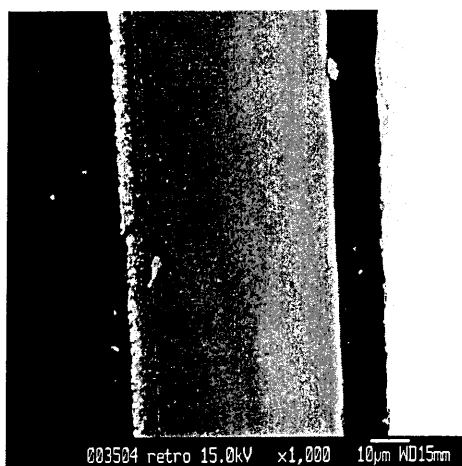
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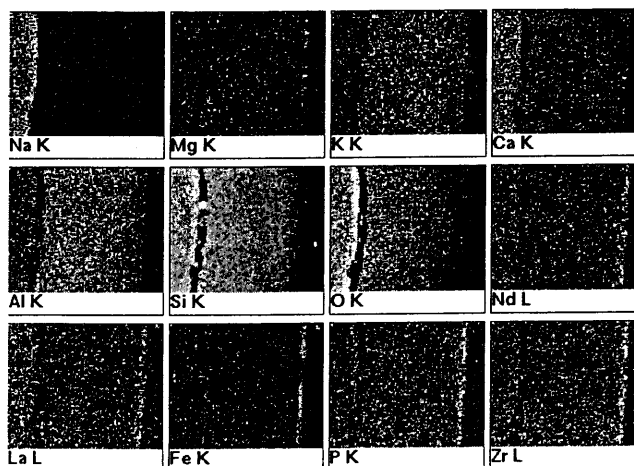
CORALUS II: Module A - Boom clay (5)

90°C - 1 year

polished section



EDS analysis



altered layer: 50 to 60 µm

CORALUS - October 30th 2003

8



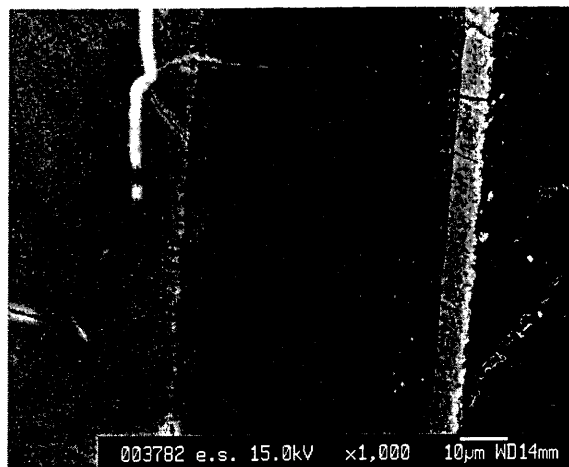
CORALUS II: Module A - Boom clay (6)

90°C - 16 months

semi profile



polished section



outer layer $\approx 6 \mu\text{m}$ (Si, Al, Ca, Fe, REE)

CORALUS - October 30th 2003

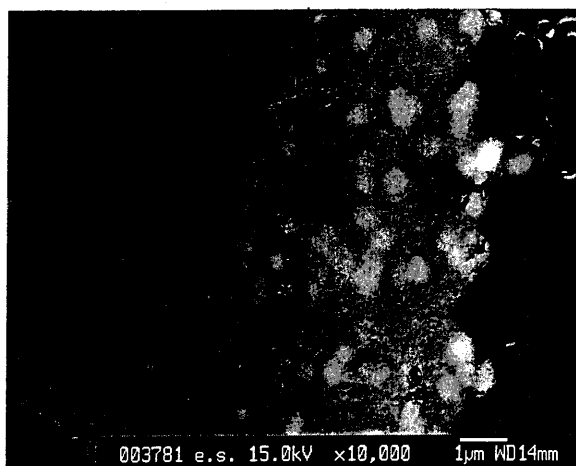
9



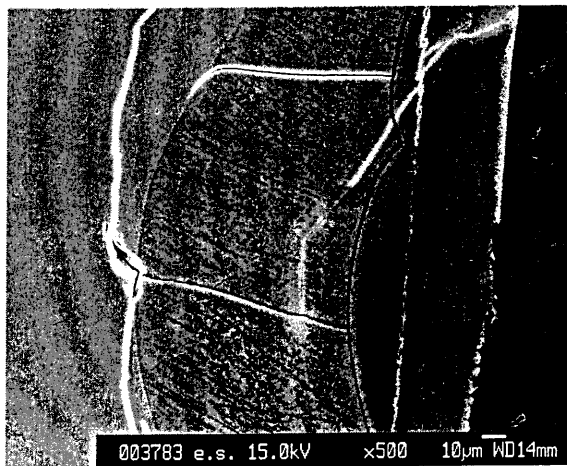
CORALUS II: Module A - Boom clay (7)

90°C - 16 months

polished section



polished section



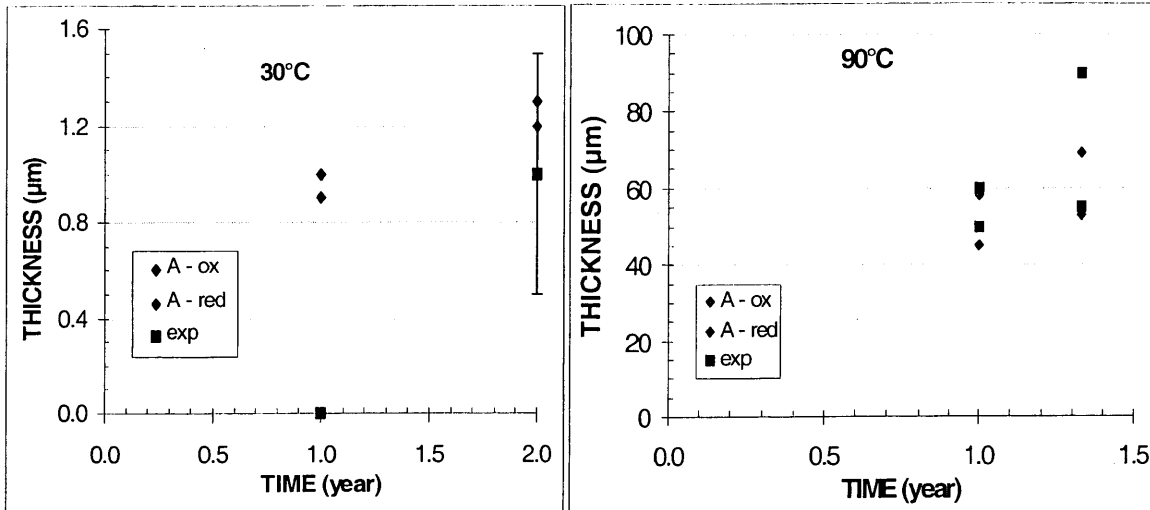
altered layer: 55 to 90 μm

CORALUS - October 30th 2003

10



CORALUS II: Module A - Boom clay (8)



CORALUS - October 30th 2003

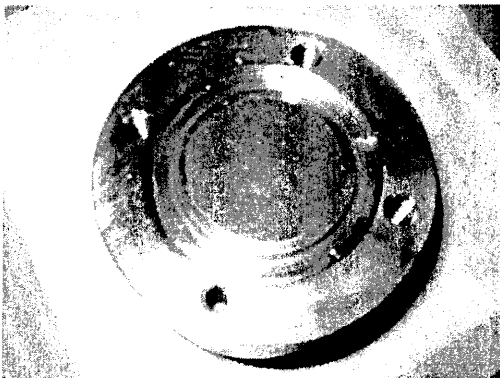
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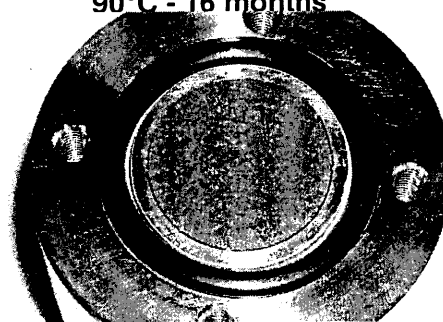
CORALUS II: Module B - PRACLAY (1)

PRACLAY mixture - above side

30°C - 2 years



90°C - 16 months



CORALUS - October 30th 2003

12

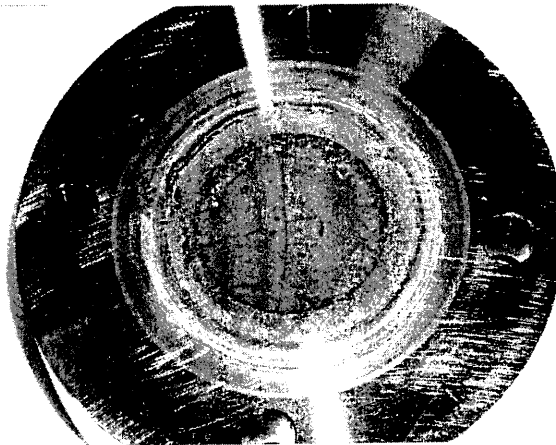
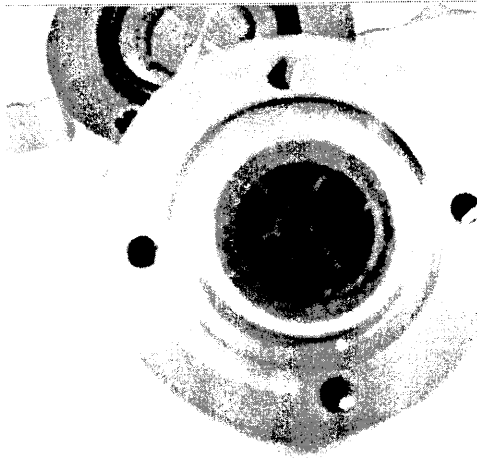


CORALUS II: Module B - PRACLAY (2)

PRACLAY mixture - bottom side

30°C - 2 years

90°C - 16 months



CORALUS - October 30th 2003

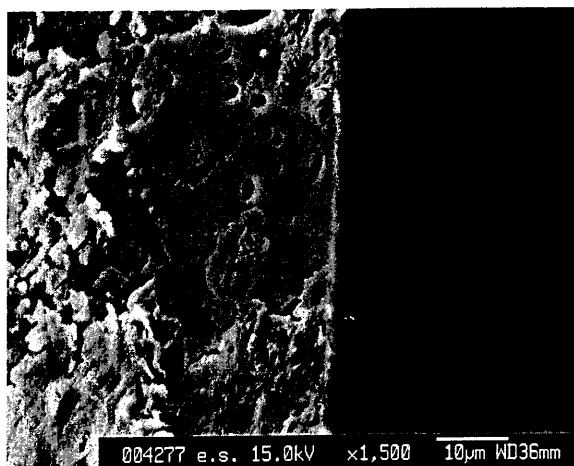
13



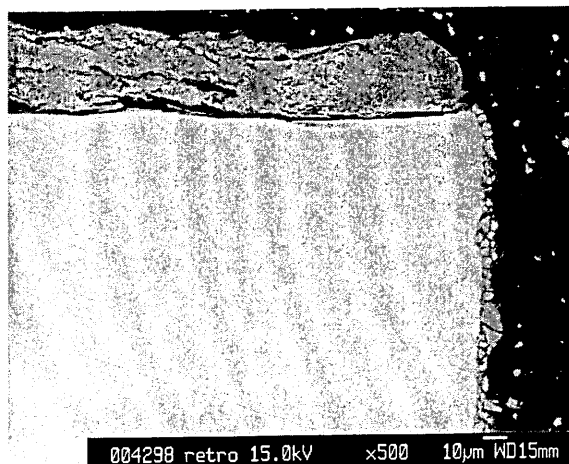
CORALUS II: Module B - PRACLAY (3)

30°C - 2 years

semi profile



polished section



altered layer ? ($< 0.25 \mu\text{m}$)

CORALUS - October 30th 2003

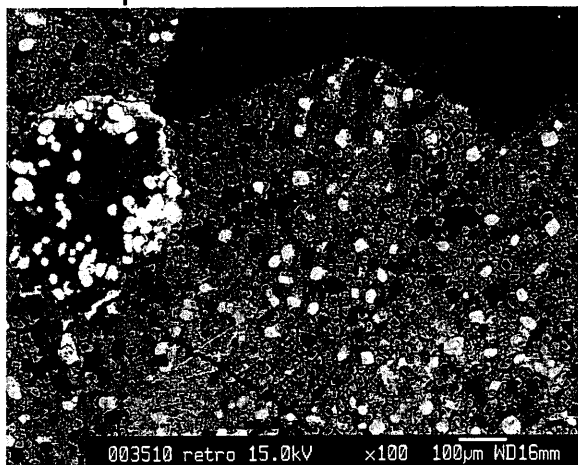
14



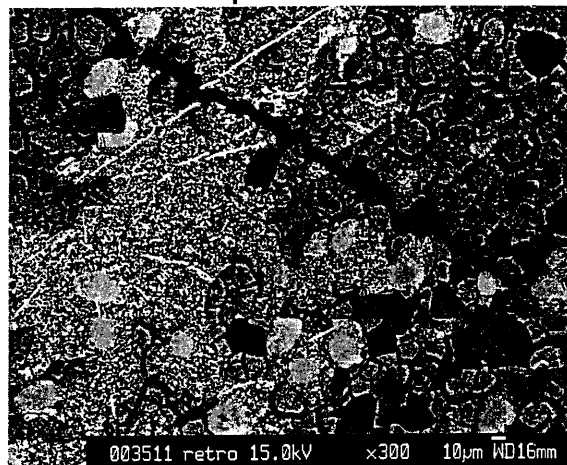
CORALUS II: Module B - PRACLAY (4)

90°C - 1 year

semi profile



semi profile



same composition for nodules (~ 1 µm) and packs (~ 30 µm): Si, Ca, REE

CORALUS - October 30th 2003

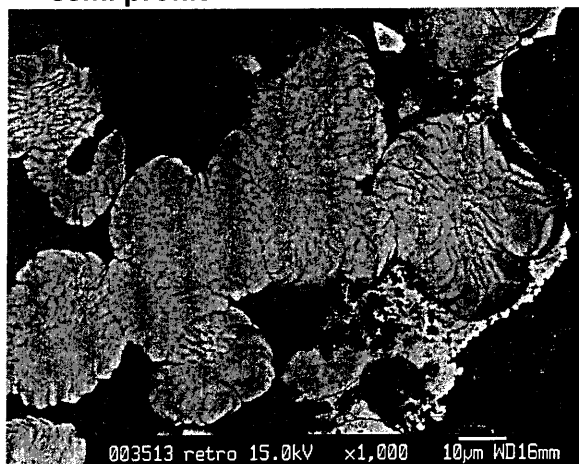
15



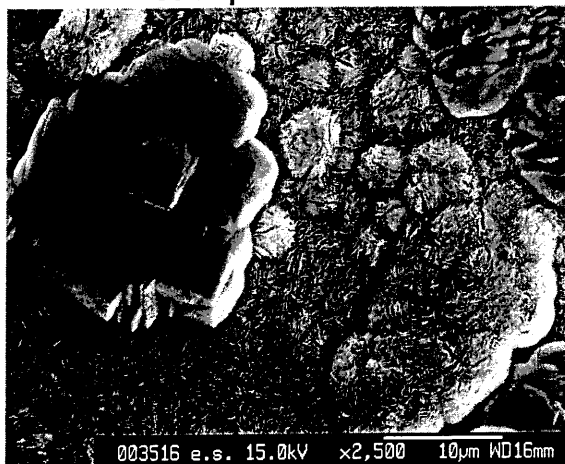
CORALUS II: Module B - PRACLAY (5)

90°C - 1 year

semi profile



semi profile



crystals : P, Ca, REE

CORALUS - October 30th 2003

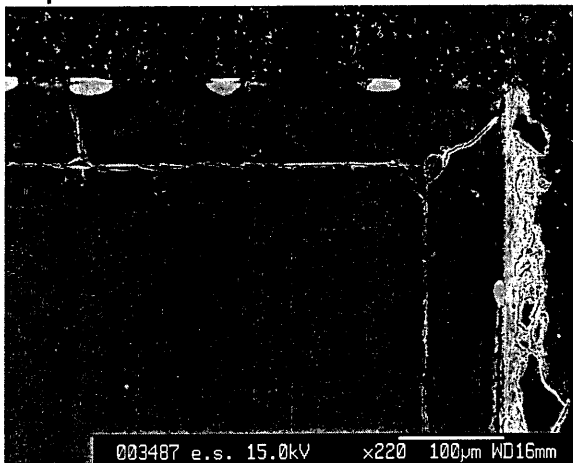
16



CORALUS II: Module B - PRACLAY (6)

90°C - 1 year

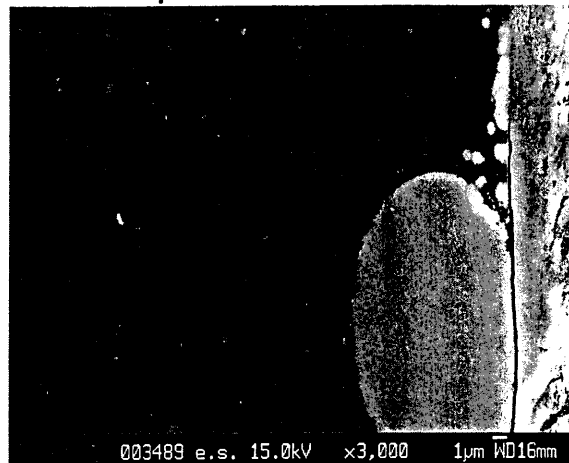
polished section



altered layer : $70 \pm 5 \mu\text{m}$

CORALUS - October 30th 2003

polished section



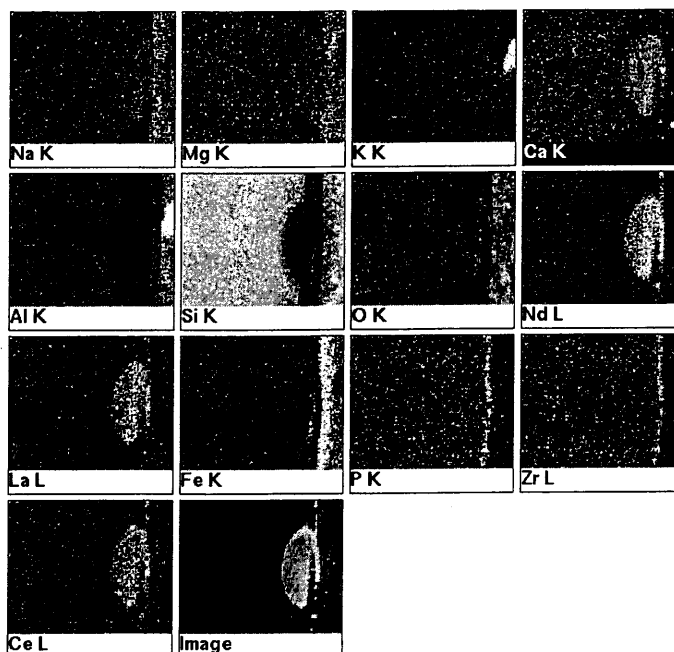
17



CORALUS II: Module B - PRACLAY (7)

90°C - 1 year

EDS analysis



CORALUS - October 30th 2003

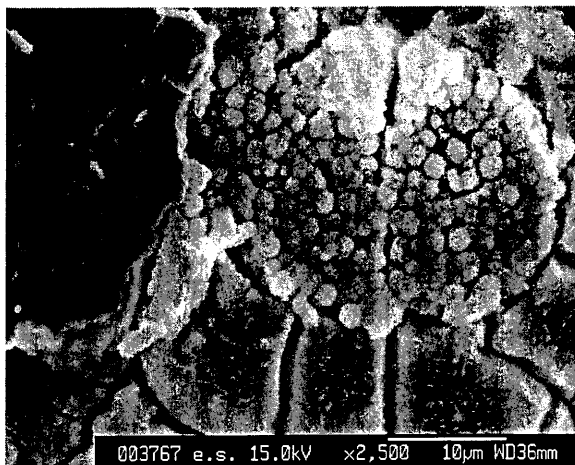
18



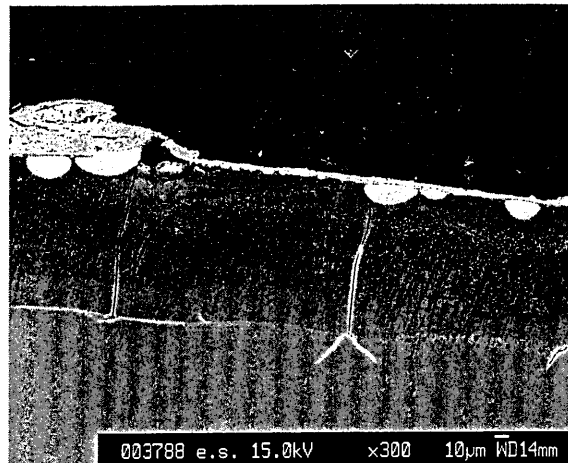
CORALUS II: Module B - PRACLAY (8)

90°C - 16 months

semi profile



polished section



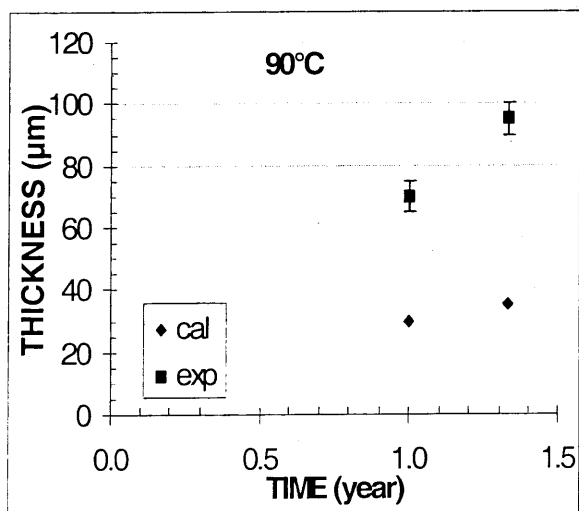
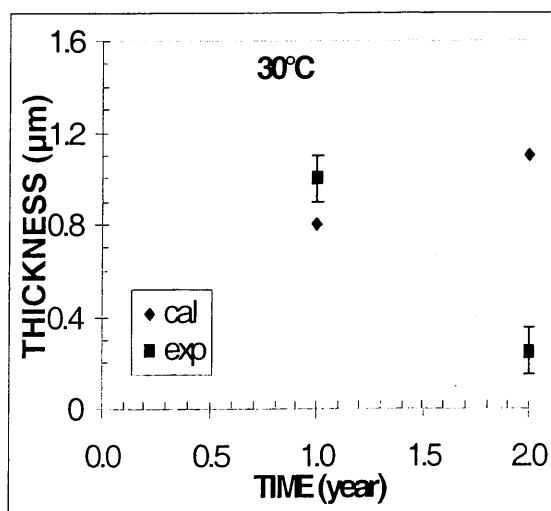
altered layer : $95 \pm 5 \mu\text{m}$

CORALUS - October 30th 2003

19



CORALUS II: Module B - PRACLAY (9)



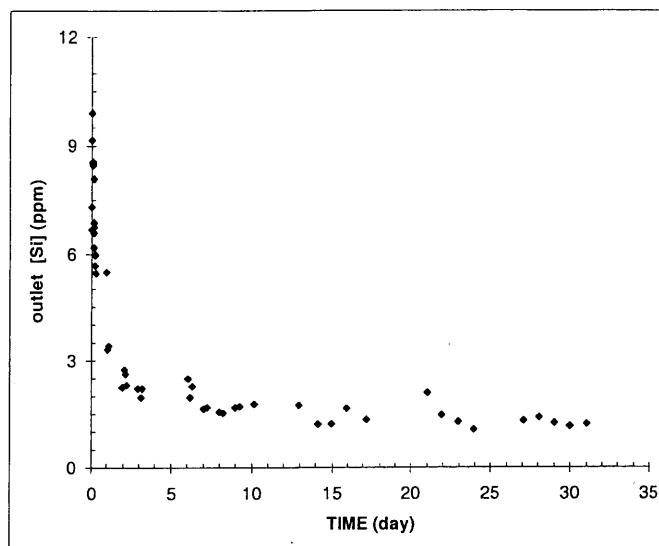
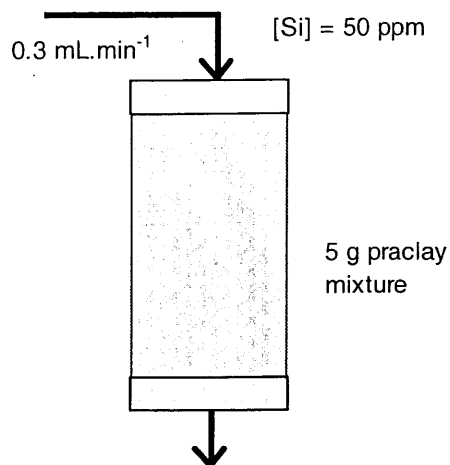
CORALUS - October 30th 2003

20



CORALUS II: PRACLAY complementary laboratory tests

- K_d measurement of praclay mixture at 90°C

CORALUS - October 30th 2003

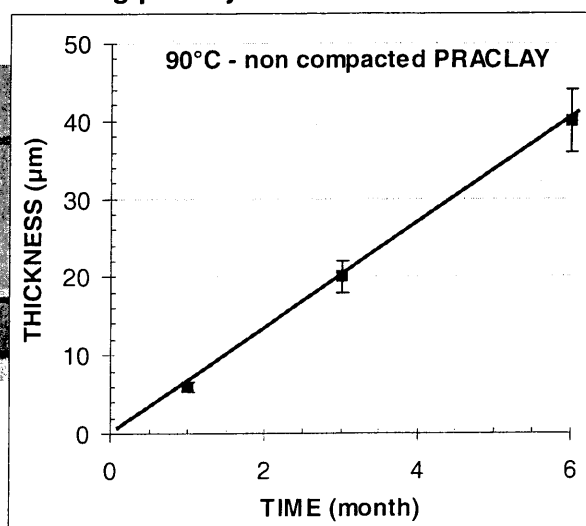
21



CORALUS II: PRACLAY complementary laboratory tests

- Non compacted tests to estimate D_g value with PRACLAY mixture
- T = 90°C, 1, 3 and 6 months

50 g praclay with 15 ml DW

CORALUS - October 30th 2003

22

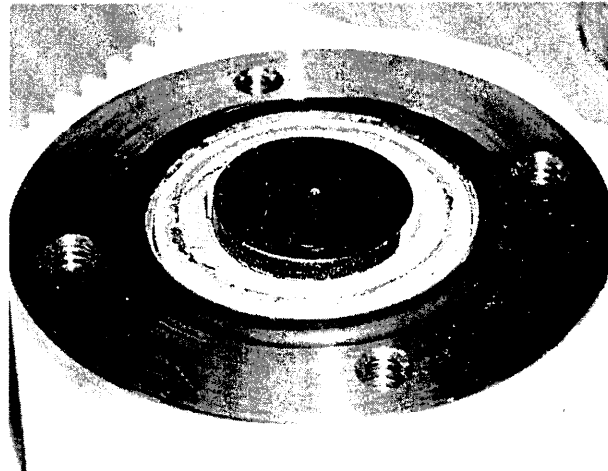
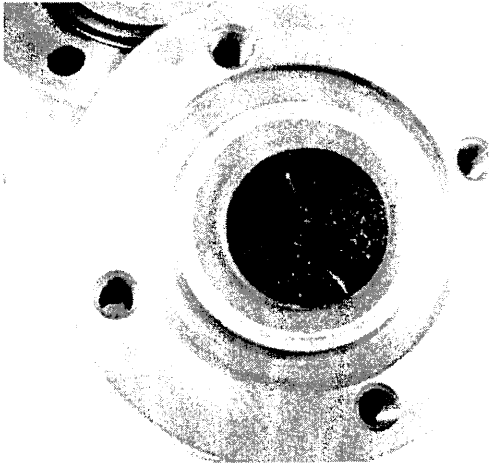


CORALUS II: Module C - FoCa (1)

FoCa7 clay + glass frit

30°C - 2 years

90°C - 16 months



CORALUS - October 30th 2003

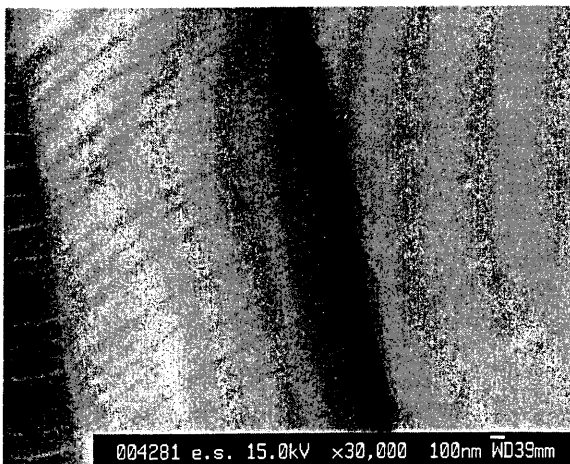
23



CORALUS II: Module C - FoCa (2)

30°C - 2 years

polished section



altered layer ? (~ 50 nm)

CORALUS - October 30th 2003

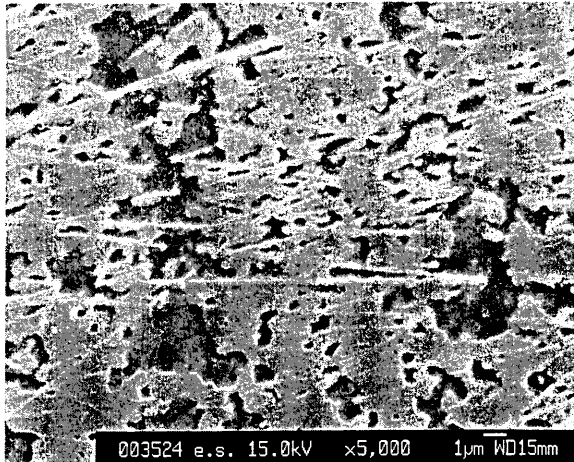
24



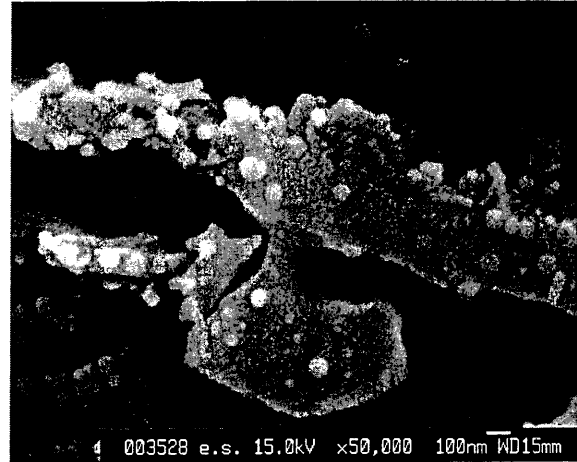
CORALUS II: Module C - FoCa (3)

90°C - 1 year

semi profile



semi profile



non uniform layer (~ 100 nm) with nodules (~ 50 nm)
estimated altered layer : 0.1 to 0.2 µm
CORALUS - October 30th 2003

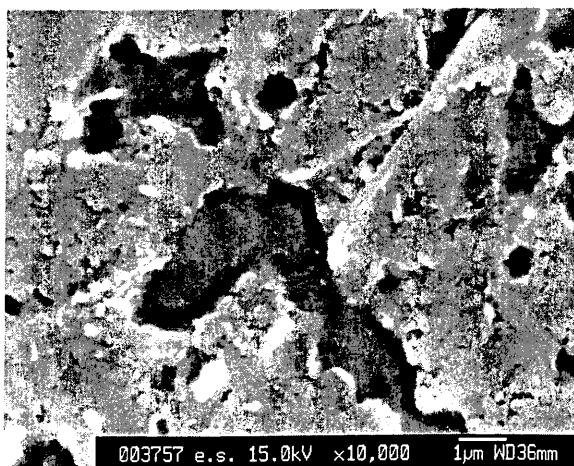
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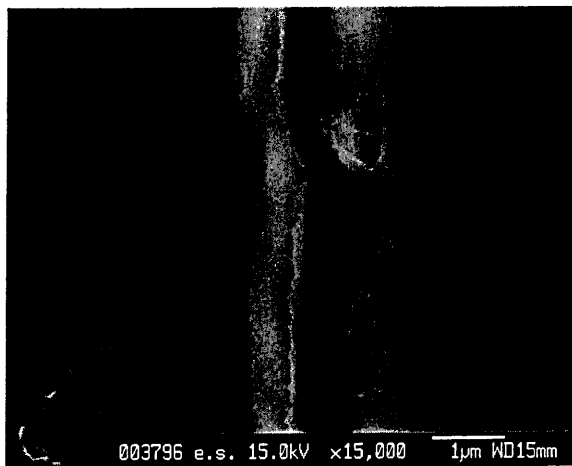
CORALUS II: Module C - FoCa (4)

90°C - 16 months

semi profile



polished section



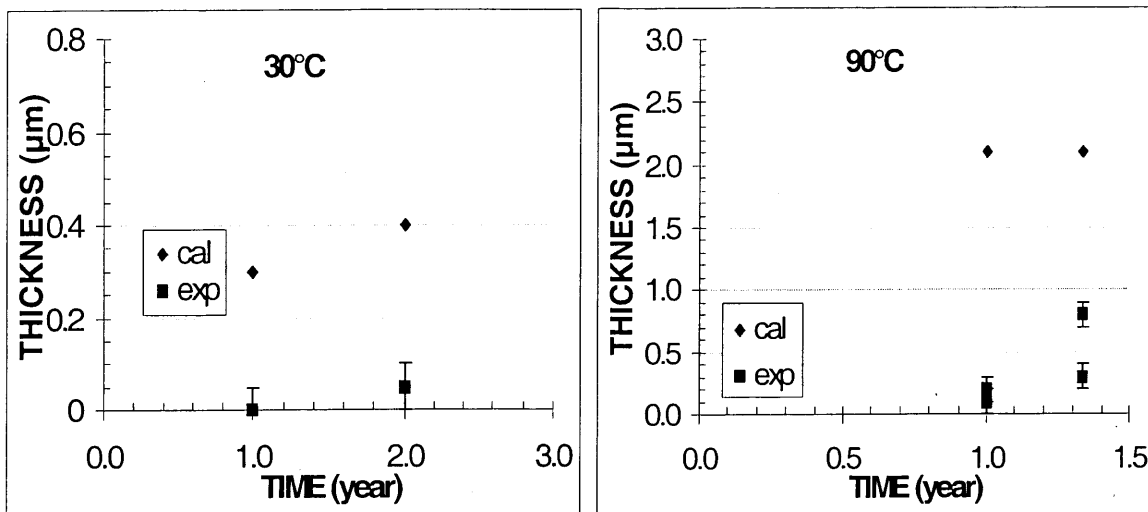
altered layer : 0.3 to 0.8 µm

CORALUS - October 30th 2003

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CORALUS II: Module C - FoCa (5)

CORALUS - October 30th 2003

27



CONCLUSION

- At 30°C, it's difficult to see an altered layer for all materials (< 1 μm after 2 years)
- At 30°C, good agreement between calculations and experiments for the 3 materials
- At 90°C, good agreement between calculations et experiments for modules A (~75 μm after 16 months) and C (<1 μm after 16 months)
- At 90°C, for Praclay mixture, the experimental thicknesses (~95 μm after 16 months) are higher than the calculated ones

⇒ K_d measure

estimation of D_g with non compacted experiments at short durations

CORALUS - October 30th 2003

28



CORALUS-II Activities 2002-2003

Elie Valcke, Steven Smets, Serge Labat,
Pierre Van Iseghem

SCK•CEN
Mol, Belgium

Cluster meeting CORALUS Glastab
Mercure Hotel, Avignon

1

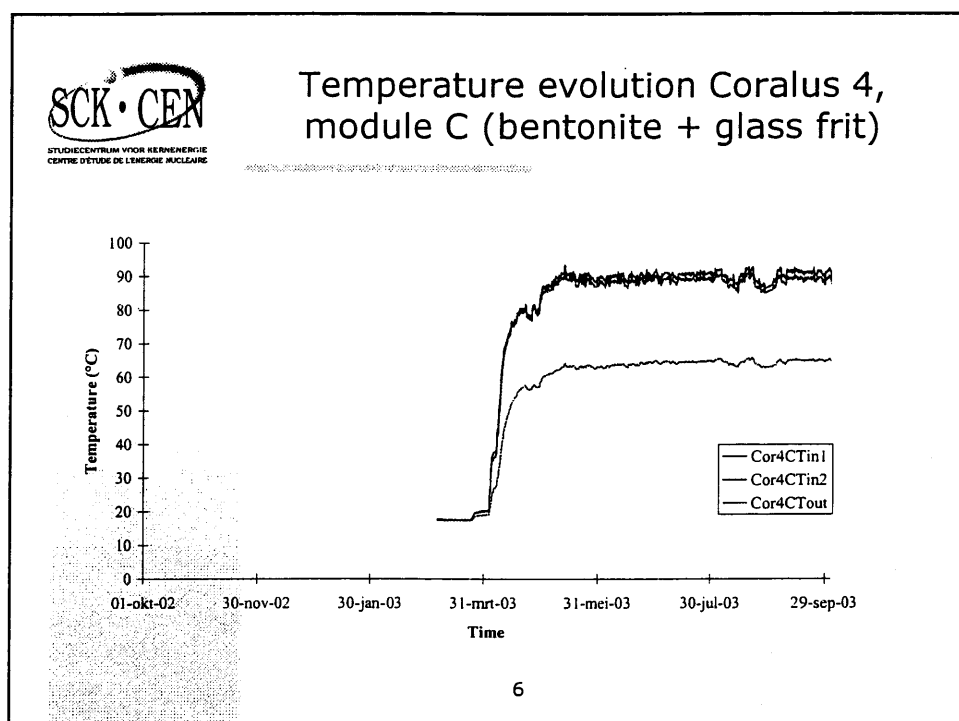
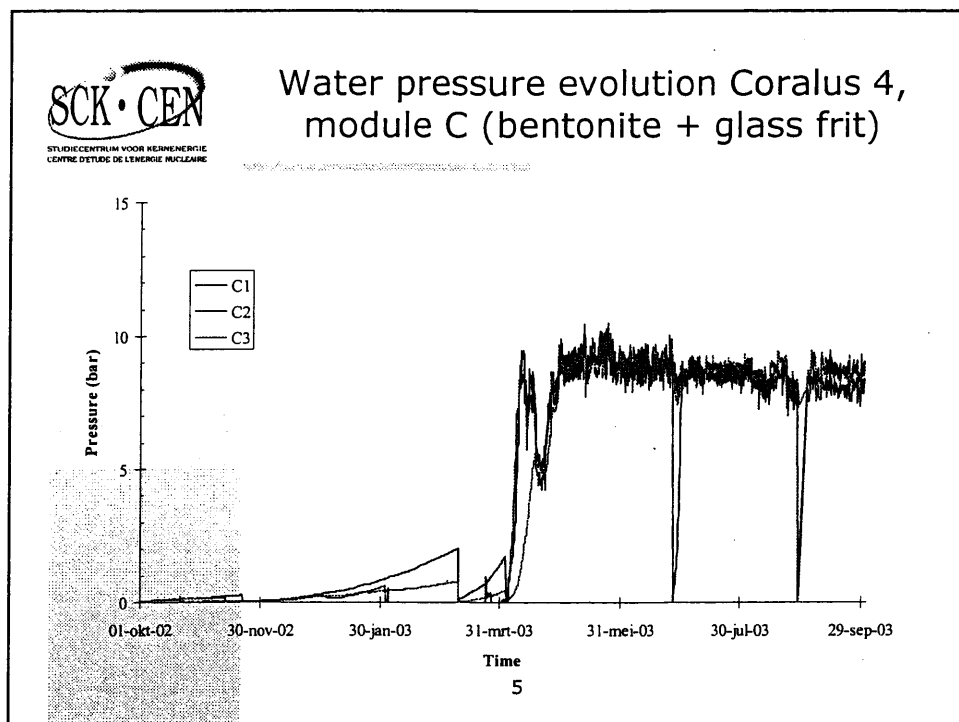
October 29-30, 2003



CORALUS-II divided in 8 WPs

- WP1 Assembly and installation of tubes 3 and 4 (SCK)
- WP2 Operation of test tubes (SCK, GRS)
- WP3 Retrieval and dismantling of tubes 2 and 3 (SCK)
- WP4 Transport of radioactive glass samples (SCK, CEA)
- WP5 Analyses on glasses and clay (SCK, CEA)
- WP6 Gas generation measurements (GRS)
- WP7 Laboratory glass alteration tests (CEA)
- WP8 Interpretation of results (SCK, CEA, GRS)

2



WP2 Operation of the test tubes

- Test tube 3: results

- Total alpha:

- ♣ ~ 0.5 - 0.7 Bq/l Boom clay ($^{234/235/238}\text{U}$, ^{232}Th ??),
 - ♣ < 0.3 - 0.5 Bq/l for bentonite-based backfills

- Composition:

- ♣ Higher in circulated (ph+Eh) than in not-circulated solutions (due to higher KCl + ion exchange ?)
 - ♣ Higher in inner piezometers (higher temperature)
 - ♣ High total DOC, Na^+ , SO_4^{2-} , (K^+ , Cl^-)

- Dissolved gases:

- ♣ CO_2 higher (3 - 5 ×) than at 30 °C: ~12 to ~20 mM total DIC
=> lower pH ?
 - ♣ CH_4 similar as at 30 °C
 - ♣ H_2 : diverging

9

WP2 Operation of the test tubes

Module/piezometer	pH	Eh (mV)
A1 - A2	6.5 - 6.5 [7.9; 7.8]	-40 and -80 [-340; -300]
B1 - B2	6.0 - 5.5 [7.3; (8.3)]	0 and -80 [-310; -280]
C1 - C2	6.7 (6.1?) - 7.0 [6.8; (7.8)]	-80 and -80 [-200; (-60)]

Numbers in brackets, in blue, are for test tube 2 (30 °C) and test tube 1 (90 °C), respectively

10



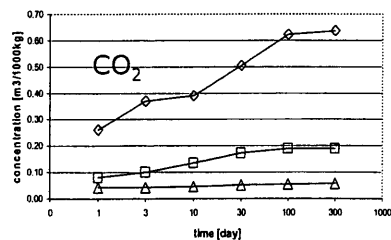
Other work packages

- **WP4** preparation of **transport of radioactive samples** to CEA (samples and clays of module C) and PSI (SIMS)
- **WP6 thermal gas generation** at 90 °C (GRS) : measurement after 1000 days in November 2003
- **WP7 laboratory glass alteration tests** in conditions similar to those of CORALUS (same backfill, Boom clay water for saturation, same temperature, same duration, but no ^{60}Co sources)

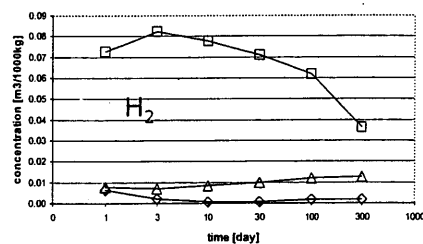
13



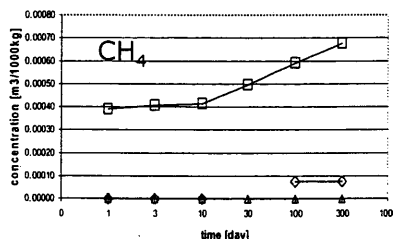
WP6 – thermal gas generation



—♦— backfill A —□— backfill B —△— backfill C



—♦— backfill A —□— backfill B —△— backfill C



—♦— backfill A —□— backfill B —△— backfill C

5.3 GLASTABプロジェクト

Agenda - GLASTAB final meeting



October, 29th

- 8h30 - 10h30 Gel characterisation (JLC)
- 10h30 - 11h00 Break (*copy of overheads*)
- 11h00 - 13h00 Scientific modelling (BG)
- 13h00 - 14h30 Lunch
- 14h30 - 16h15 Alteration under near-field conditions (KL)
- 16h15 - 16h45 Break
- 16h45 - 18h30 Operational modelling and PA (IR)
- 19h40 Dinner (meeting in the hall of the hotel)

October, 30th am

- 8h30 - 10h30 RN sorption & coprecipitation (RB)
- 10h30 - 11h00 Break (*copy of overheads*)
- 11h00 - 13h00 General conclusions, final organisation
- 13h00 - 14h30 Lunch

CEA /DEN/VRH/DIEC/SESC/LCLT/Isabelle RIBET

GLASTAB - October 29-30, 2003

1

Objectives



Synthesize the results
Discuss the conclusions
Prepare the final report

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GLASTAB - October 29-30, 2003

2



WP 4.1

Preparation of integral alteration mockups to determine the alteration gel stability domain at 50°C in a reducing alkaline medium in the presence of realistic corrosion products and realistic barrier clay

study how the relative positions of the glass and of the environmental material influence the gel development.

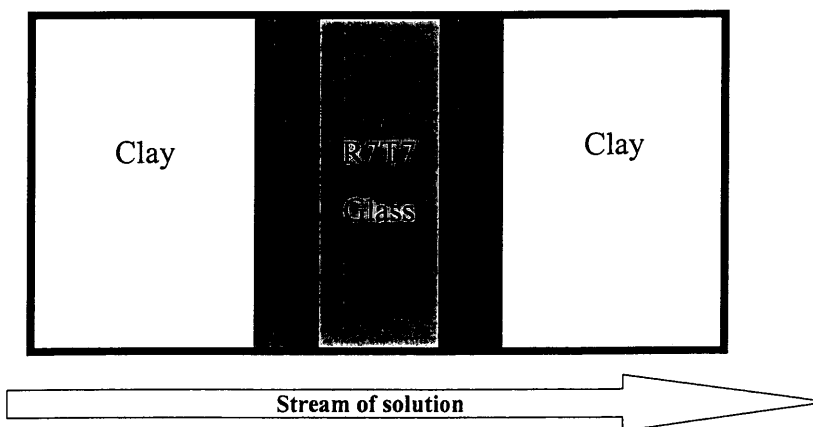
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1



Design of the mockup



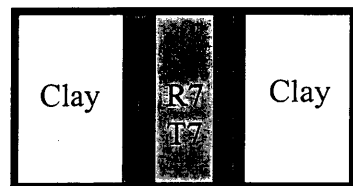
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2



Experimental conditions



Compacted FoCa clay

Mixture of 1/3 Siderite (iron carbonate forming during the alteration of the container in the contact of clay), 1/3 Fe, 1/3 FoCa clay

R7T7 glass powder

Anoxic conditions

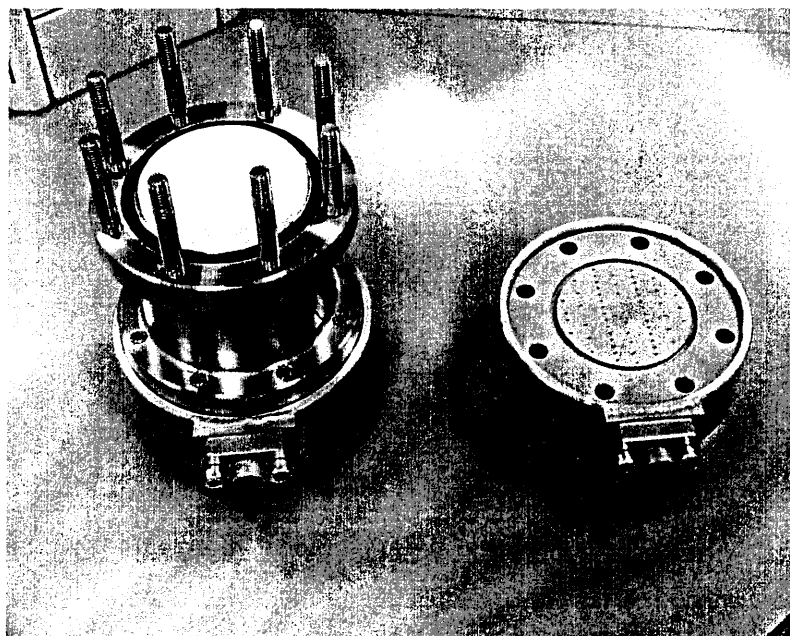
90°C

Pure water (0.1ml/day)

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3



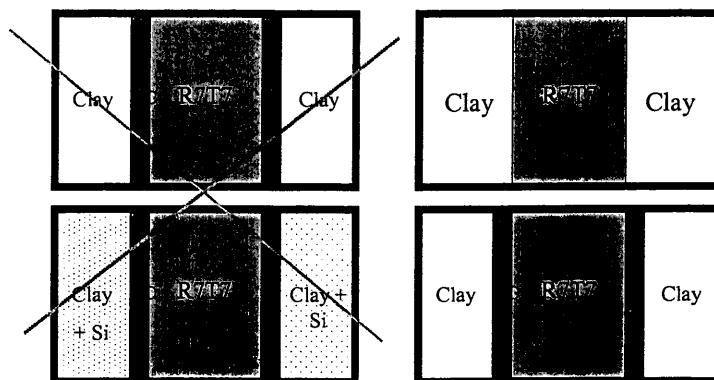
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4



4 tests were performed (1 for GLASTAB),
2 only functioned well
(problems of water circulation according to preferential ways)

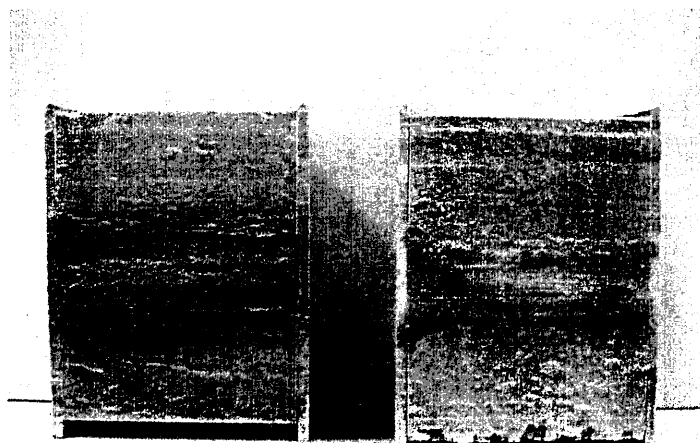


Influence of the environment on the gel formation and on the glass alteration kinetics

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5



Sample with various places of the glass powder characterization of the gel
(MEB, SEM ...): thickness, composition, structure ...

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6



Planning

Running the test : 6 months

Stopping the test : October 2003

Analysis and treatment of the results : from
October 2003 to January 2004

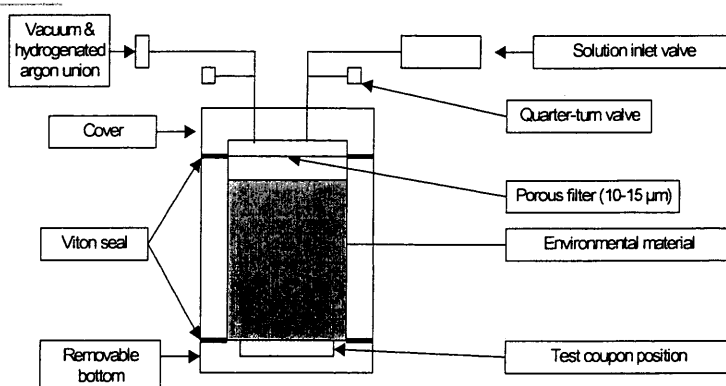
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7



Coralus-like experiment at 50°C (material C)



measured gel thickness: $\approx 0.5 \mu\text{m}$

calculated gel thickness: $0.40 \mu\text{m}$ ($D_g = 7.4 \cdot 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ $C^* = 10^{-3.01} \text{ mol} \cdot \text{L}^{-1}$)

good agreement between calculated and experimental thicknesses but only one point

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8

WPU 13



Performance calculations Long-term glass package behaviour under integral conditions

Operational modelling

CEA / DEN / VRH / DIEC / SESC / LCLT / Isabelle RIBET

Operational modelling - Final meeting GLASTAB - October 29th, 2003 1

Operational modelling / Scientific modelling



Glass package in near-field
conditions

Prediction of glass source
term

Tradeoffs between realism
and simplicity

Choice of phenomena,
hypotheses, numerical
values, uncertainties

Known glass surface in
controlled environment

Prediction of rate for
comparison with experiments

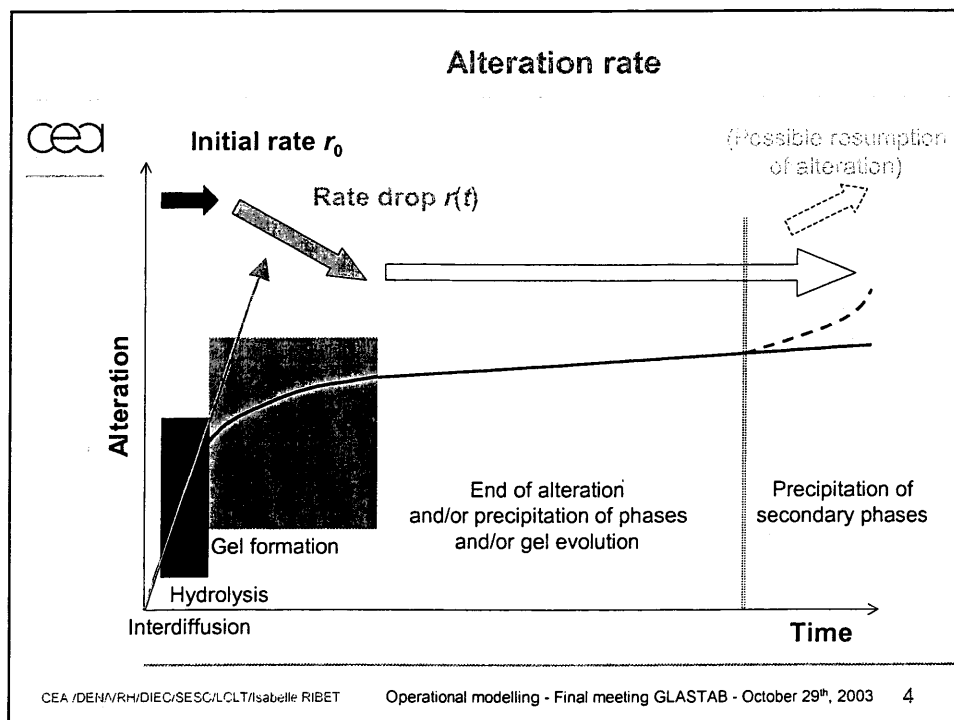
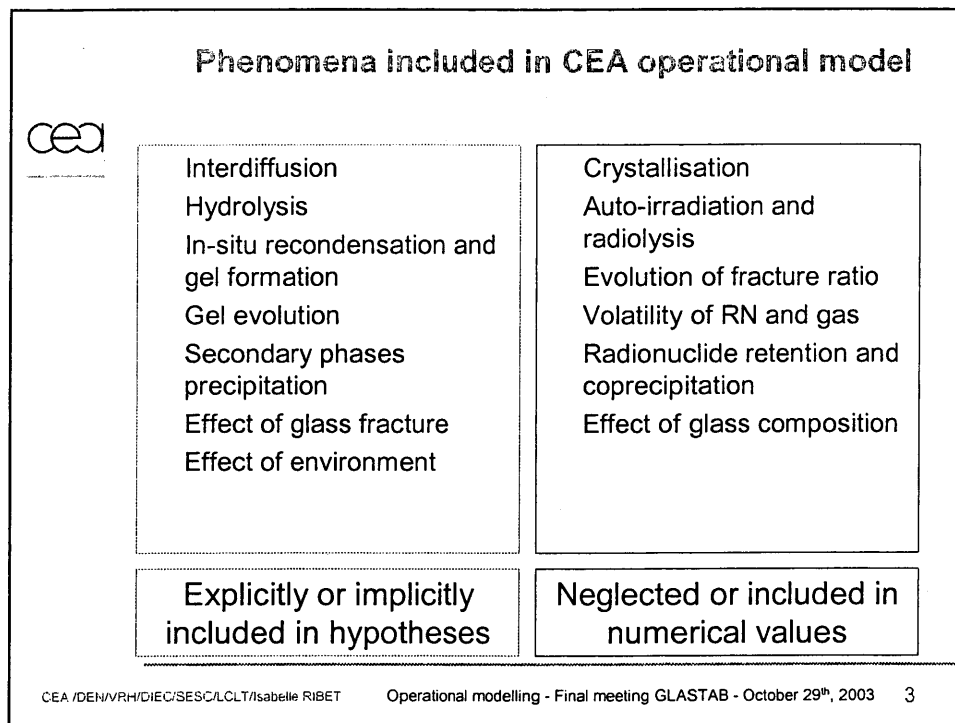
Realism

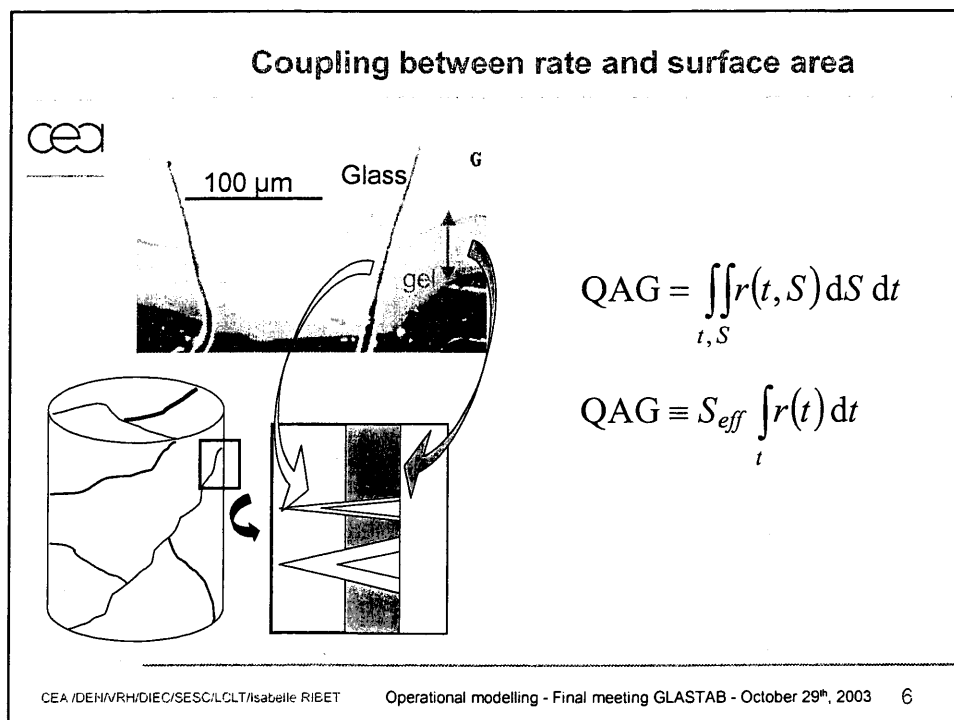
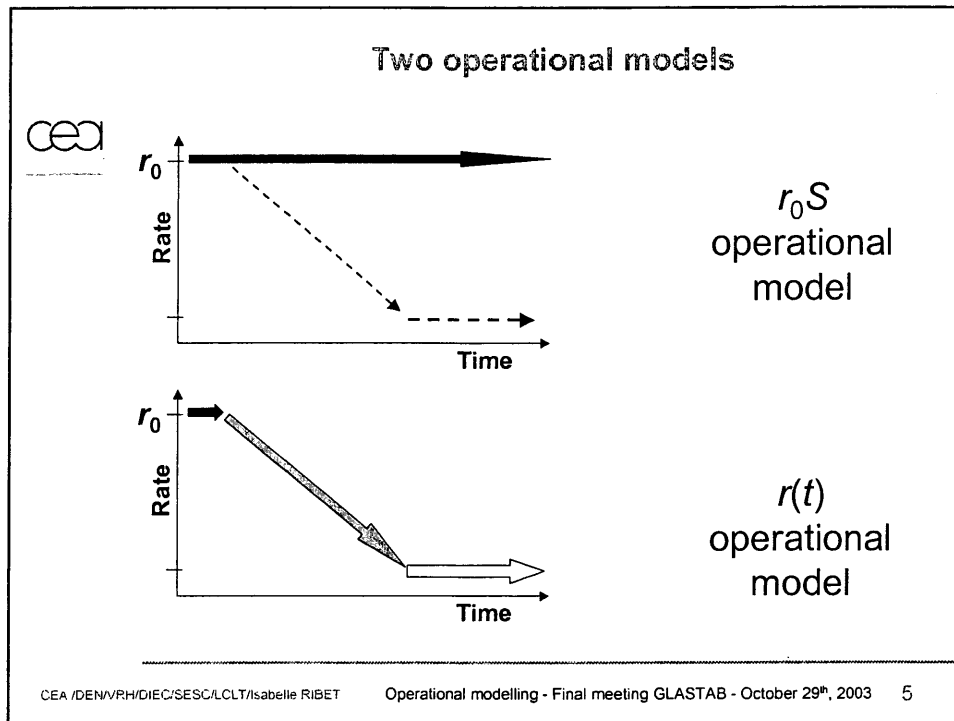
Test of hypotheses,
determination of numerical
values

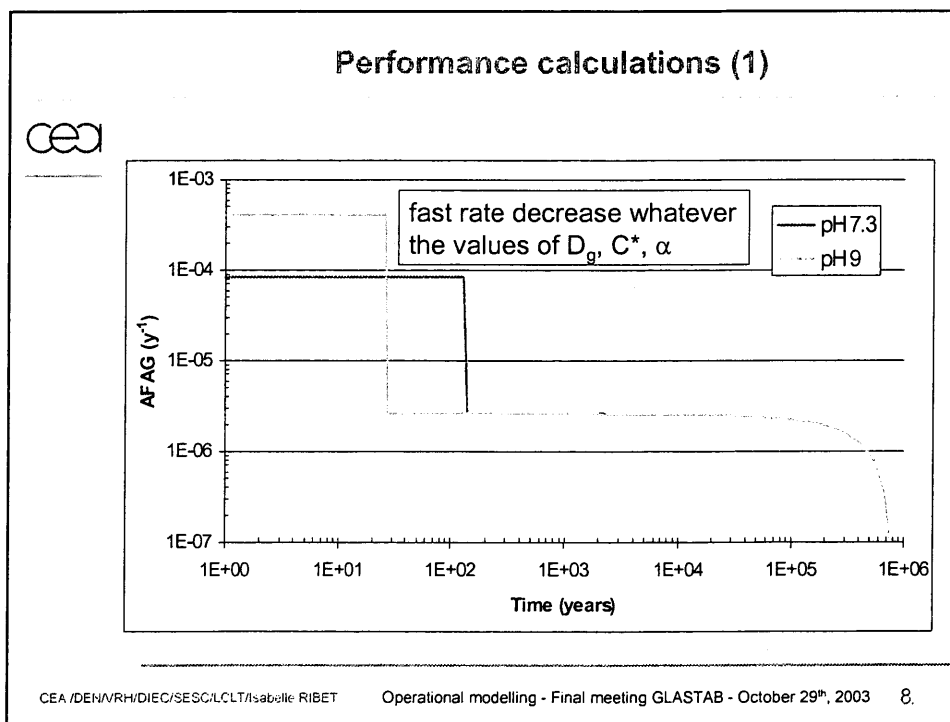
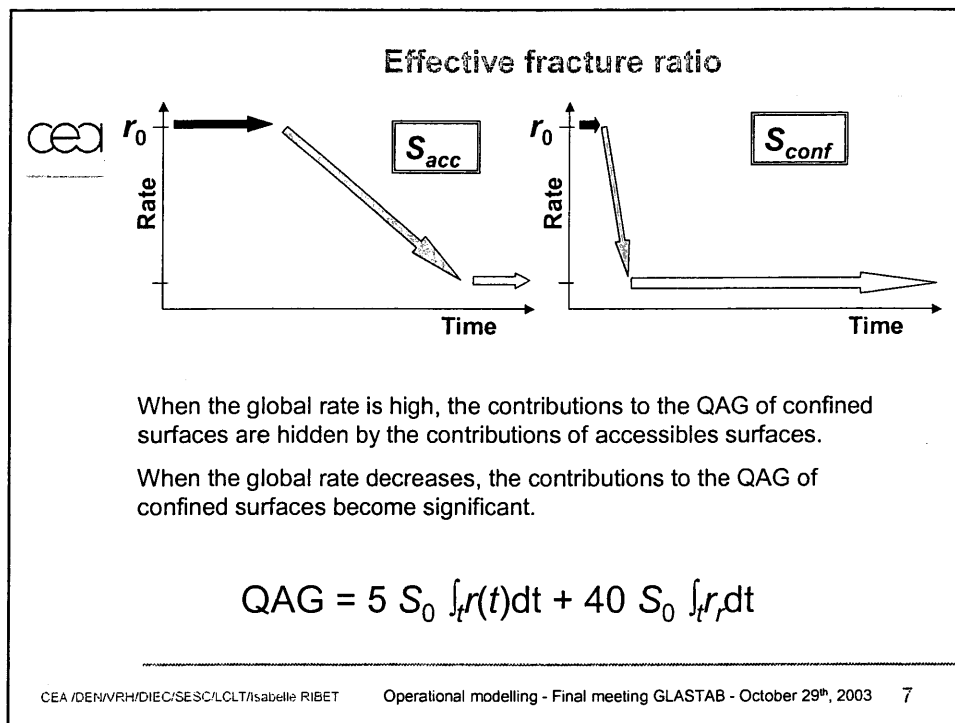
$$QAG = \iint_{t,S} r(t,S) dS dt$$

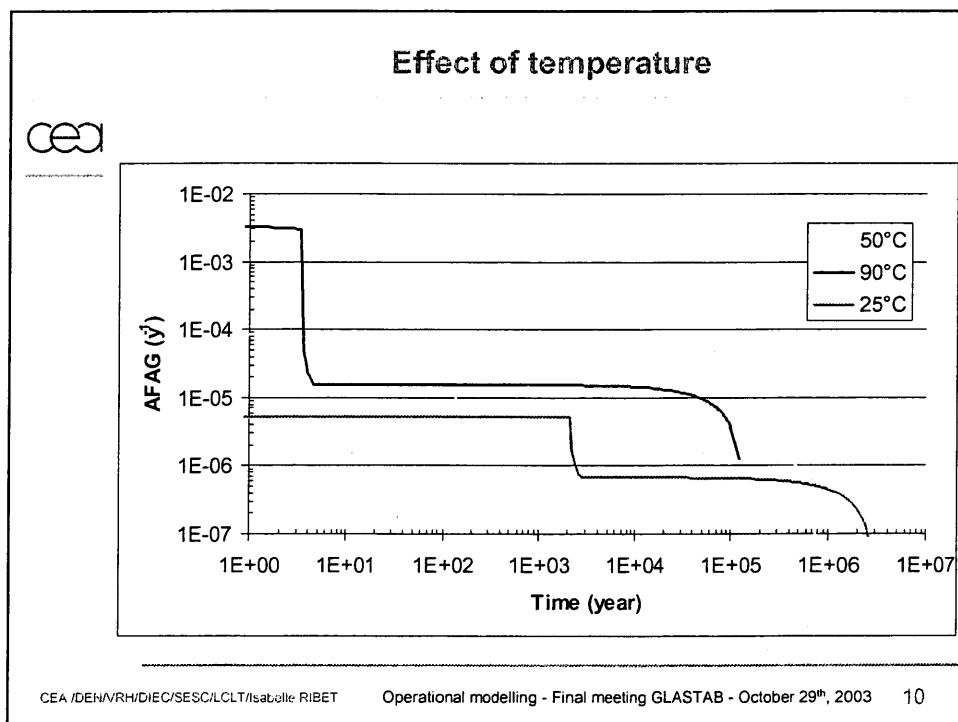
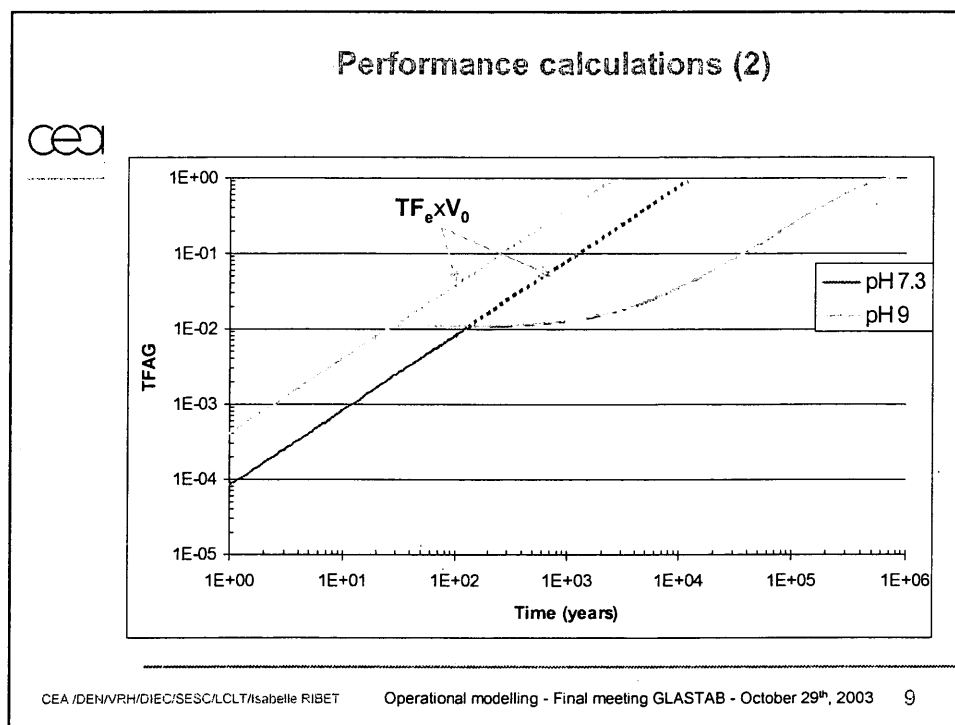
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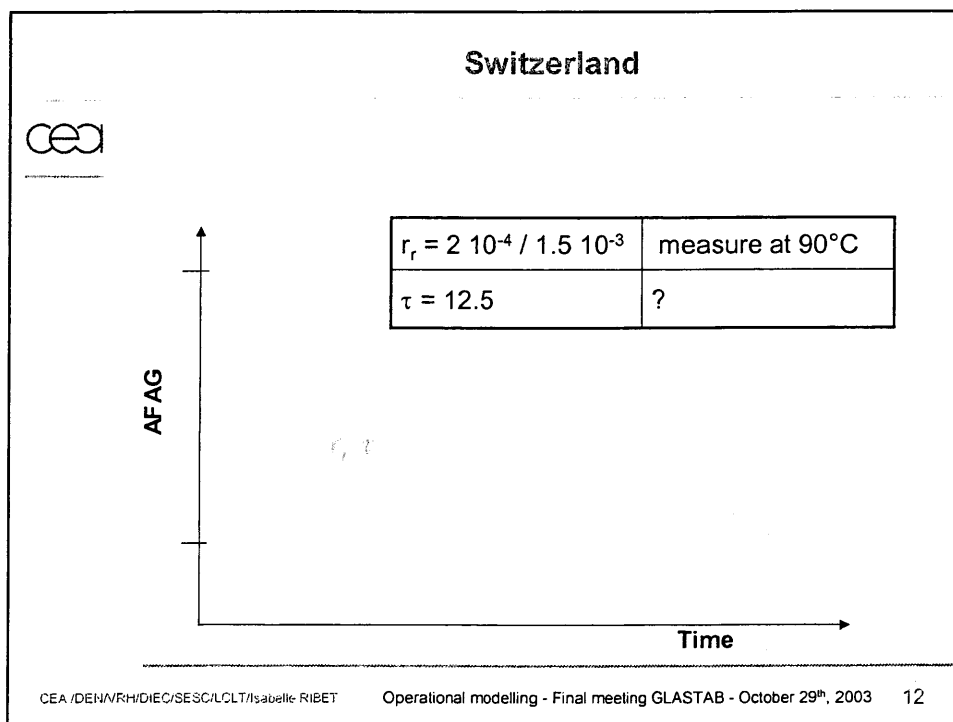
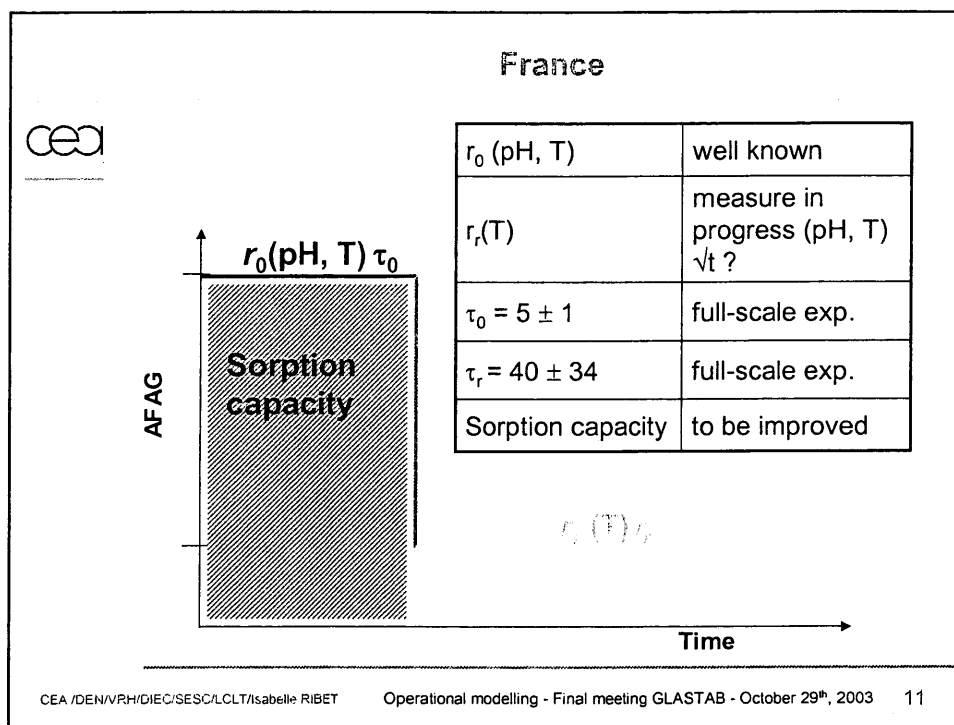
Operational modelling - Final meeting GLASTAB - October 29th, 2003 2

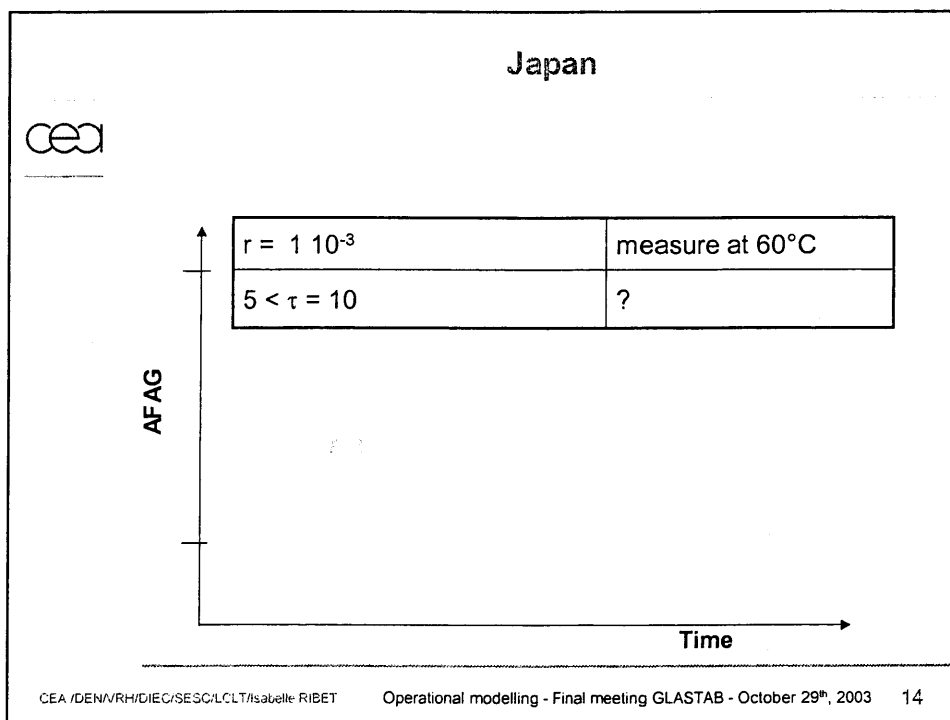
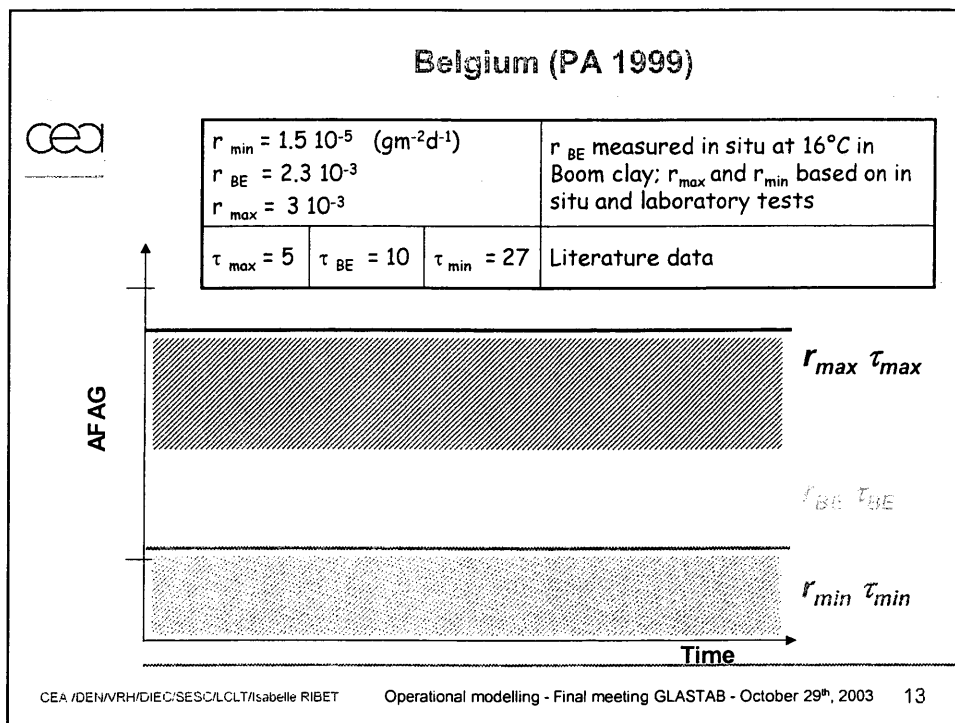


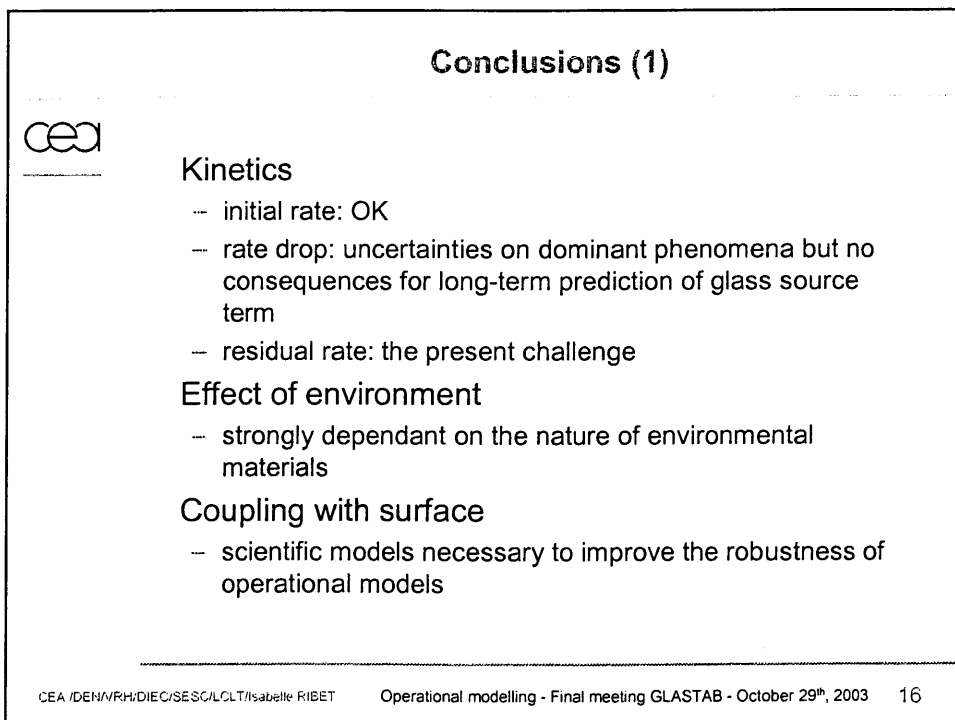
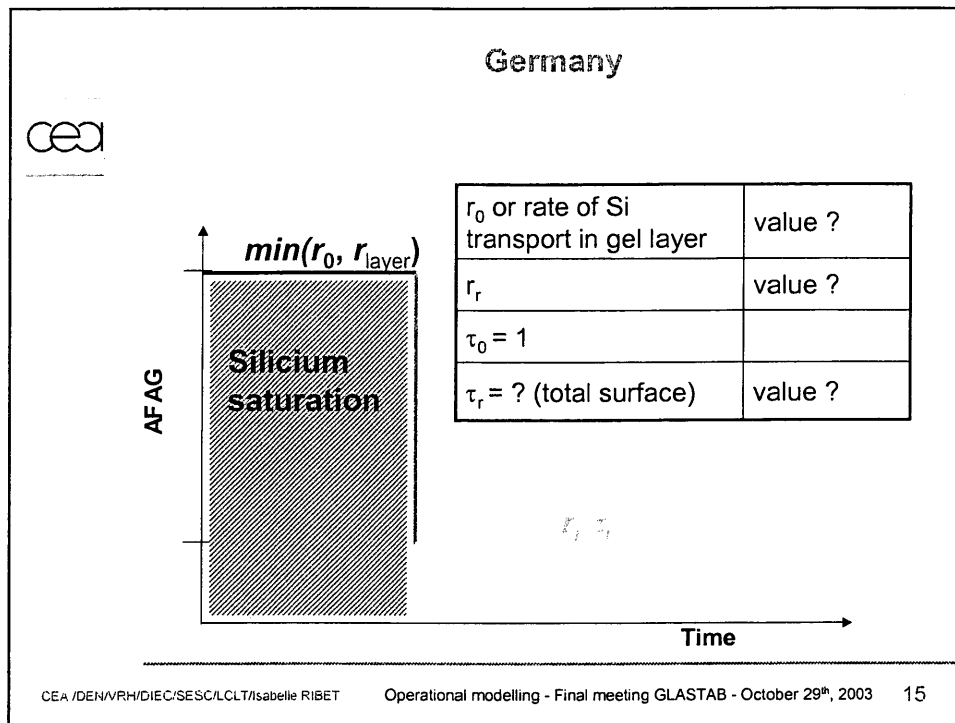












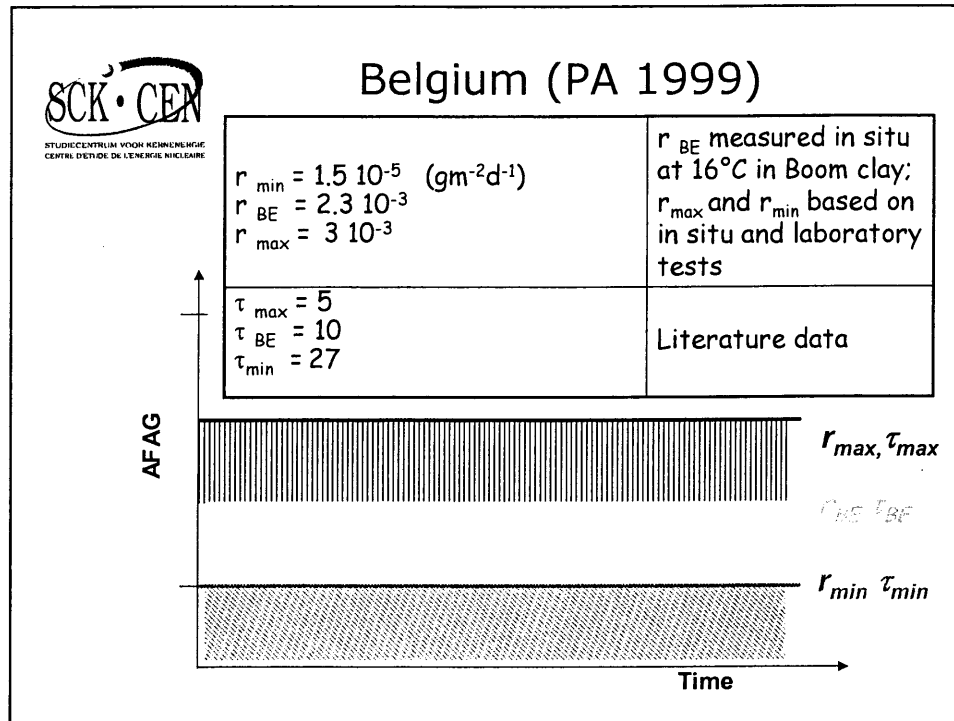
Conclusions (2)



Is the glass a good confinement matrix ?

Under which conditions ?

Are we able to propose a value of minimal glass performance ?



**Belgium
suggestion for PA update**

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

- keep constant rate model with other values for $r_{\max, \text{BE}, \min}$
 e.g. $r_{\text{BE}} = 0.05 - 1 \cdot 10^{-2} \text{ gm}^{-2}\text{d}^{-1}$ (test 30°C in solid Boom Clay)
 $r_{\max} = 2 \times r_{\text{BE}}$ (uncertainty on r_{BE})
 $r_{\min} = 10^{-4} - 10^{-5} \text{ gm}^{-2}\text{d}^{-1}$ (tests with glass frit, TAV in Boom Clay, ...)
- use operational code (SCK•CEN code or other) with 'worst case', 'best estimate' and 'best case' parameter values
- No new information concerning the effective glass surface area

Communication



Summary document for the public: new proposal

- list and comments on documents available on websites
- interest, targeted audience, ...

Euradwaste'04

- Paper due for December, 15th
- Content: conclusions of the 3 meetings (GLASTAB, CORALUS, GLAMOR)

Preparation of an information brochure on the Euratom Research programme on the Geological Disposal of Radioactive Waste

- 2 pages on GLASTAB results
- due for December, 1st

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GLASTAB - October, 30th, 2003

1

Planning



Cost statements

- deadline: **end of December**
- eligible costs: until end of October (official end of the contract)

Technological Implementation Plan

- e-TIP: completed as mid-term TIP
- deadline: **end of January**

Final report

- draft from partners: **December, 15th**
- compiled draft report submitted to partners: January, 25th
- proof-reading by partners: **end of February**
- Final version: **end of March**

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GLASTAB - October, 30th, 2003

2

Final report



The final technical report should consolidate and summarise the work carried out and the results obtained by all the partners

- up to **50 pages**, including figures

Plan

- Executive publishable summary
- **Scientific and technical description of the results**
 - 5 technical parts as discussed among GLASTAB partners
 - no more than 10 pages for each chapter, including figures
- Assessment of Results and Conclusions
- Management final report

General conclusions - Outlook



Gel observation and characterisation

Modelling of alteration kinetics and gel formation

Radionuclide retention

Glass alteration in near-field conditions

Performance calculations

Final report

2 Modelling of alteration kinetics and gel formation

Literature review	WP2-2, WP5-1
Kinetics modelling	WP3-1, WP3-2
Solid-solution modelling	WP2-1, WP2-3-4
KIRMAT	WP2-4, WP2-5 (+ chapter 3)
Monte-Carlo modelling	WP2-9, (WP5-7 ? or chapter 4)
B. Grambow, J.L. Crovisier, P. Jollivet + I. Ribet + Y. Minet, M. Aerstens	

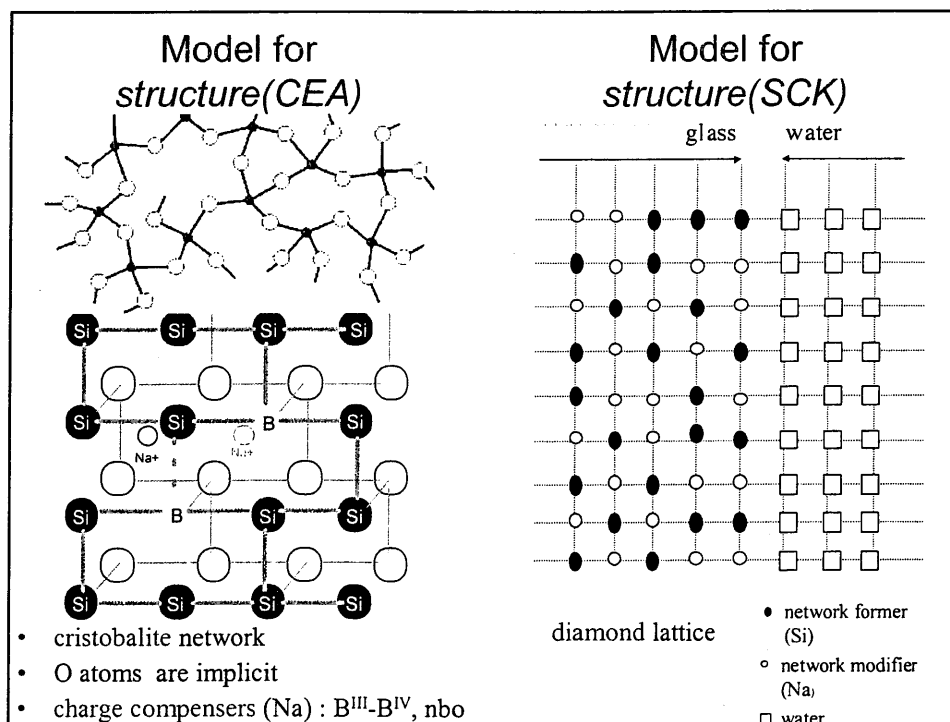
Literature review 2 pages
 Monte Carlo modeling of initial reaction/saturation and gel formation: 3 pages
 Thermodynamic modelling of gel formation: 3 pages
 Modeling of porosity evolution and of mass transfert in gel
 Overall modeling of kinetic reaction scheme

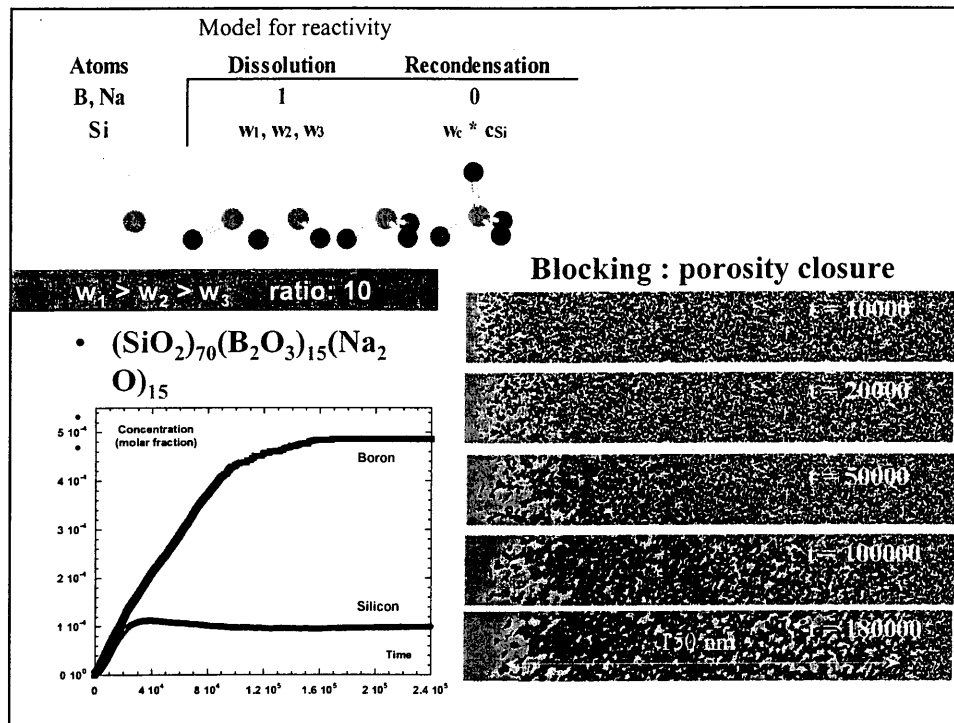
Literature review

n°	Task	Responsible
33	WP2-2 Bibliographic survey of solid-solution model applied to volcanic glasses (natural analogues)	CGS
116	WP5-1 Bibliographic survey of prior simulation approaches and review of unknowns, contradictions and uncertainties	CEA; SUBATECH
- Biblio is ready, very detailed model description, needs to be shortened significantly for final report: - Proposition: maximal 3 pages for all - Refer to GLAMOR for more detailed review		

Monte Carlo modeling of initial reaction/saturation and gel formation

68	WP2-9 Qualitative assessment of sealing and passivating properties of the gel by Monte-Carlo modelling	
69	WP2-9-1 Calculation of the pore structure	SCK
70	WP2-9-2 Comparison CEA - SCK	SCK; CEA
125	WP5-7 Monte-Carlo modelling to improve the understanding of glass-backfill environment interactions	SCK





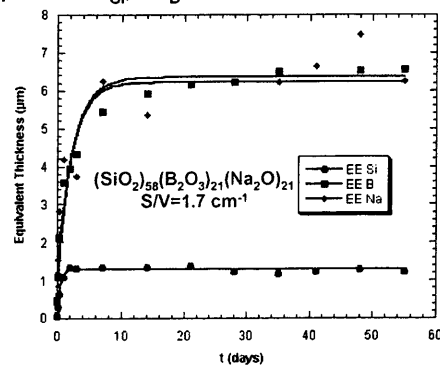
MC parameters adjustment

- MC parameters are fitted on experimental data :
 kinetic of leaching : initial rate of leaching
 amount of solubilized species : c_{Si} , ET_B

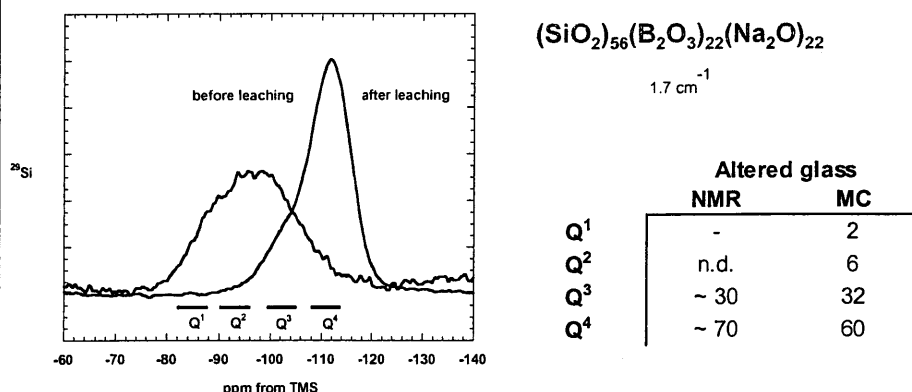
Leached glasses
 $(SiO_2)_{1-2x}(B_2O_3)_x(Na_2O)_x$
 x from 11 to 24 (mol. %)

Experimental conditions

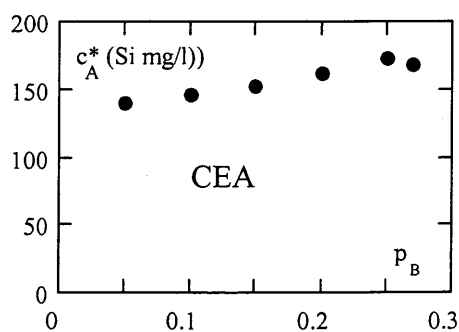
- pH = 8.5
- T = 90°C
- calibrated powders
- S/V from 1.7 cm⁻¹ up to 30 cm⁻¹



*Qualitative agreement with morphological
data : **NMR***

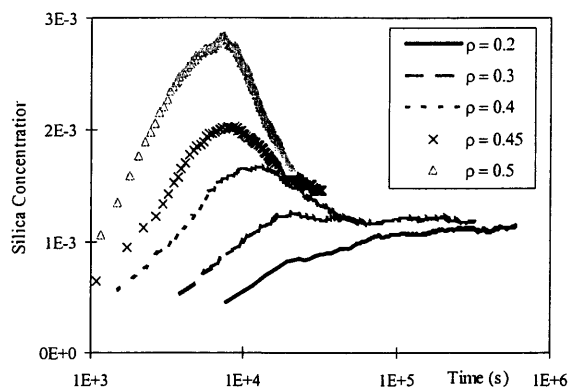


**Static tests: silica solubility
vs sodium fraction**



CEA: silica solubility approximately independent
of sodium fraction
SCK: similar result

Evolution towards Si saturation



Depending on sodium fraction, Si diffusion and surface to volume ratio, SCK observes supersaturation
CEA ?

Conclusions and perspectives

- Monte Carlo models are able to reproduce quantitatively the experimentally observed short term leaching phenomenology for simple glasses:
 - Initial congruent leaching
 - Formation of gel and gel cross-link density
 - Saturation of Si
 - Reduction of release rates of B, Na well after saturation of Si, but related to saturation of Si
- Efforts have to be made on
 - altered layer morphology prediction
 - More complex glasses
 - Long term evolution
 - Distinguish between Si and H2O diffusion control

Thermodynamic modelling of gel formation

32	WP2-1 Evaluation of the geochemical models (KINDIS and KIRMAT codes) to simulate the gel layers by coprecipitation, based on ideal solid solutions, during aqueous alteration of nuclear glasses	CEA; CGS
33	WP2-2 Bibliographic survey of solid-solution model applied to volcanic glasses (natural analogues)	CGS
34	WP2-3 Comparison of geochemical model findings with alteration gels characterised by TEM and SIMS, obtained during alteration experiments with 2 simplified glasses	
38	WP2-3-4 Modelling	CGS

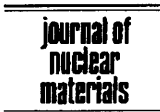


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Journal of Nuclear Materials xxx (2003) xxx–xxx



www.elsevier.com/locate/jnucmat

Modelling the alteration gel composition of simplified borosilicate glasses by precipitation of an ideal solid solution in equilibrium with the leachant

I. Munier ^{a,*}, J.-L. Crovisier ^a, B. Grambow ^b, B. Fritz ^a, A. Clément ^a

^a *Ecole et Observatoire des Sciences de la Terre, Centre de Géochimie de la Surface, ULP, CNRS, Strasbourg, France*
^b *Ecole des Mines, SUBATECH, Nantes, France*

Received 1 August 2002; accepted 26 August 2003

Table 3
Dissolution equations and free enthalpies of dissolution (kJ/mol) at 363 K

Dissolution equations	log K_{diss}
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4 \rightleftharpoons \text{SiO}_4$	-2.25
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SiO}_3$	-2.96
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$	-3.19
$\text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$	-8.95
$\text{Na}_2\text{O} + 2\text{H}^+ \rightleftharpoons 2\text{Na}^+ + \text{H}_2\text{O}$	56.39
$\text{CaO} + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{O}$	26.56
$\text{B}_2\text{O}_3 + 3\text{H}_2\text{O} \rightleftharpoons 2\text{B(OH)}_3$	5.08
$\text{Al}_2\text{O}_3 + 5\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_3 + 2\text{H}^+$	-24.54
$\text{ZrO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_4$	-11.6*
$\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$	6.87
$\text{Ca(OH)}_2 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 2\text{H}_2\text{O}$	18.63
$\text{Al(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_4^- + \text{H}^+$	-12.51
$\text{Zr(OH)}_4 \rightleftharpoons \text{Zr(OH)}_4$	-3.9*
$\text{Na}_2\text{SiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+ + \text{H}_4\text{SiO}_4$	17.75
$\text{CaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$	8.83
$\text{ZrSiO}_4 + 4\text{H}^+ \rightleftharpoons \text{Zr(OH)}_4 + \text{H}_4\text{SiO}_4$	-17.76*

* At 298 K.

Modeling results for gel composition

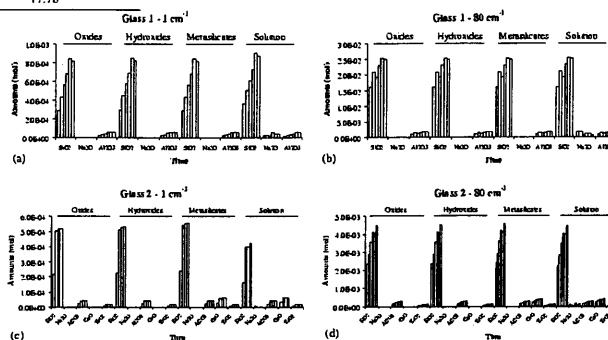


Fig. 14. Molar compositions of the simulated alteration gels according to the end-members and molar composition of the gels deduced from the solution analyses (mol) versus the alteration time (from left to right: 30, 60, 90, 120, 150 and 180 days, except for glass 2 at 1 cm³: 30, 60, 90 and 180 days).

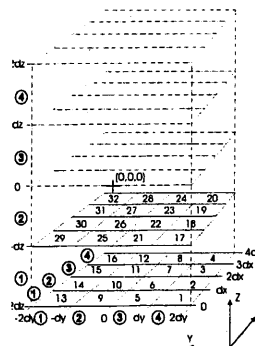
Modeling of porosity evolution and of mass transfert in gel

39	WP2-4 Modelling by reactive dispersion/advection with KIRMAT on micro/nanometer scale of the glass hydration, the formation of a gel and the variation of its porosity, the dissolution of the glass matrix, the ion exchange and the reactive Si transport	
40	WP2-4-1 Building of the model	SUBATECH; CGS

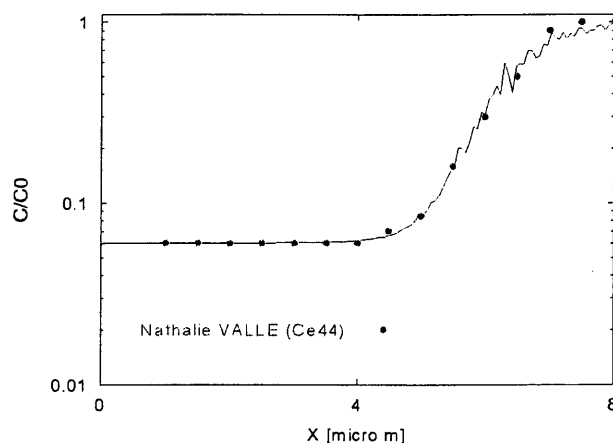
The stochastic model RW3D

C. Fleurant/B. Grambow

- "particle tracking" + "random walk" mechanism.
- Glass = porous medium.
- Glass constituents and the water molecules represented by individual particles with different diffusivities.
- Position of a particle in space (coordinates X,Y,Z) and time $t+\Delta t$:
- $X(t+\Delta t) = X(t) + U\Delta t + Z_1(6D_m\Delta t)^{1/2}$
- $Y(t+\Delta t) = Y(t) + Z_2(6D_m\Delta t)^{1/2}$
- $Z(t+\Delta t) = Z(t) + Z_3(6D_m\Delta t)^{1/2}$



Experimental Na release profile in R7T7 type glass at high S/V: comparison to stochastic model

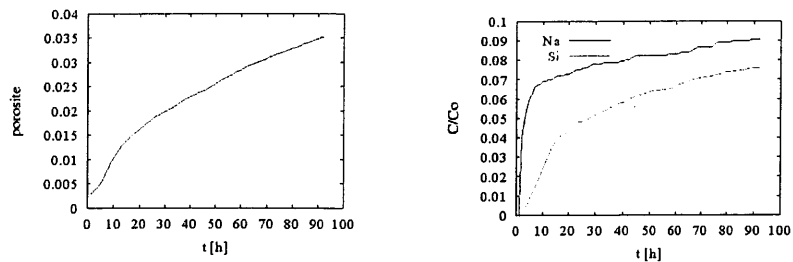


Application of the model to experimental data of N. Valle 2000.

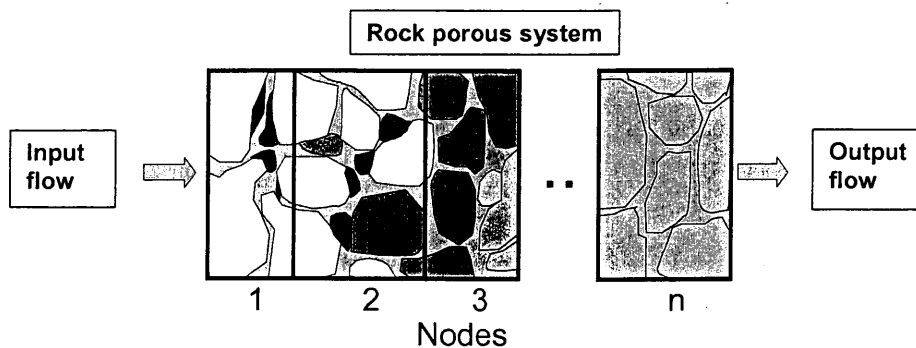
The concentration profile of Na is calculated for 3 month.

The fit of the experimental data was done with an apparent diffusion coefficient of $3.85 \cdot 10^{-19} \text{ m}^2/\text{s}$.

Stochastic prediction of parameter variation

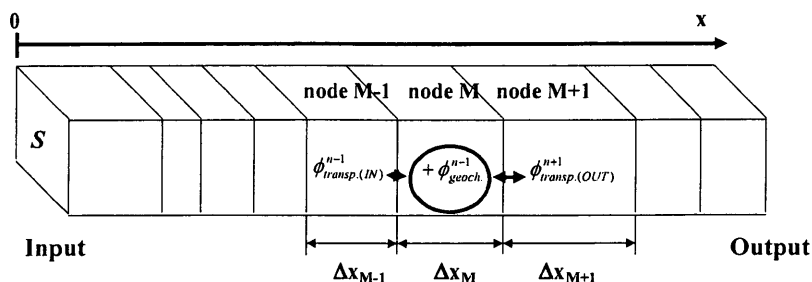


Introduction to KIRMAT (CGS)



The thermo-kinetic hydro chemical code Kirmat has been developed from the reaction path model Kindis by keeping all its geochemical formulation and its numerical method to solve chemical equations.

Calculations



Φ : geochemical flow per unit of total rock volume ($\text{mole L}^{-3} \text{T}^{-1}$).

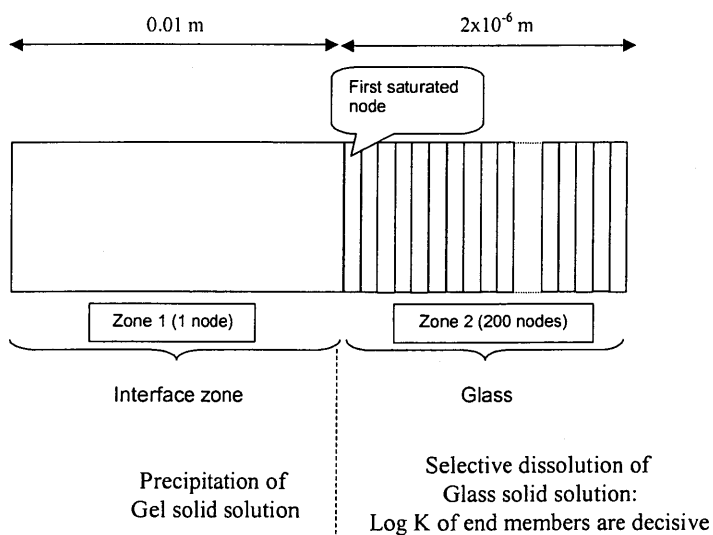
- Each node can have different mineral volume fractions, mineral reaction rates, water compositions and porosities
- Evolution of these parameters with reaction progress and transport

Modifications for GLASTAB

- Initial Kirmat designed to simulate a porous medium saturated with an initial solution. The code was modified
 - The user specifies the n first nodes of the system that are to be considered as saturated with an initial given solution. The other $N-n$ nodes are inactive.
 - During the simulation at the beginning of a new Δt step, a new node i is considered as saturated if:

$$(U \Delta t) + L(\text{init}) \geq L(i)$$
 - Where $L(i)$ represents the length of the system until (and including) node i , $L(\text{init})$ is the initial length of the saturated zone and U is the Darcy's rate.
 - Then the new active node is initialized:
 - o Aqueous species concentrations are computed and Saturation indexes of minerals and kinetic rates are calculated
 - o After node i , a null dispersive flow boundary condition is fixed (Neumann's condition) i.e. as if node i was the end of the system
 - The new node is included in the common set of active nodes and the process resumes.

Application to glass dissolution



- 119 WP5-4 Geochemical modelling (KIRMAT) of the interrelation of (i) formation of crystalline and amorphous solid reaction products, (ii) variation of surface layer porosity, (iii) variation of pore fluid composition, (iv) kinetics and (v) fluid advection/dispersion

SUBATECH;
CGS

Parameter selection

Transport coefficients:

Parameter	Zone 1	Zone 2
Porosity	0.9	0.01
Permeability (m^2)	10^{-9}	10^{-11}
Coef. of diffusion ($m^2/year$)	0.0315	10^{-15}
Dispersivity (m)	0.01	10^{-8}
Factor of cementation	2	2
Darcy's rate (m/year)	3×10^{-8}	3×10^{-8}

Mineralogical composition:

Mineral	Zone 2			
	Molar fraction	Molar volume	Surface reaction (m^2)	Kinetic constant (neutral k_0)
SiO ₂	.51	22.69	7.93×10^{-6}	0.01
B ₂ O ₃	.2	27.26	3.75×10^{-6}	1.
Al ₂ O ₃	.05	25.58	8.39×10^{-7}	0.01
Na ₂ SiO ₃	.16	128.49	1.39×10^{-5}	1.
CaSiO ₃	.07	39.94	1.96×10^{-6}	0.01
ZrSiO ₄	.01	176.11	1.61×10^{-6}	0.01

Physical and chemical parameters:

Parameter	Zone 1	Zone 2
Temperature ($^{\circ}C$)	90	90
pH	5.9	5.9
pCO ₂	3.02×10^{-4}	1.8×10^{-5}
Total concentrations (moles/kg H ₂ O)		
Al	10^{-11}	10^{-11}
Na	10^{-7}	10^{-7}
Ca	10^{-10}	10^{-10}
Zr	10^{-13}	10^{-13}
B	10^{-11}	10^{-11}
Si	10^{-10}	10^{-10}
C	10^{-10}	5×10^{-7}
Cl	10^{-10}	10^{-10}

Preliminary results

- Calculations up to 1 yr,
- Complete dissolution of Na and B from nodes close to bulk water, Si little mobile, Zr, Al almost immobile.
- Porewater pH 9.4, solution pH 9.0
- Problems :
 - overall feed-back of porosity change, mineral surface area change, permeability change,
 - mass balance at interface of very small and very large cells

Overall modeling of kinetic reaction scheme

71	WP3 Integrating the physico-chemical properties of the gel and glass in the alteration kinetics	
72	WP3-1 Balance of intrinsic glass kinetic parameters: kinetic constants, catalytic effects and inhibiting effects, diffusion coefficients in the gel, water interdiffusion coefficient in the pristine glass	SUBATECH; CEA
73	WP3-2 Measurement of free enthalpy of formation of SON68 glass by viscometry and calorimetry; quantification of the role of chemical affinity on the dissolution kinetics described by a first-order law	
74	WP3-2-1 Thermochemical measurements	CEA
75	WP3-2-2 Test of the solubility equilibrium between the glass and the solution	CEA

Phenomenological description of models

- Empirical description of the decrease of reaction rates with time
- Quantification by combination of
 - Forward rate k_+
 - Silica retention in gel f_{si} or a
 - Silica diffusion in gel D_{Si}
 - Si-saturation/First order rate law $\log K_{sat}$
 - Long-term rate r_{fin}
- Consens
 - Concept provides a good base for operational models
- Model uncertainty -> see GLAMOR
 - Significance of saturation constant in first order law
 - Parametrisation of long-term Si-diffusion in the transition to final rate
- Progress in GLASTAB
 - Evidence for and quantification of water diffusion D_{H2O}

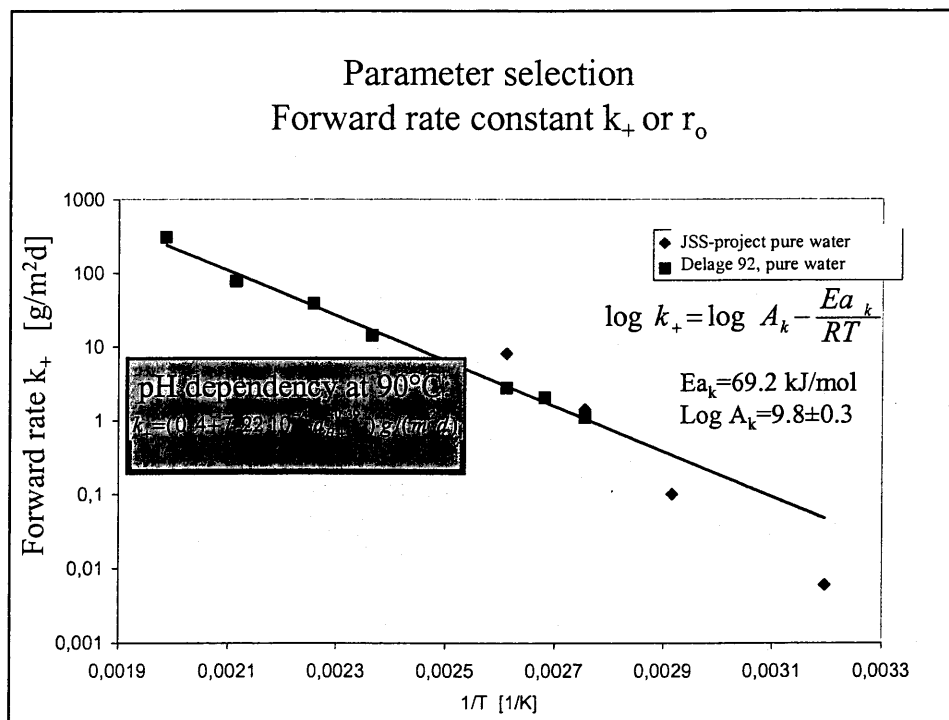
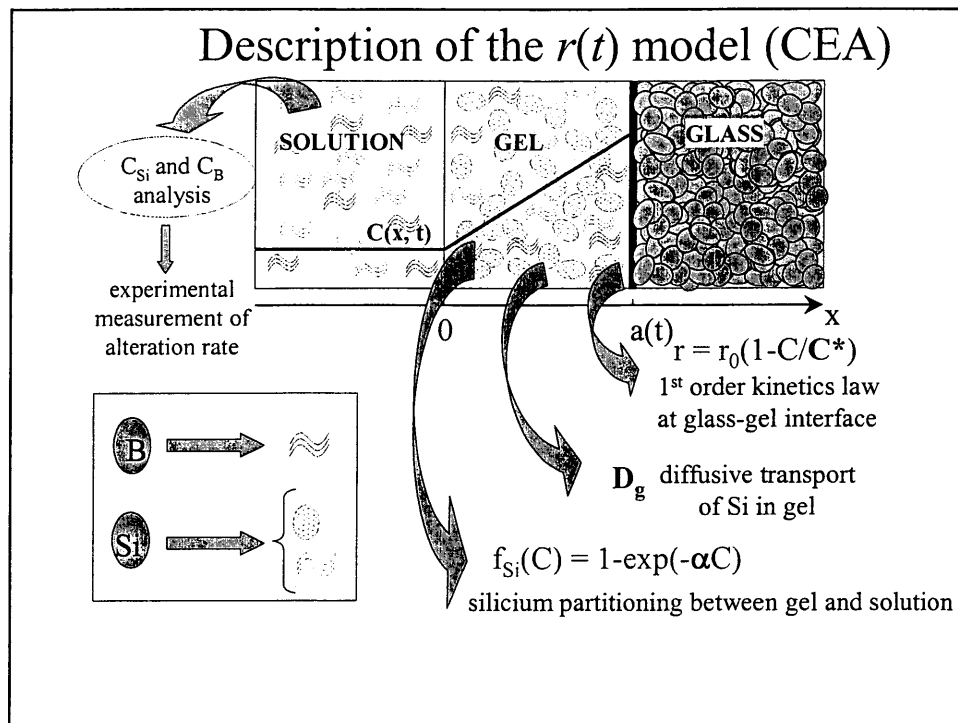
Steps in gel formation/surface alteration

- | | | | |
|---|---|----|---|
| Covered
by
1 st order
dissolution | { | 1. | Glass dissol. with k^+ , retention of metal oxyhydrates and small fraction of Si |
| | | 2. | Increased Si retention, decrease of rate by Si-diffusion and by affinity reduction |
| | | 3. | Stabilisation of gel close to saturation, rate of Si transport close to zero |
| | | 4. | Continuing water diffusion/ion exchange becomes rate determining forming a hydrated glass |
| | | 5. | Transformation of hydrated glass to gel, if solubility of water in glass is exceeded |

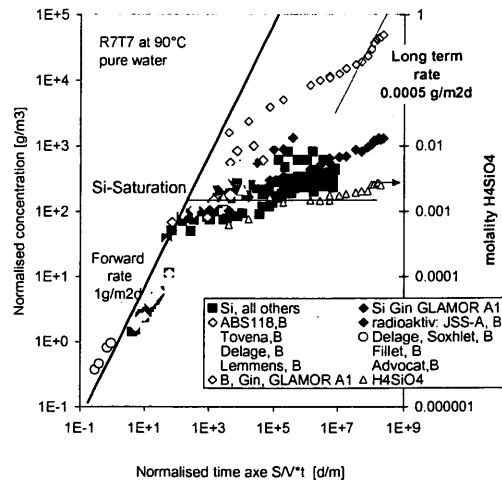
Terms: « gel » = amorphous product, phase separated into network+water

« hydrated glass » = amorphous glass-like phase with water in solid solution

Question: is step 5 governing long term rate???



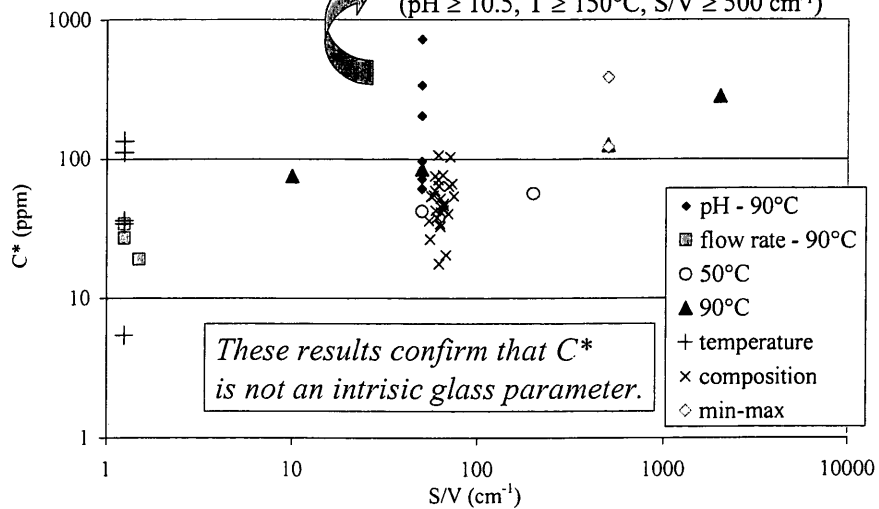
Si-saturation



C* versus leaching conditions

$$d, a = r(t) = r_0 \left(1 - \frac{C(x=a(t), t)}{C^*} \right)$$

"extreme" alteration conditions
(pH ≥ 10.5, T ≥ 150°C, S/V ≥ 500 cm⁻¹)



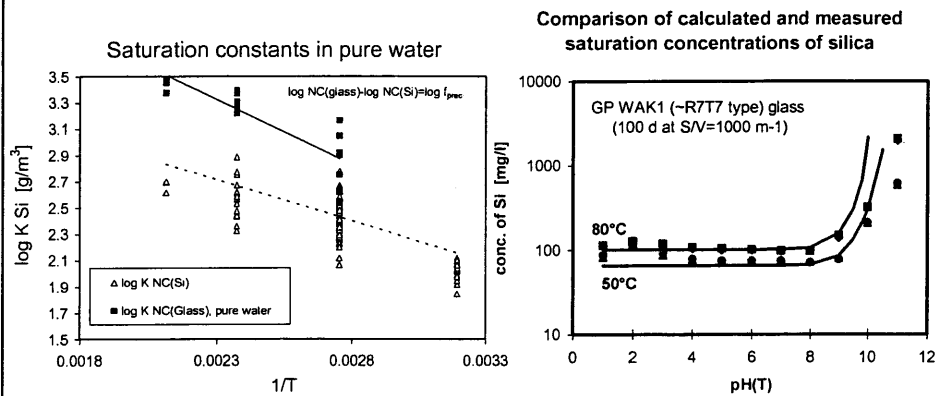
Saturation as a function of T et pH

$$\log K_{\text{SiO}_2, \text{glass}}(T) = \log K_{\text{SiO}_2, \text{glass}}^{\circ} + \frac{\Delta H_{\text{SiO}_2, \text{glass}}^{\circ}}{2.303 \cdot R} \left(\frac{1}{T^{\circ}} - \frac{1}{T} \right)$$

$$\Delta H_{\text{SiO}_2, \text{glass}}^{\circ} = 2.4 \pm 4.0 \text{ kJ/mol}$$

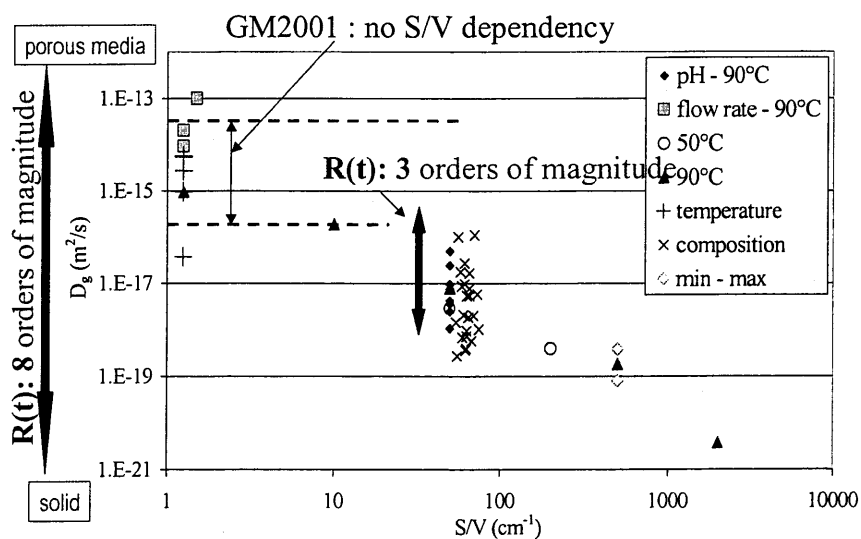
$$\log K_{\text{NC}(\text{Si-sat})}(T) = \log K_{\text{NC}(\text{Si-sat})}^{\circ} + \frac{\Delta H_{\text{SiO}_2, \text{glass}}^{\circ}}{2.303 \cdot R} \left(\frac{1}{T^{\circ}} - \frac{1}{T} \right)$$

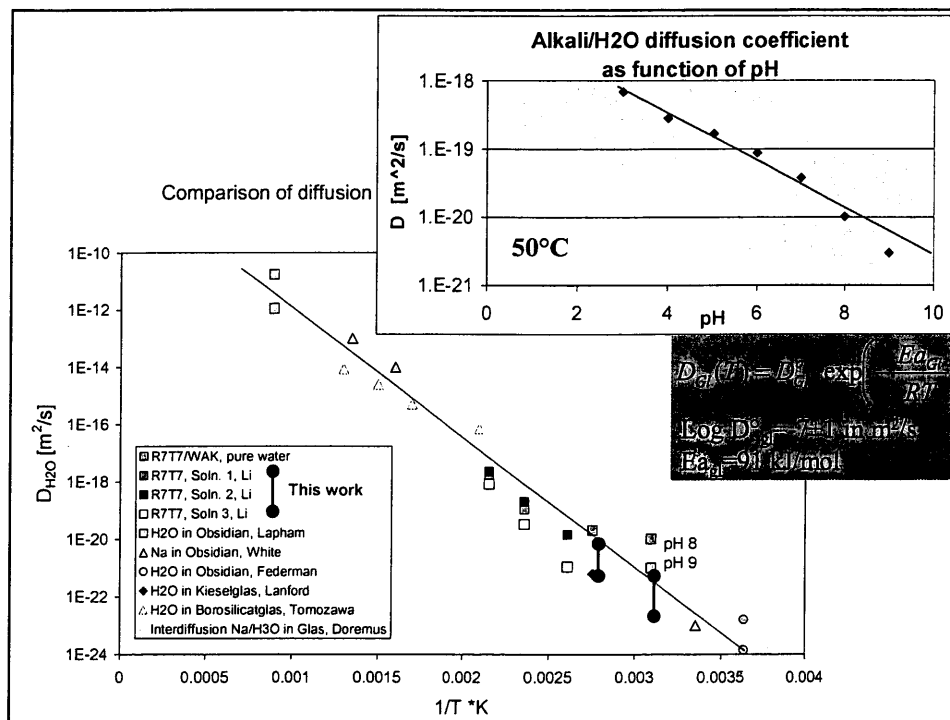
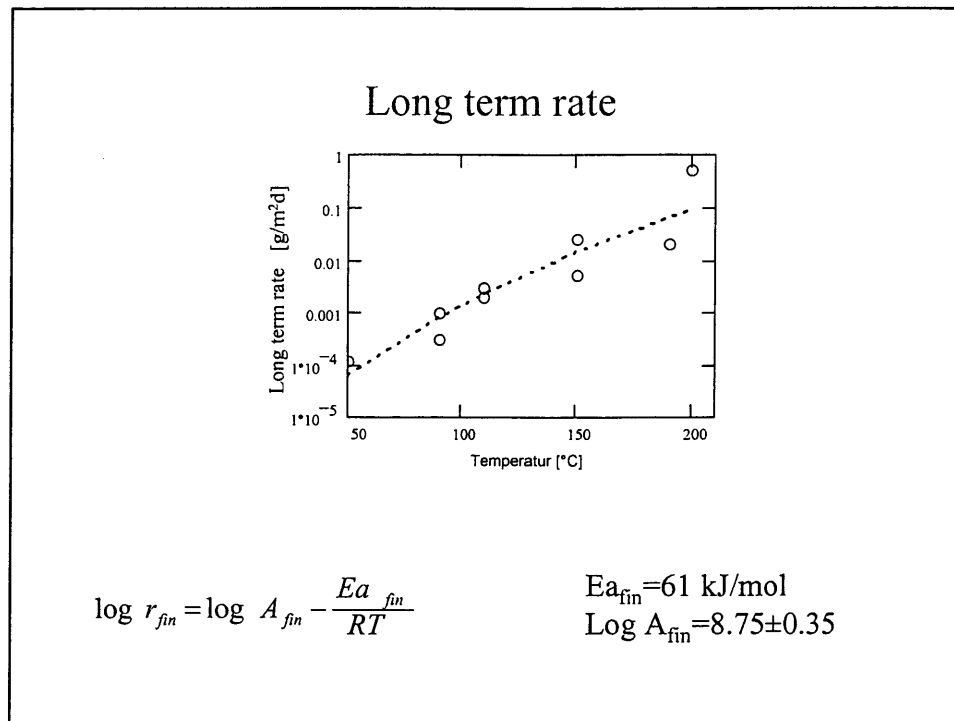
$$\log K_{\text{SiO}_2, \text{glass}}^{\circ} = -3.07 \pm 0.5 \text{ mol-BASiO}_4/\text{L}$$



D_g ou D_{si} versus leaching conditions

$$\partial_t C(x,t) = D_g \partial_x^2 C(x,t)$$





GLAMOR : Contribution of SUBATECH

Contribution to data base : OK
Model comparison/selection: OK
Use of models

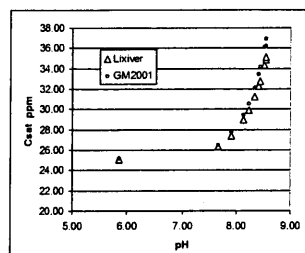
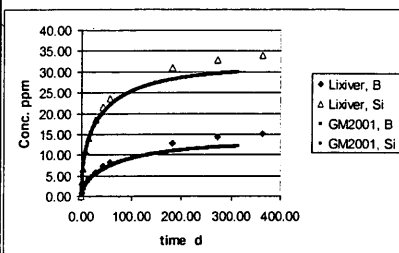
GLAMOR WP3: Model selection

- Decision last meeting: only few representative models
- Choice sufficient large to assess model uncertainty
 - Uncertainty to affinity law
 - Uncertainty to affinity non-related protective layer effect
 - Evaluation: Presentation of conceptual model- critics-defense
 - What about « constant long term rate »
- Until now: r(t) (CEA) and GM2001 (SUBATECH)

A17: Comparison

Small, but clear deviation in B conc.!

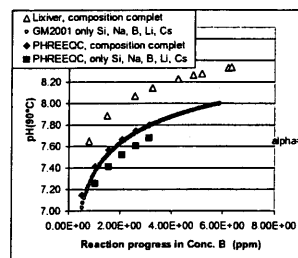
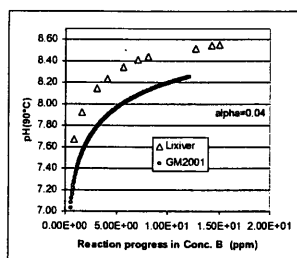
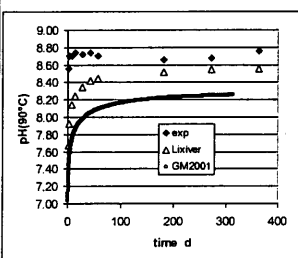
Is the difference caused by different SiO₂ solubility?



No!

Clear deviation in pH!

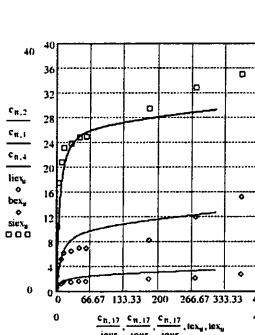
Is the difference caused by geochemical representation of reaction progress? Yes!



A17, continuation

With water diffusion, pH variable

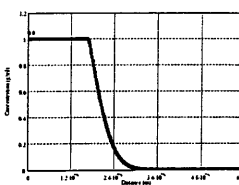
Summary of principal variables



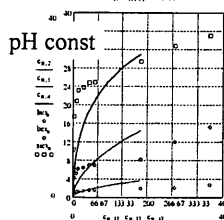
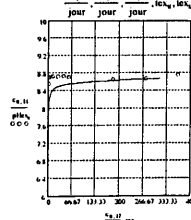
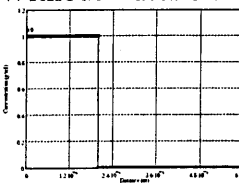
Summary of physical variables

Initial pH, force ionique	$\text{pH}_0 = 6$	$10 = 1 \cdot 10^{-4}$
Surface to volume ratio	$\text{SV} = 50 \text{ m}^2$	
Flow rate	$F = 0.03 \text{ kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$	
Solution volume	$V_{\text{ext}} = 6 \text{ klitre}$	$\log \text{CO}_2 = -4$
Initial Si +B concentration	$\text{NCCB} = 0.06 \text{ mol} \cdot \text{kg}^{-1}$	$\text{C}_{\text{B}0} = 0.06 \text{ mol} \cdot \text{kg}^{-1}$
Diff. Coefficient Water in glass	$D = 5 \cdot 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$	
Diff. Coefficient Si in gel	$D_{\text{Si}}(T, A_0, K_{\text{Si}}, T_{\text{ref}}, W_{\text{Si}}) = 5 \cdot 219 \cdot 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$	
Retention factor Si sorbed in gel	$\theta = 1$	$\theta = 0.8$
retention factor B	$k_{\text{B}} = 160 \text{ kg} \cdot \text{m}^{-3}$	
retention factor Li	$k_{\text{Li}} = 10 \text{ kg} \cdot \text{m}^{-3}$	
porosity of gel	$\phi = 0.2$	
forward rate	$k_1(T, A_0, K_{\text{H}}, T_{\text{ref}}, \text{pH}_0, 10) = 2999 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	
Si Saturation constant in mg/L	$K_{\text{H}}(T, A_0, K_{\text{H}}, T_{\text{ref}}, \text{pH}_0, 10) = 2999 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	17.758
$\log K_{\text{SiO}_2(\text{T})}$	$\log \left(\frac{K_{\text{H}}(T, A_0, K_{\text{H}}, T_{\text{ref}}, \text{pH}_0, 10)}{\frac{\text{mol}}{\text{kg}}} \right) = -3.198$	
$\log K_{\text{SiO}_2(25^\circ\text{C})}$	$\log K_{\text{H}}(T_{\text{ref}}) = -3.93$	

With water diffusion



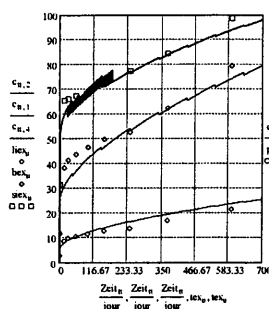
Without water diffusion



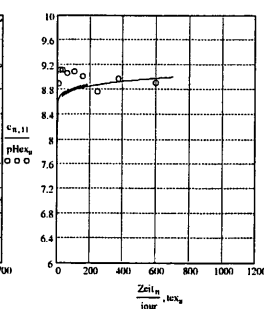
Static leaching, high S/V: A2

pH variable

Solution concentration of
Si, Li and B in mg/L



pH(at temperature)



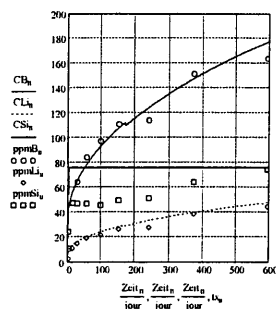
Summary of principal variables

Initial pH, force ionique	pHo = 6	Io = 1 × 10 ⁻⁴
Surface to volume ratio	SV = 5 × 10 ³ m ⁻¹	
Flow rate	F = 0 kg jour ⁻¹	
Solution volume	V _{leer} = 0.035 litre	logpCO2 = -3.5
Initial Si + B concentration	m _{CCB} = 0 mole kg ⁻¹	C _{Ba} = 0 mole kg ⁻¹
Diff. Coefficient Water in glass	D = 5 × 10 ⁻²³ m ² sec ⁻¹	
Diff. Coefficient Si in gel	DS(T, A _D , R ₇₇ , I ₅₀) = 5.219 × 10 ⁻¹⁴ m ² sec ⁻¹	
fraction of Si sorbed in gel	f _{pc} = 1	f _l = 0 f _x = 2.1
retention factor B	kd _B = 70 kg m ⁻³	
retention factor Li	kd _{Li} = 10 kg m ⁻³	
porosity of gel	φ = 0.2	
forward rate	kf(T, A _R , 77) = 7.005 × 10 ⁻⁴ kg m ⁻² jour ⁻¹	
Si Saturation constant in mg/L	Ks(T, log, K _R , 77) 28000 kg mole ⁻¹ = 34.587	
	KspH(T, log, K _R , 77, pHo, Io) 28000 kg mole ⁻¹ = 34.626	
	log((Ks(T, log, K _R , 77) $\frac{kg}{mole}$)) = -2.908	

Static leaching, high S/V: A3

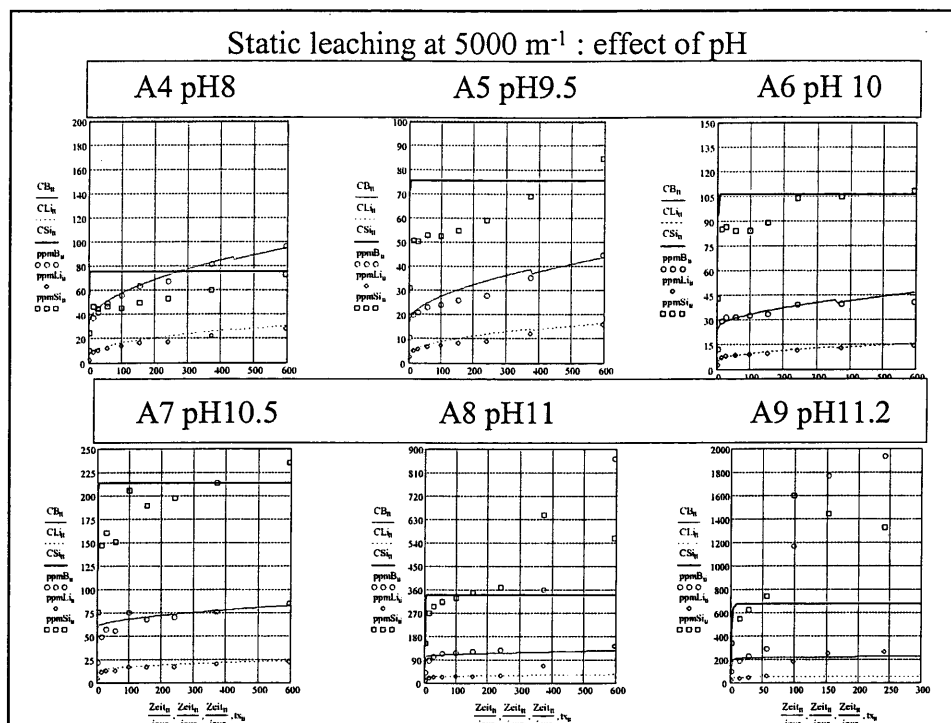
constant pH

Solution concentration of
Si, Li and B in mg/L

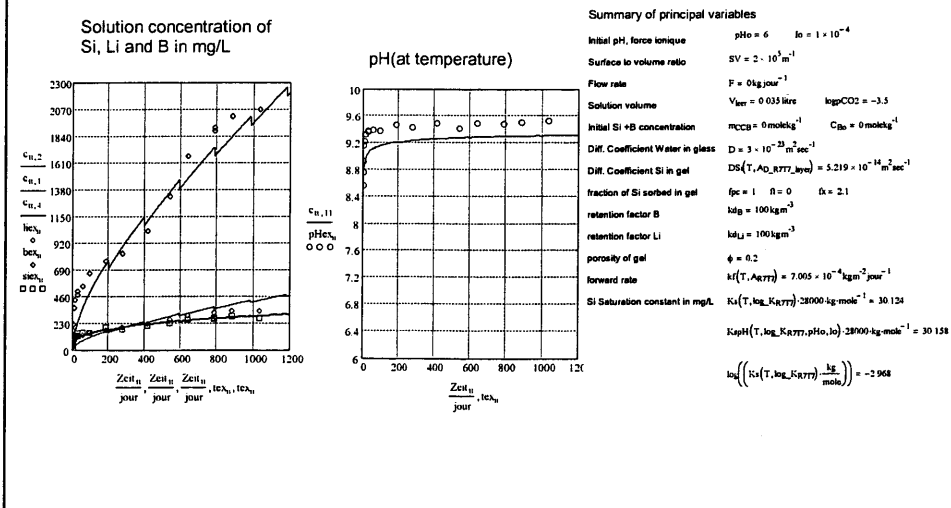


Summary of principal variables

Surface to volume ratio	SV = 5 × 10 ³ m ⁻¹	
Flow rate	F = 0 kg jour ⁻¹	
Solution volume	V _{leer} = 0.08 litre	
Initial Si concentration	m _{CCB} = 0 mole kg ⁻¹	
Diff. Coefficient Water in glass	D = 3 × 10 ⁻²² m ² sec ⁻¹	
Diff. Coefficient Si in gel	DS(T, A _D , R ₇₇ , I ₅₀) = 5.219 × 10 ⁻¹⁵ m ² sec ⁻¹	
fraction of Si sorbed in gel	f _{pc} = 1	f _l = 0 f _x = 1.5
retention factor B	kd _B = 30 kg m ⁻³	
retention factor Li	kd _{Li} = 10 kg m ⁻³	
porosity of gel	φ = 0.2	
forward rate	kf(T, A _R , 77) = 7.005 × 10 ⁻⁴ kg m ⁻² jour ⁻¹	
Si Saturation constant in mg/L	Ks(T, log, K _R , 77) 28000 kg mole ⁻¹ = 75.667	



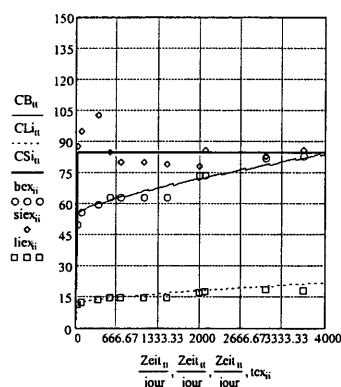
Static leaching, very high S/V: A1 pH variabel



Static very long term test

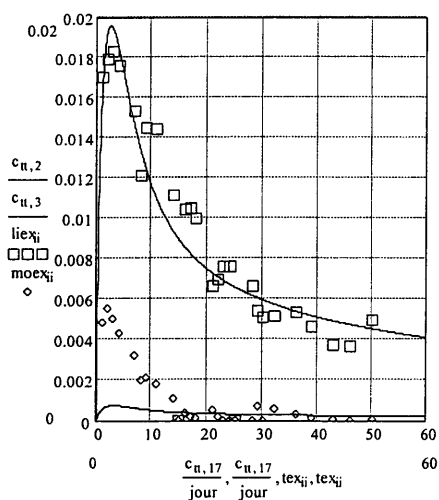
PSI data

Solution concentration of
Si, Li and B in mg/L



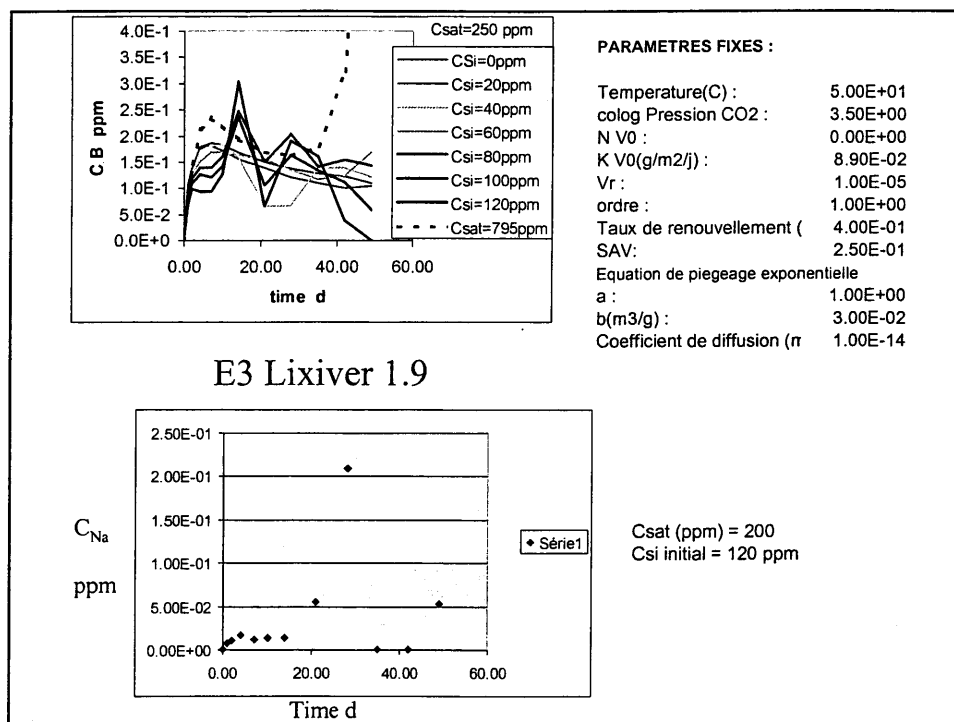
Flow test under Si saturated conditions : E3/ 50°C

pH 9	PHREEQC		
	25°C	50°C	90°C
pH	7	6.8	8.9
logpCO ₂	-3.5	-3.24	-2.67
Na	2392 ppm		
Si	120 ppm		
B	380 ppm		



Summary of principal variables

Initial pH, ionic strength	pH = 7	Io = 0.01
Surface to volume ratio	SV = 25.714 m ⁻¹	
Flow rate	F = 0.014 kg jour ⁻¹	
Solution volume	V _{seer} = 0.035 litre	
Initial Si + B concentration	m _{CCB} = 4.4 × 10 ⁻³ mole kg ⁻¹	C _{B0} = 0.01 mole kg ⁻¹
Diff. Coefficient Water in glass	D = 2.5 × 10 ⁻²¹ m ² sec ⁻¹	
Diff. Coefficient Si in gel	DSi(T, A _{D,R777,lay}) = 2.822 × 10 ⁻¹⁴ m ² sec ⁻¹	
fraction of Si sorbed in gel	f _{pc} = 1	Ω = 0
retention factor B	k _{dB} = 100 kg m ⁻³	fx = 0.6
retention factor Li	k _{dLi} = 10 kg m ⁻³	α = 0.049
porosity of gel	φ = 0.2	
forward rate	kf(T, A _{K777}) = 8.932 × 10 ⁻⁵ kg m ⁻² jour ⁻¹	
Si Saturation constant in mg/L	K _{spH} (T, log _{R777} , pHo, Io) 28000 kg·mole ⁻¹ = 12.166	
	log(K _s (T, log _{R777})) = -3.364	
	log _{R777} = -3.68	
	T = 323.15 K	

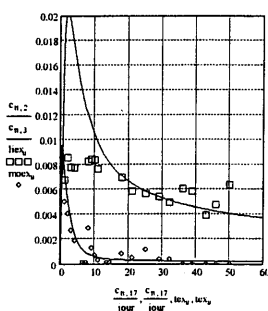


Flow tests in Si saturated soln.

Slow flow rate 14 mL/day

pH 9	PHREEQC
	25°C 50°C 90°C
pH	9.7 9.38 8.9
logpCO ₂	-3.5 -3.08 -2.67
Na	2392 ppm
Si	120 ppm
B	380 ppm

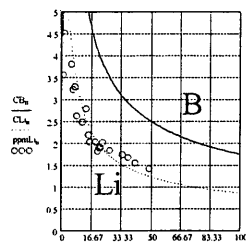
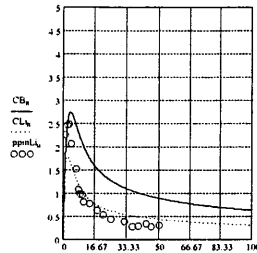
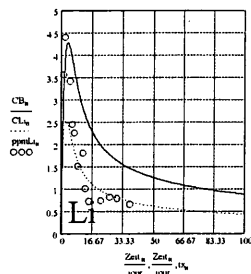
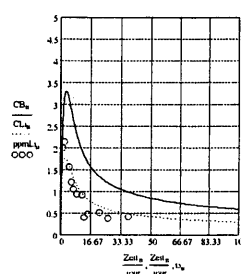
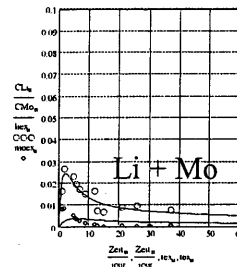
E16/ S/V 26 m⁻¹, pH 8.9



Summary of principal variables

Initial pH, ionic strength	pHo = 8.9	Io = 0.1
Surface to volume ratio	SV = 25.714 m ⁻¹	
Flow rate	F = 0.014 kg jour ⁻¹	
Solution volume	V _{sol} = 0.035 litre	logpCO ₂ = -2.67
Initial Si + B concentration	mCCB = 4.4 × 10 ⁻³ mole kg ⁻¹	C _{B0} = 0.01 mole kg ⁻¹
Diff. Coefficient Water in glass	D = 2 × 10 ⁻²¹ m ² sec ⁻¹	
Diff. Coefficient Si in gel	DS(T, A _D , R ₇₇₇ , w _{gel}) = 5.211 × 10 ⁻¹³ m ² sec ⁻¹	
fraction of Si sorbed in gel	f _{pc} = 1	β = 0
retention factor B	k _{dB} = 60 kg m ⁻³	f _c = 0.999
retention factor Li	k _{dLi} = 10 kg m ⁻³	α = 0.014
porosity of gel	φ = 0.2	
forward rate	k _f (T, A _{R777}) = 2.084 × 10 ⁻³ kg m ⁻² jour ⁻¹	
Si Saturation constant in mg/L	K _{spH} (T, log _{R777} , pHo, Io) = 28000 kg·mole ⁻¹ = 70.265	
	log((K _{sp} (T, log _{R777}) · (kg/mole))) = -3.103	
	log _{R777} = -3.88	
	T = 368.15 K	

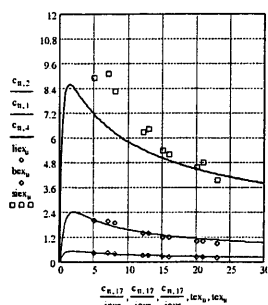
Other slow flow tests under Si-saturated conditions

E9/ pH7 12000 m⁻¹E15/ pH8.9 12000 m⁻¹E12/ pH8.1 12000 m⁻¹E11/ pH8.1 4700 m⁻¹E13/ pH8.1 26 m⁻¹

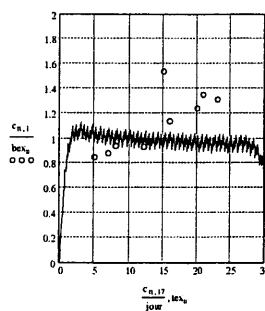
Flow test as a function of Si conc. at pH 8

fast flow 144 mL/day

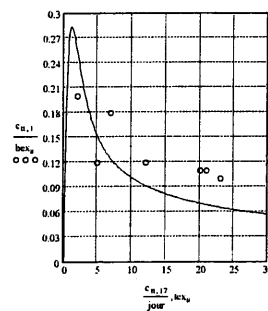
A10: 0 ppm Si

Solution concentration of
Si, Li and B in mg/L

A11: 60 ppm Si

Solution concentration of
Si, Li and B in mg/L

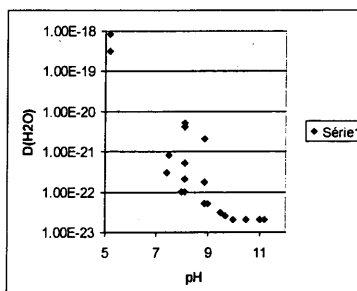
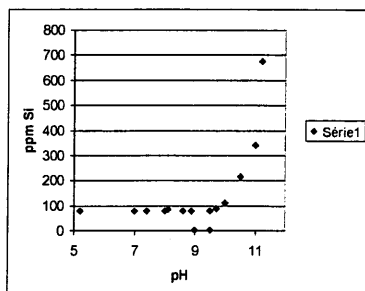
A12: 120 ppm Si

Solution concentration of
Si, Li and B in mg/L

Summary of parameters

	tmax d	pH	SV m-1	F mL/j	mccb ppm	Dsi m2/s	DH2O m2/s	Si sat ppm	KdB	KdLi	fx	k+ g/m2d	rfin	log Ksi (90C)	logKsi(25C)
A1	1200	9.5	200000	0	0	5.20E-14	3.00E-23	f(pH)	100	100	2.1	0.7	7.00E-08	-2.97	-3.7
A2	600	9	5000	0	0	5.20E-14	5.00E-23	f(pH)	70	10	2.1	0.7	7.00E-08	-2.91	-3.64
A3	600	7.4	5000	0	0	5.20E-14	3.00E-22	75.6	30	10	1.5	0.7	7.00E-08	-2.78	-3.52
A4	600	8	5000	0	0	5.20E-14	1.00E-22	75.6	60	10	1.5	0.7	7.00E-08		
A5	600	9.5	5000	0	0	5.20E-14	3.00E-23	75.6	100	10	0	0.7	7.00E-08		
A6	600	10	5000	0	0	5.20E-14	2.00E-23	106.9	100	10	0	0.7	7.00E-08		
A7	600	10.5	5000	0	0	5.20E-14	2.00E-23	213.3	100	10	0.8	0.7	7.00E-08		
A8	600	11	5000	0	0	5.20E-14	2.00E-23	338	100	10	0.8	0.7	7.00E-08		
A9	240	11.2	5000	0	0	5.20E-14	2.00E-23	674	100	10	0.8	0.7	7.00E-08		
Curti	3600	9.7	1200	0	0	5.20E-14	2.50E-23	84.9	100	10	2.1	0.7	7.00E-08		
E9	48	7.5	12000	14.4	120	5.20E-14	8.00E-22	75.6	100	10		0.7	7.00E-08		
E10-a	30	5.2	26	14.4	120	5.20E-14	8.00E-19	75.6	100	10		0.7	7.00E-08		
E10-a	50	5.2	26	14.4	120	5.20E-14	3.00E-19	75.6	100	10		0.7	7.00E-08		
E11	37	8.1	4330	14.4	120	5.20E-14	5.00E-22	75.6	100	10		0.7	7.00E-08		
E12	37	8.1	12000	14.4	120	5.20E-14	2.00E-22	75.6	100	10		0.7	7.00E-08		
E13	37	8.1	26	14.4	120	5.20E-14	4.00E-21	75.6	100	10		0.7	7.00E-08		
E15-a	10	8.9	12000	14.4	120	5.20E-14	1.70E-22	75.6	100	10		0.7	7.00E-08		
E15-b	50	8.9	12000	14.4	120	5.20E-14	5.00E-23	75.6	100	10		0.7	7.00E-08		
E16	50	8.9	26	14.4	120	5.20E-14	2.00E-21	75.6	100	10		0.7	7.00E-08	-3.1	-3.88
A10	23	8.1	150	144	0	1.70E-13	1.00E-22	84	30	10	3.5	0.7	7.00E-08	-2.88	3.62
A11	23	8.1	150	144	60	7.00E-14	5.00E-21	84	30	10	3.5	0.7	7.00E-08	-2.61	-3.3
A12	23	8.1	150	144	120	7.00E-14	5.00E-21	84	30	10		0.7	7.00E-08		
A17	370		50	0	0	5.20E-13	5.00E-21	f(pH)	100	10	0.8	0.7	7.00E-08	-3.2	-3.93

Overall dependencies at 90C



Framework of WP 3.3 : Long term impact assessment of water diffusion processes in the pristine glass versus hydrolysis reaction by means of leach tests at imposed pH

Materials used

- powders of SON 68
 - a) Particles with a diameter lower than 20 μm
SA = 0.51 $\text{m}^2.\text{g}^{-1}$ measured by BET method (Kr)
 - b) Particles with a diameter equal to 5 μm
SA = 1.39 $\text{m}^2.\text{g}^{-1}$ given by CEA
- Chips : 2.4 cm x 2.4 cm x 100 μm

Experimental conditions

- Dynamic system
flow = 0.6 mL.h⁻¹
- Temperature : 50°C or 90°C
- Solution saturated in silicon,
boron and sodium
pH = 4.8 or 7.2 or 9.8

Dissolution of SON 68 in a static system at 90°C with S/V = 20000 m⁻¹ (Tovena 1995)

Days	NL(Si)	NL(B)	NL(Na)	NL(Li)	NL(Mo)	pH
189	0.03	0.43	0.42	0.66	0.19	9.53

NL in g.m⁻²

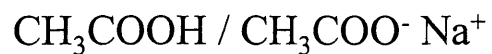
Composition of the synthetic solution

Chemicals	[Na] (g/L)	[B] (g/L)	[Si] (g/L)
$\text{Na}_2\text{B}_4\text{O}_7$	0.3988	0.3815	
SiO_2 , NaOH	0.0805		0.1275
NaOH (1M)	0.5347		

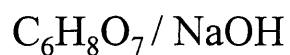
[Na] = 1015 mg.L⁻¹[B] = 381 mg.L⁻¹[Si] = 127 mg.L⁻¹pH_i = 12

- pH 9.8 in equilibrium with atmosphere obtained by bubbling with Ar / CO₂(90 / 10)

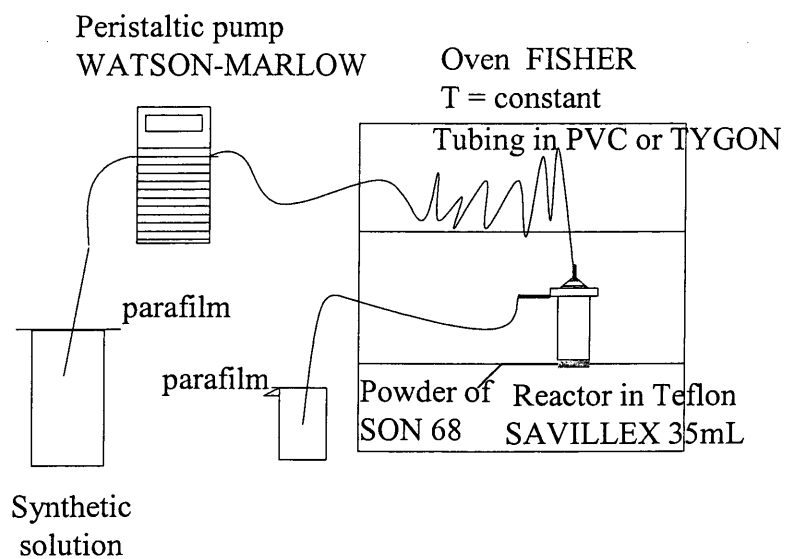
- pH 4.8 obtained by using a chemical buffer



- pH 7.2 obtained by using a chemical buffer



Experiment



Leaching dissolution rate in $\text{g.m}^{-2}.\text{d}^{-1}$

$$NL_{t+1} = \frac{\left(\frac{NC_t - NC_{t+1}}{((t+1) - t)} \right) + \left(F/V \times NC_{t+1} \right)}{S/V}$$

$$\text{With } NC = \frac{C_{\text{element}}}{\% \text{ element in pristine glass}}$$

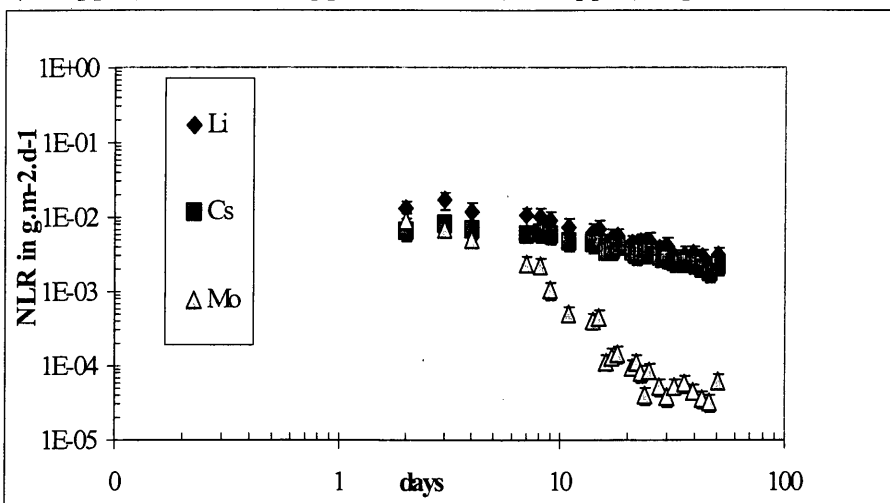
Estimation of the uncertainty according to the error's propagation

$$\Delta NL/NL = \sqrt{\frac{\left[\Delta NC_t^2 + \Delta NC_{t+1}^2 + \left(\frac{F}{V} \times NC_{t+1} \right)^2 \times \left[\left(\frac{\Delta F}{F} \right)^2 + \left(\frac{\Delta V}{V} \right)^2 + \left(\frac{\Delta NC_{t+1}}{NC_{t+1}} \right)^2 \right] \right]}{\left(\frac{NC_t - NC_{t+1}}{(t+1) - t} + \frac{F}{V} \times NC_{t+1} \right)^2}} + \left(\frac{\Delta V}{V} \right)^2 + \left(\frac{\Delta S}{S} \right)^2$$

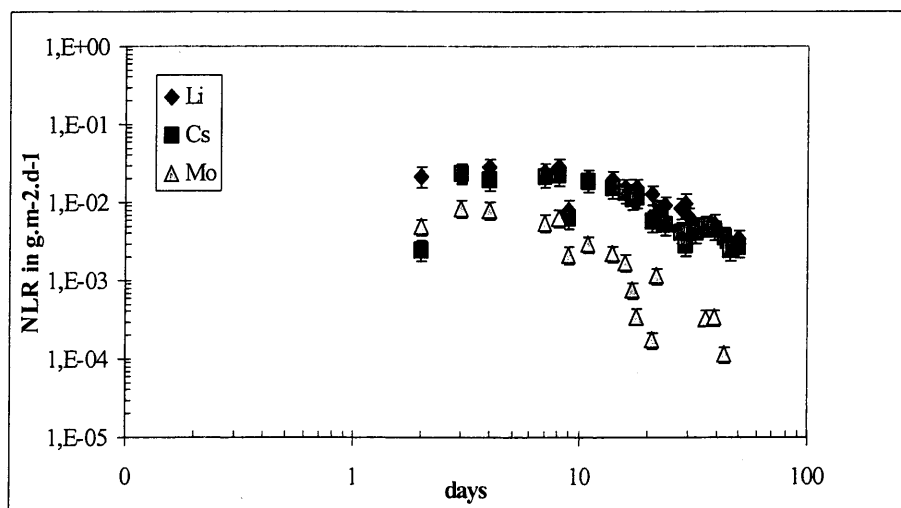
Uncertainty in % in the case of experiments in a dynamic system at 50°C with a synthetic solution saturated in silicon (120 ppm), boron (380 ppm) and sodium (1015 ppm)

Material	pH								
	4.8			7.2			9.8		
	Li	Cs	Mo	Li	Cs	Mo	Li	Cs	Mo
Powder d20	27	27	25	28	26	25	26	26	25
Powder d5	27	27	25	26	29	29			
chip	28	28	24	30	32	31	24	25	23

Normalised leaching rates as a function of time for the dissolution at **50°C** of the **powder d20** with a synthetic solution saturated in silicon (120 ppm), boron (380 ppm), sodium (1015 ppm) at pH 4.8



Normalised leaching rates as a function of time for the dissolution at **50°C** of the **chip** with a synthetic solution saturated in silicon (120 ppm), boron (380 ppm), sodium (1015 ppm) at pH 4.8

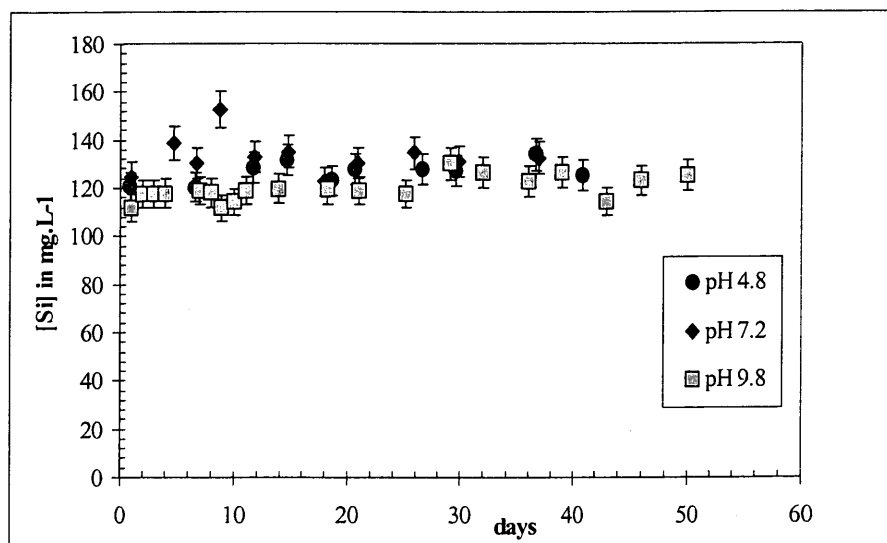


Final corrosion rates in $\text{g.m}^{-2}.\text{d}^{-1}$

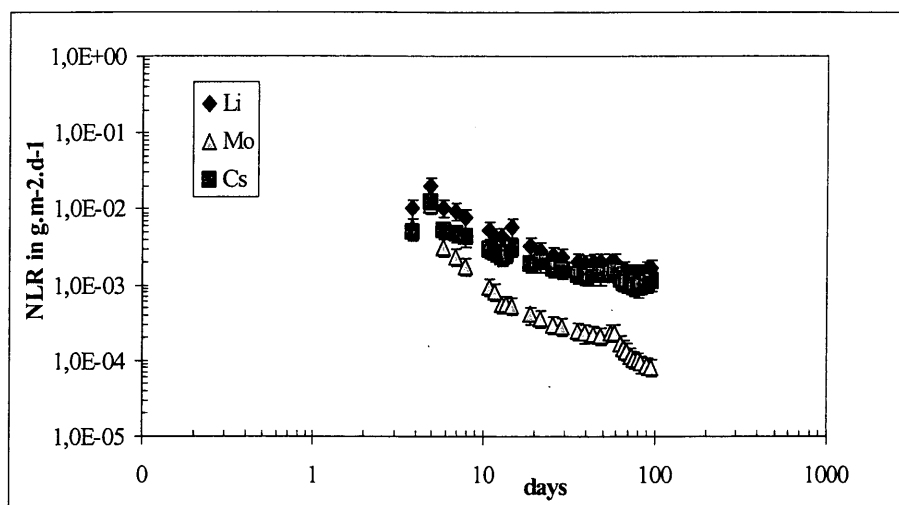
Material	Element	50°C			90°C		
		pH			pH		
		4.8	7.2	9.8	4.8	7.2	9.8
Chip	Li	2.10^{-3}	3.10^{-3}	-	5.10^{-3}	5.10^{-3}	10^{-2}
	Mo	5.10^{-5}	-	10^{-4}	2.10^{-5*}	3.10^{-4}	10^{-3}
Powder	Li	2.10^{-3}	2.10^{-3}	6.10^{-5}	5.10^{-3}	2.10^{-3}	2.10^{-3}
	Mo	3.10^{-5}	10^{-4*}	10^{-5}	2.10^{-5}	10^{-4}	3.10^{-4}

* Steady state is not reached in these experiments

Evolution of silicon concentration during experiments conducted at 90°C with the powder d20 and the synthetic solution containing 120 ppm silicon



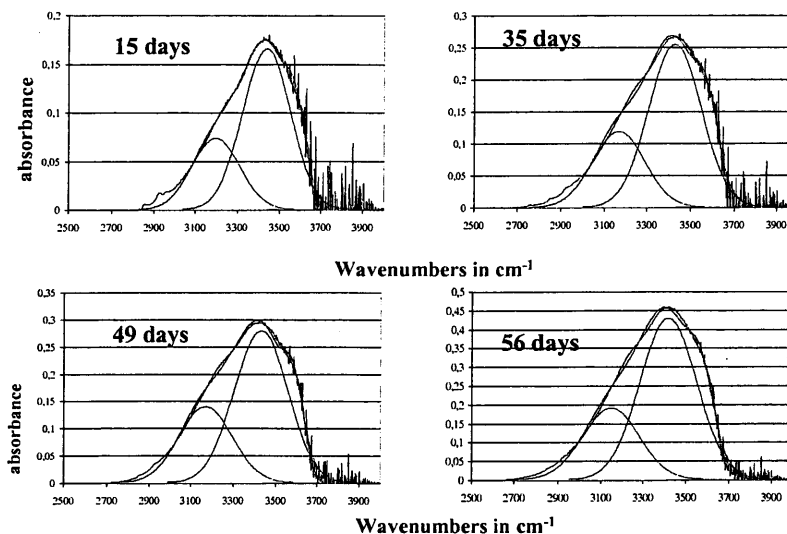
Normalised leaching rates as a function of time for the dissolution at 90°C of the **powder d20** with a synthetic solution oversaturated in silicon (240 ppm), boron (380 ppm), sodium (1015 ppm) at pH 9.8



Final corrosion rate in g.m⁻².d⁻¹ for experiments at 90°C with SON 68 powder

[Si]	120 ppm		240 ppm	
Element	Li	Mo	Li	Mo
pH 4.8	5.10 ⁻³	2.10 ⁻⁵	10 ⁻²	4.10 ⁻⁵
pH 7.2	2.10 ⁻³	10 ⁻⁴	4.10 ⁻³	10 ⁻⁴
pH 9.8	2.10 ⁻³	3.10 ⁻⁴	2.10 ⁻³	10 ⁻⁴

Evolution of spectra during alteration of powder d20 with a synthetic solution at pH 4.8



Beer – Lambert Law :

$$A = \epsilon l C$$

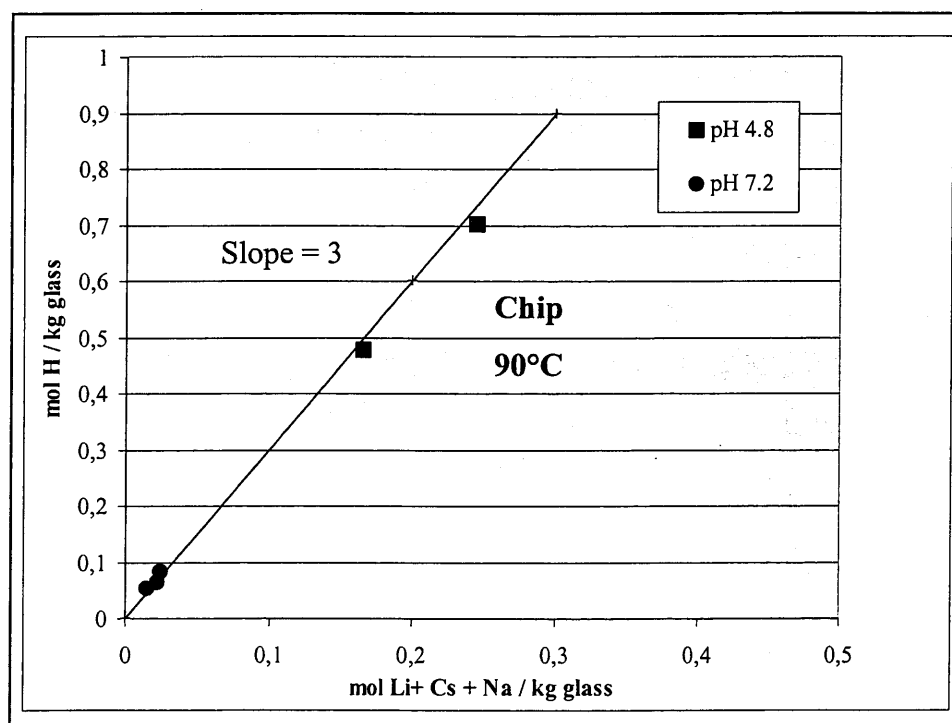
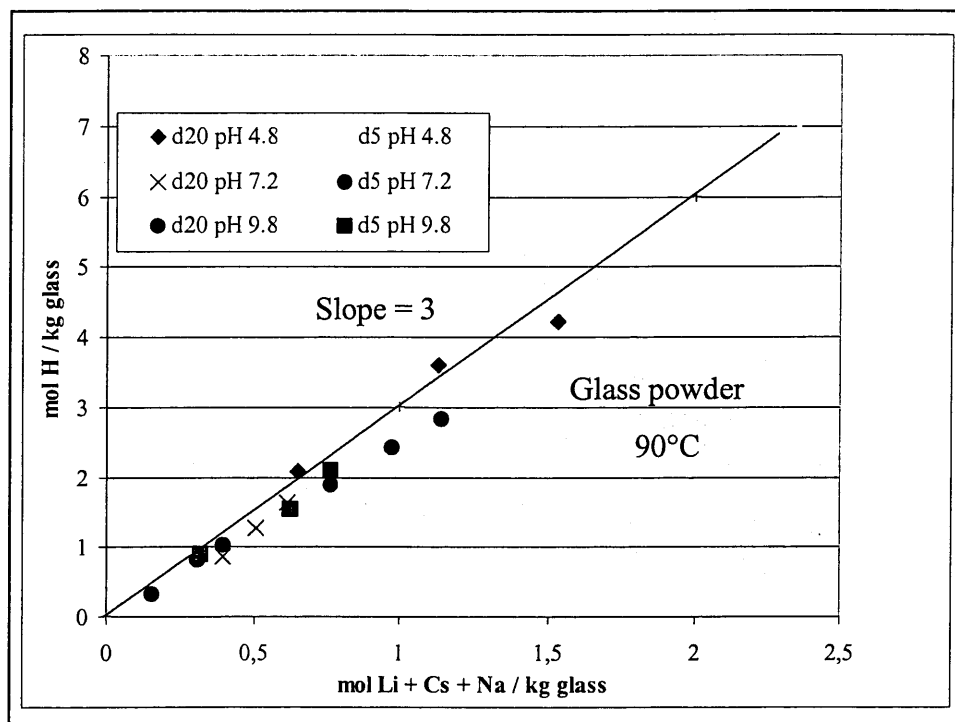
Literature extinction coefficients

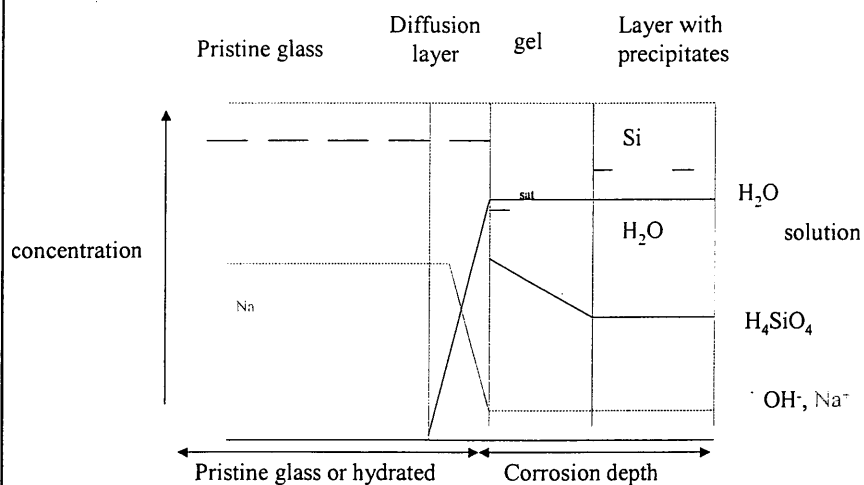
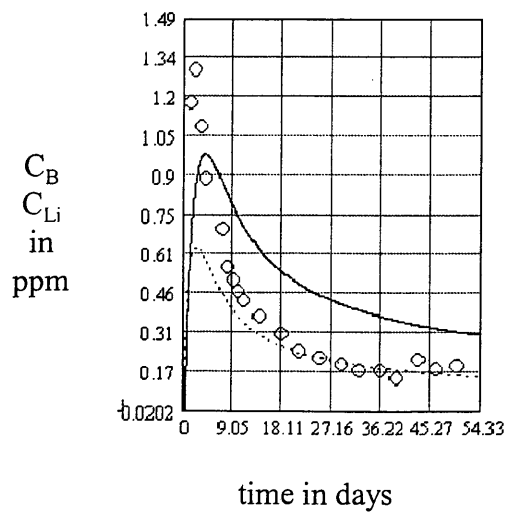
$$\epsilon_{\text{SiOH}} = 70 \text{ L.mol}^{-1}.\text{cm}^{-1} [1]$$

$$\epsilon_{\text{H}_2\text{O (I\&II)}} = 81 \text{ L.mol}^{-1}.\text{cm}^{-1} [2]$$

[1] F.Geotti-Bianchini, Geibler H., Krämer F., Smith I.H, *Glastech. Ber. Glass Sci. Technol.*, **72** n°4,(1999).

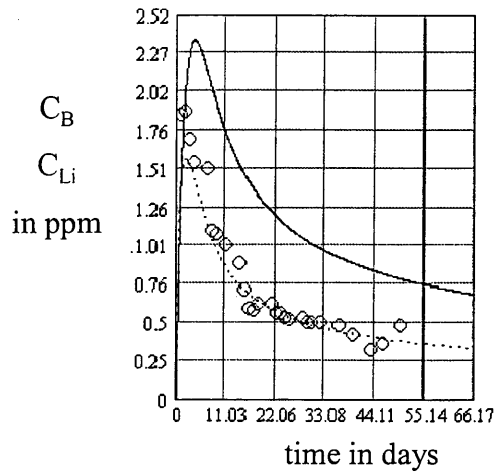
[2] N. Yanagisawa, K. Fujimoto, S. Nakashima, Y. Kurata, N. Sanada, *Geochimica and Cosmochimica Acta*, **61** n°6, pp 1165-1170, (1997).



GM 2001 model(B. Grambow, R. Müller, *Journal of Nuclear Material*, **298**, pp 112-124, 2001)
**Modeling of the results obtained during dissolution
of the powder d20 at 90°C with the synthetic solution
at pH 9.8**


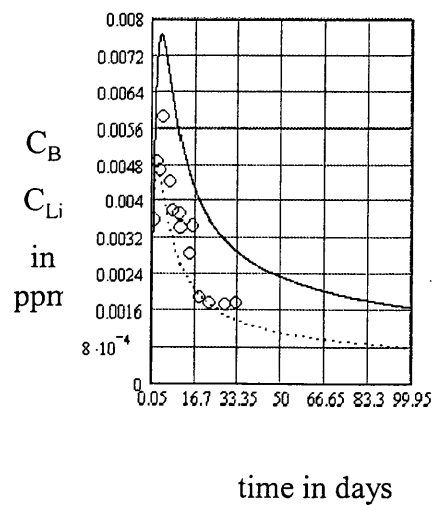
$$D_{H_2O} = 10^{-22} \text{ m}^2 \cdot \text{s}^{-1}$$

Modeling of the results obtained during dissolution of the powder d5 at 50°C with the synthetic solution at pH 4.8



$$D_{H_2O} = 8.10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$$

Modeling of the results obtained during dissolution of the chip at 50°C with the synthetic solution at pH 7.2



$$D_{H_2O} = 1.5 \cdot 10^{-22} \text{ m}^2 \cdot \text{s}^{-1}$$

**Water diffusion coefficients in $\text{m}^2\cdot\text{s}^{-1}$ for experiments
conducted at 50°C**

pH	4.8	7.2	9.8
Powder d20	$4\cdot 10^{-22}$	$6\cdot 10^{-23}$	$3\cdot 10^{-24}$
Powder d5	$8\cdot 10^{-23}$	$5.3\cdot 10^{-23}$	
Chip	$2.5\cdot 10^{-21}$	$1.5\cdot 10^{-22}$	

**Water diffusion coefficients in $\text{m}^2\cdot\text{s}^{-1}$ for experiments
conducted at 90°C**

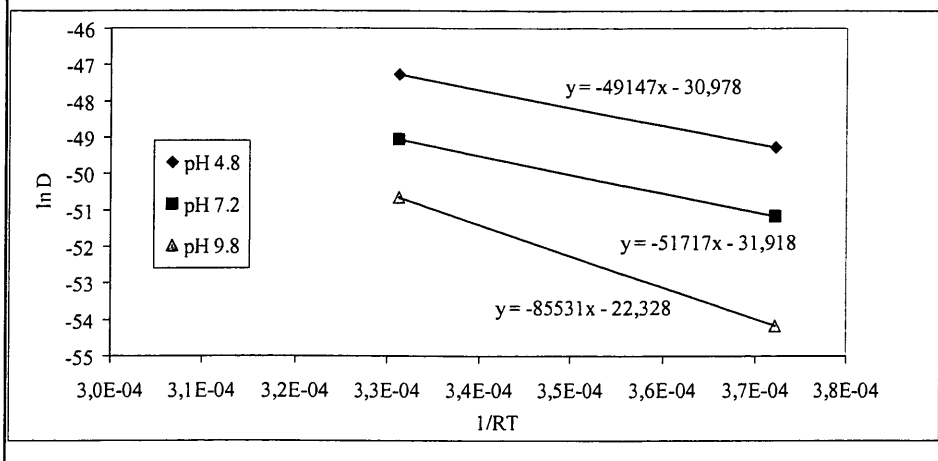
pH	4.8	7.2	9.8
Powder d20	$3\cdot 10^{-21}$	$5\cdot 10^{-22}$	10^{-22}
Powder d5	10^{-21}	$1.5\cdot 10^{-22}$	$6\cdot 10^{-23}$
Chip	$4\cdot 10^{-19}$	$4\cdot 10^{-21}$	$2\cdot 10^{-21}$

Water diffusion coefficients similar to those obtained by :

- Doremus (1975) → Baucke : experiments conducted at 50°C in a 0.1 N H₂SO₄
- Lanford (1979) : 90°C in pure water

Arrhenius law:
 $\ln D = -E_A/RT + \ln D_0$

Activation energy determined from the experiments conducted with the powder d20



Delage (1992) : $E_A = 60 \text{ kJ.mol}^{-1}$

Yanagisawa (1997) : $E_A = 60 \text{ kJ.mol}^{-1}$

Usually an activation energy between 40 and 80 kJ.mol^{-1} characterises a surface reaction but Yanagisawa considers the activation energy of 60 kJ.mol^{-1} as associated with water diffusion in a hydrated glass layer

apparent E_A

Work-Package 1:

Task No. 4 and 5: FZK-INE

Coprecipitation experiments:

To determine the maximum obtainable solution concentrations of fission products, Th and U during glass corrosion two sorts of precipitation tests were performed:

WP1-4: Dissolution of simulated HLW glass at 80°C in highly acid (HCl) and highly basic (NaOH) media followed by pH adjustment to obtain alteration gels between pH 2.5 and 10; Characterisation of the products obtained.

WP1-4-1: Glass dissolution in 0.5 M HCl (80°, 50°, 23°C)

WP1-4-2: Analyses of the precipitates(XRD, SEM/EDX)

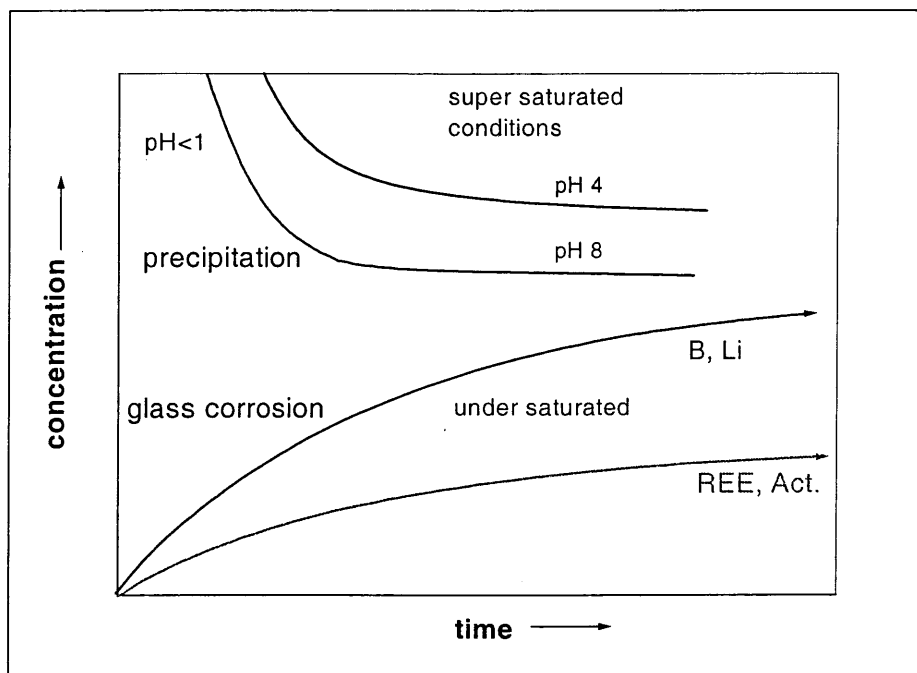
WP1-4-3: Glass dissolution in NaOH, acid MgCl₂-rich solution and in HCl under more reducing conditions (Argon)

WP1-4-4: Analyses of the precipitates

WP1-5: Preparation of acid solutions containing the glass frit components, fission products, Th and U in soluble form (Chlorides, Na₂SiO₃, B(OH)₃). Adjustment of pH to 2.5-10; Characterisation of the products obtained.

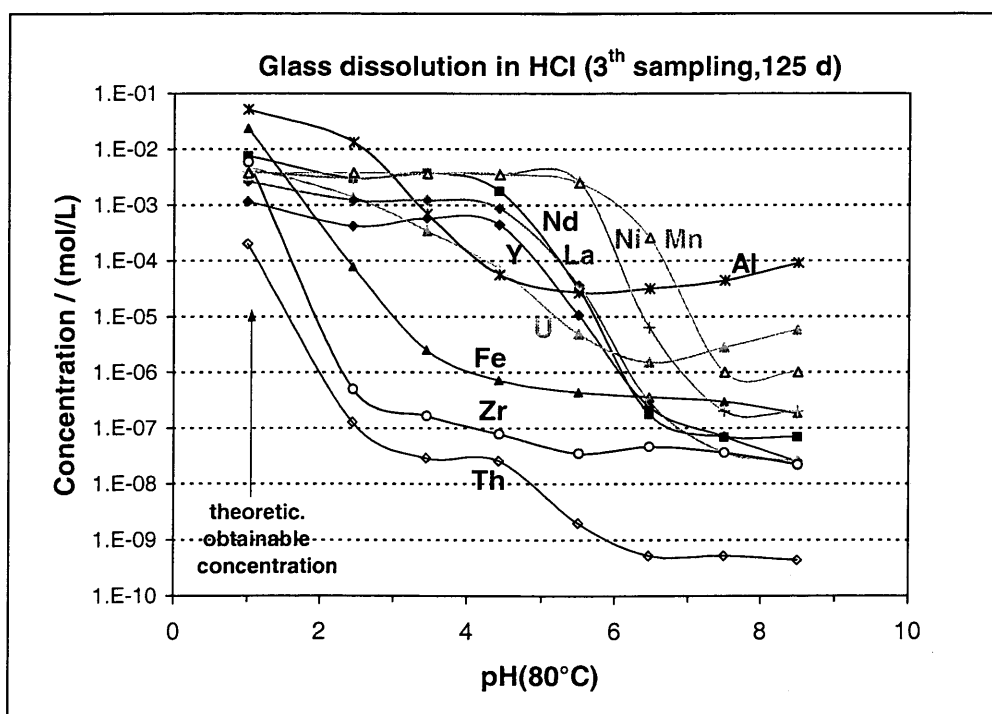
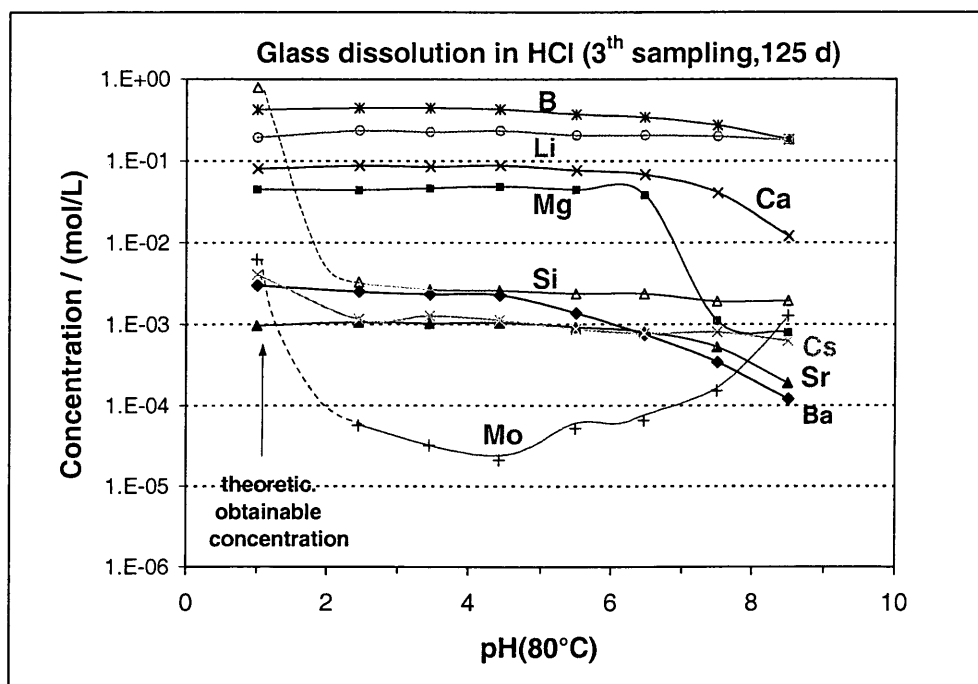
WP1-5-1: Preparation of acid solutions containing the elements in soluble form

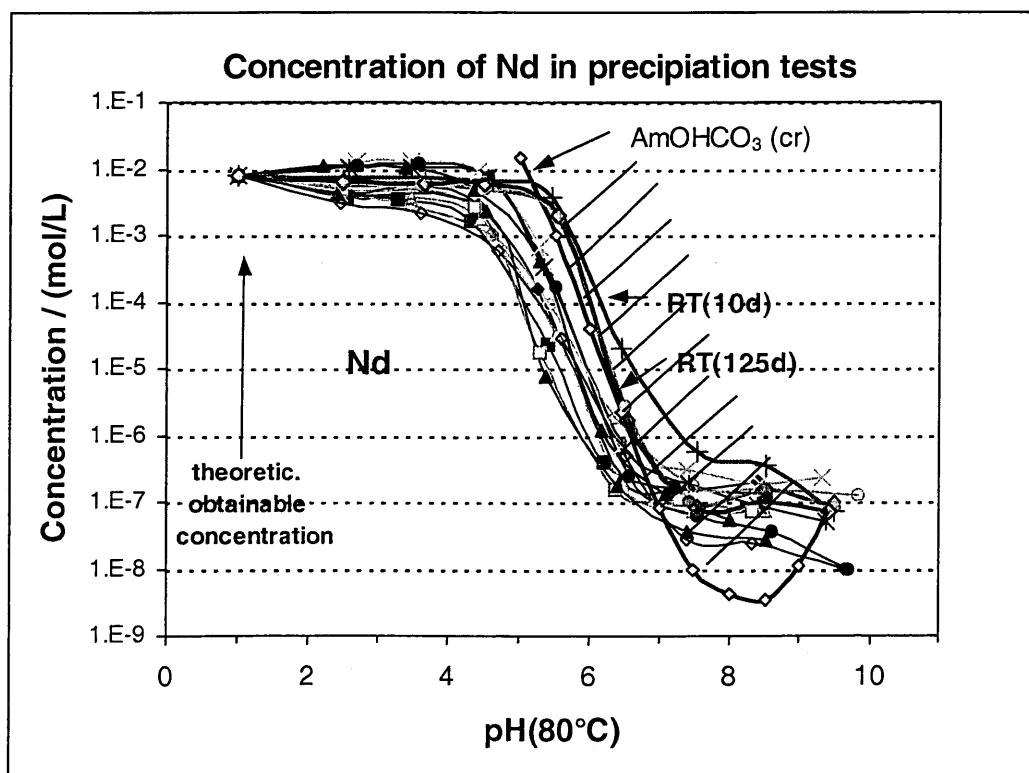
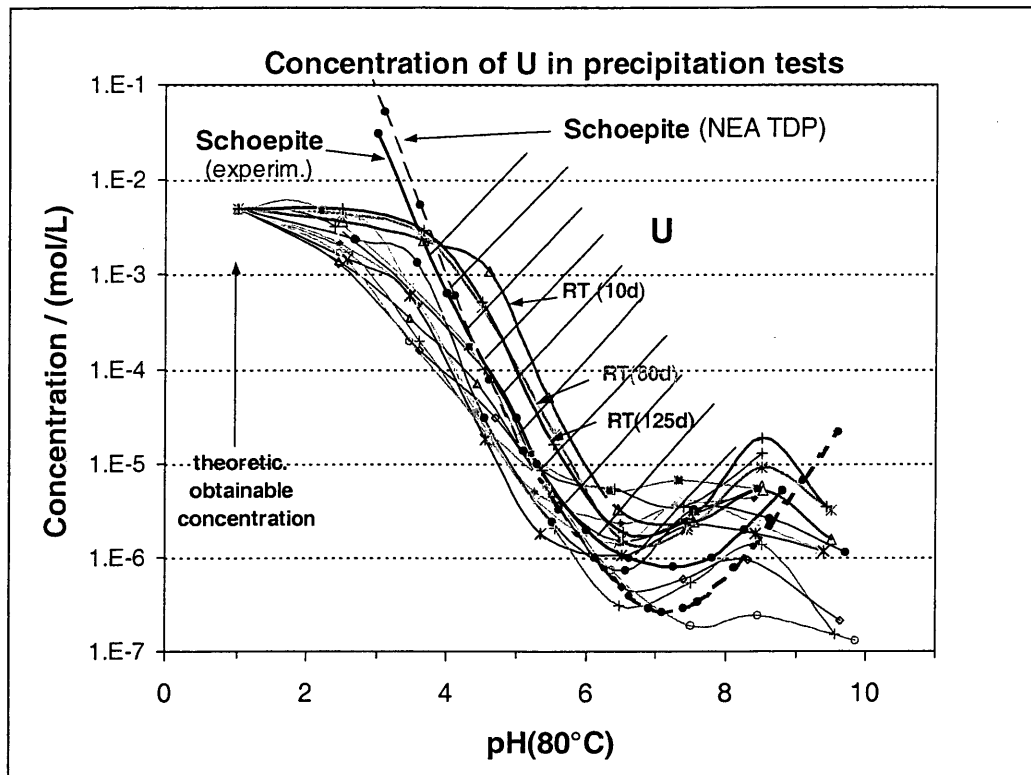
WP1-5-2: Analyses of the precipitates

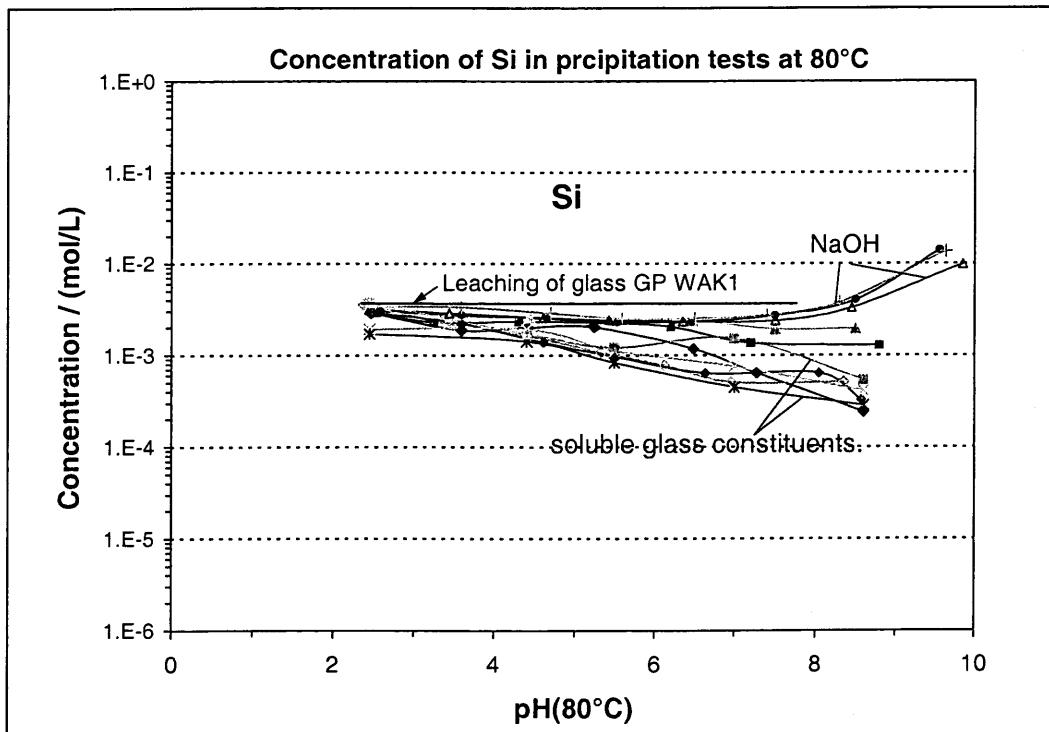
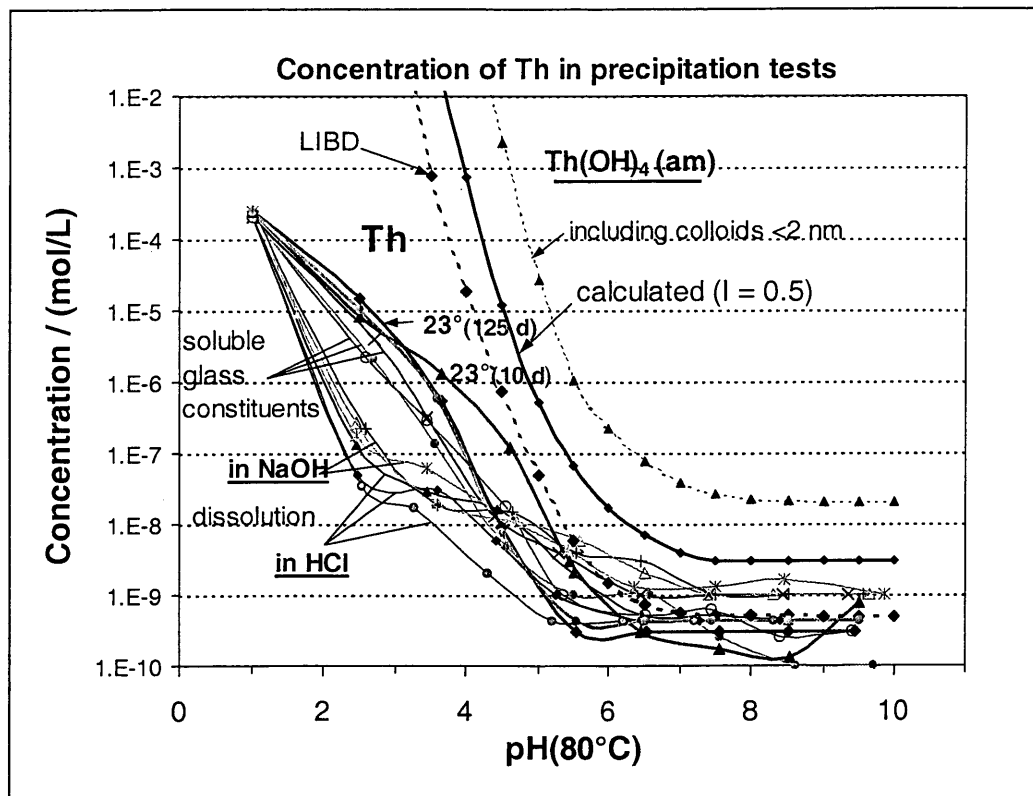


Glass dissolution tests:

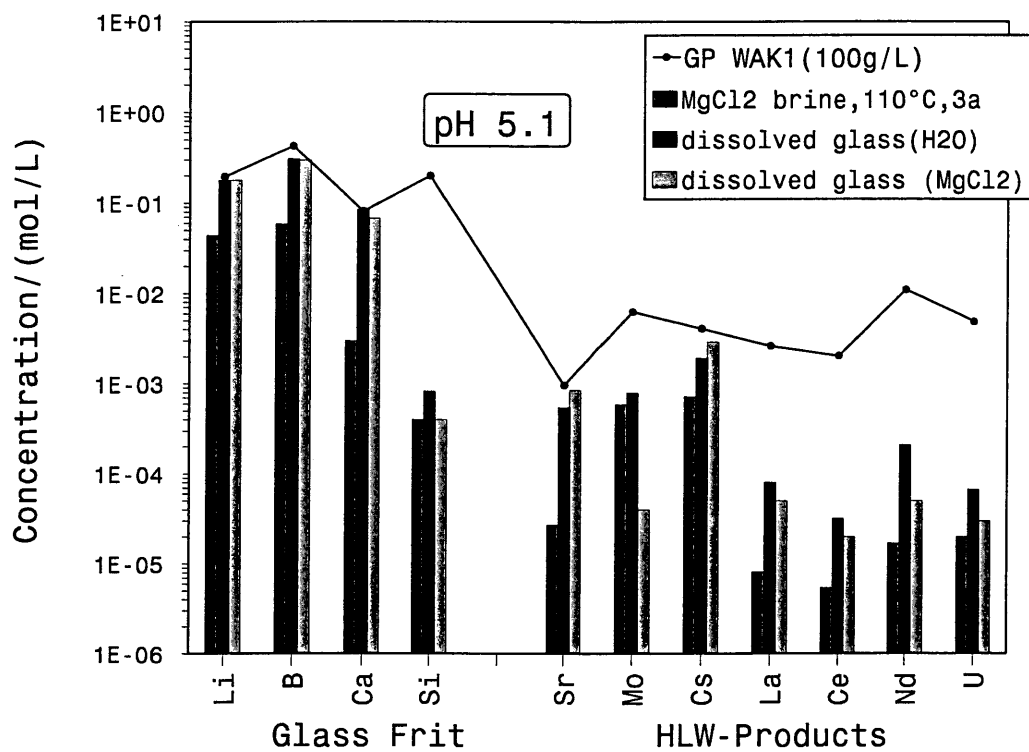
- Dissolution temperature: 80°C
- high S/V-ratio: $\geq 10000 \text{ m}^{-1}$
- Dissolution time: 30 days
- Glass sample: 5 g glass powder (<100 μm)
- Solution volume: 50 ml
- **Media:** 0.5 M HCl (pH <1), 2 M NaOH (pH~ 12.5), acid 2M MgCl_2 (pH~ 0.5)
- pH values: between 2.5 and 10
- Sampling time: after about 10, 60 and 120-150 days



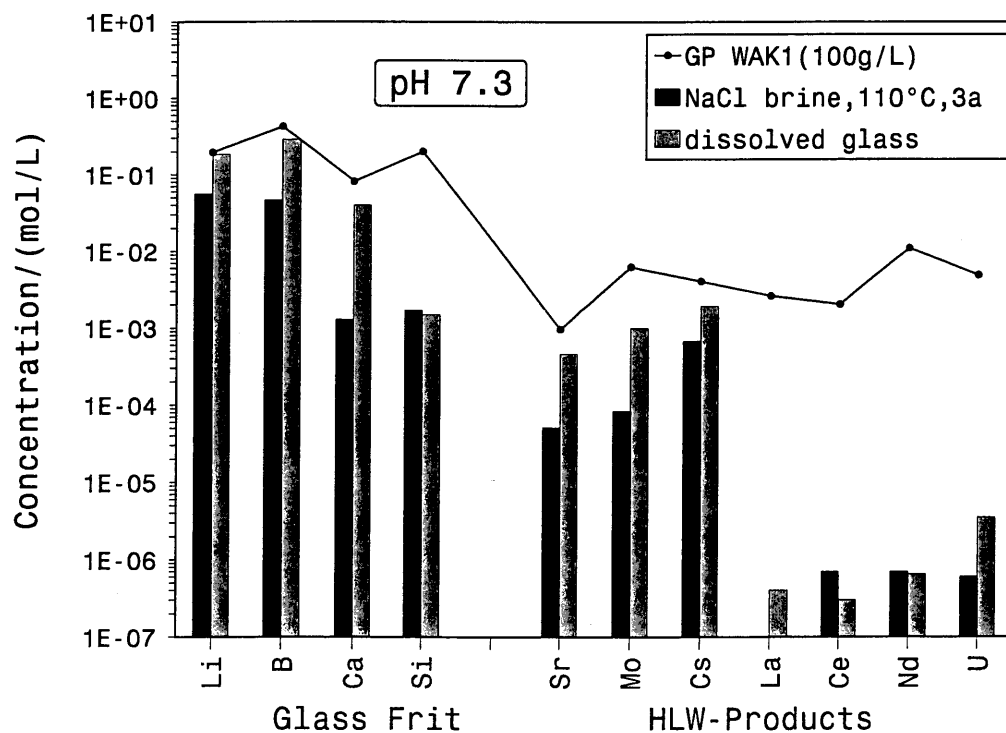




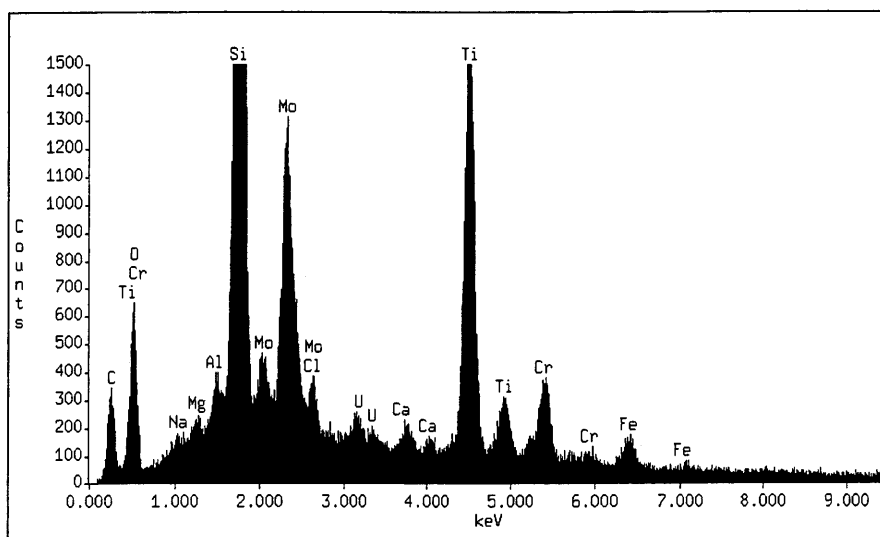
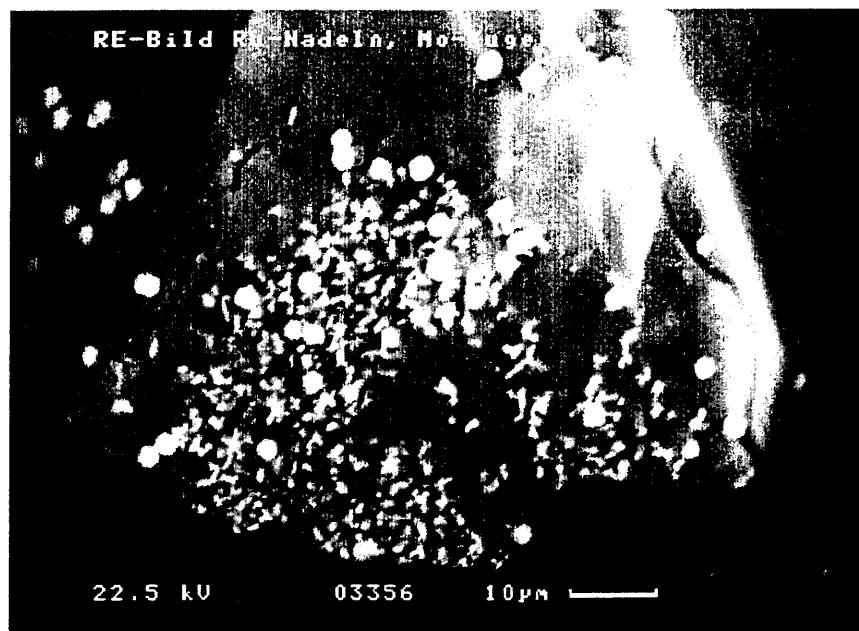
Concentration of elements in precipitation and corrosion tests



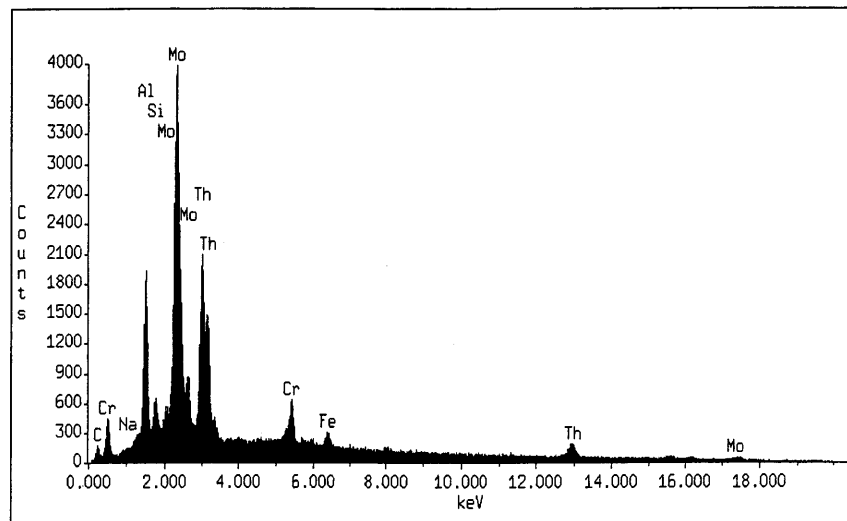
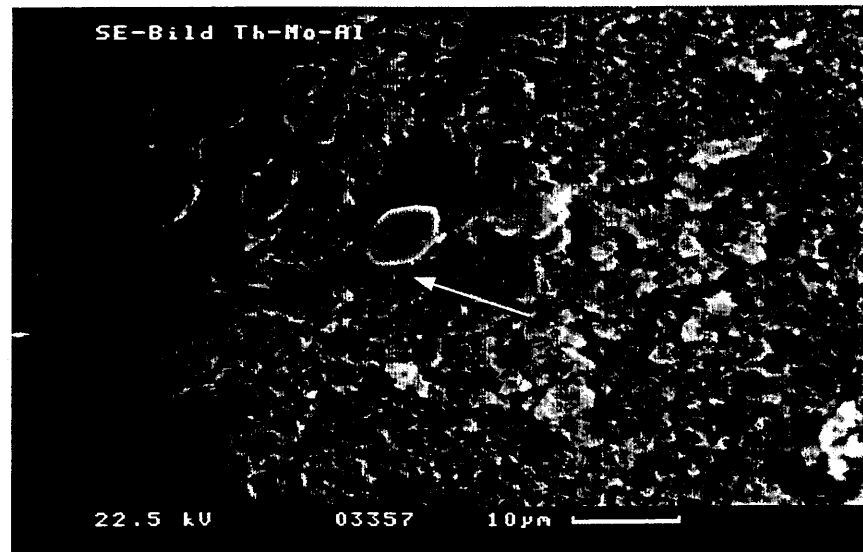
Concentration of elements in precipitation and corrosion tests



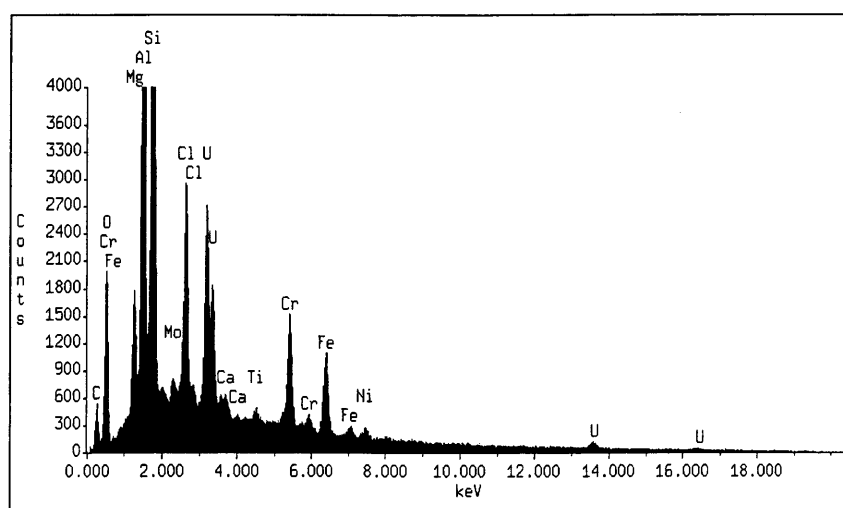
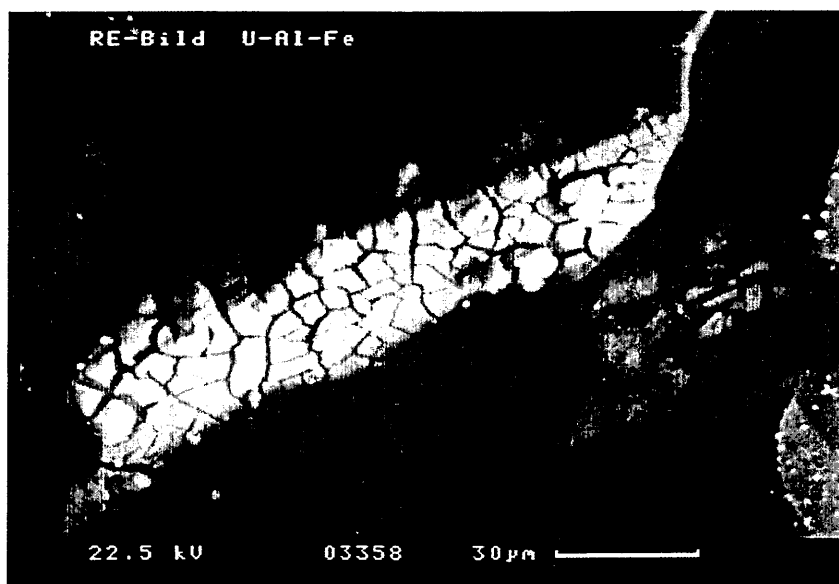
Precipitates in MgCl_2 brine, pH 1.5



Glass dissolution residues in MgCl_2 brine, pH 5.5



Glass dissolution residues in MgCl_2 brine, pH 6.5



Work-package 1:

Task No. 7:

Sorption/coprecipitation behaviour of Am^{241} on the gel layer of precorroded, simulated HLW glass GP WAK1 in water and brines.

WP1-7-1: Sorption experiments: retention factors of Am in water

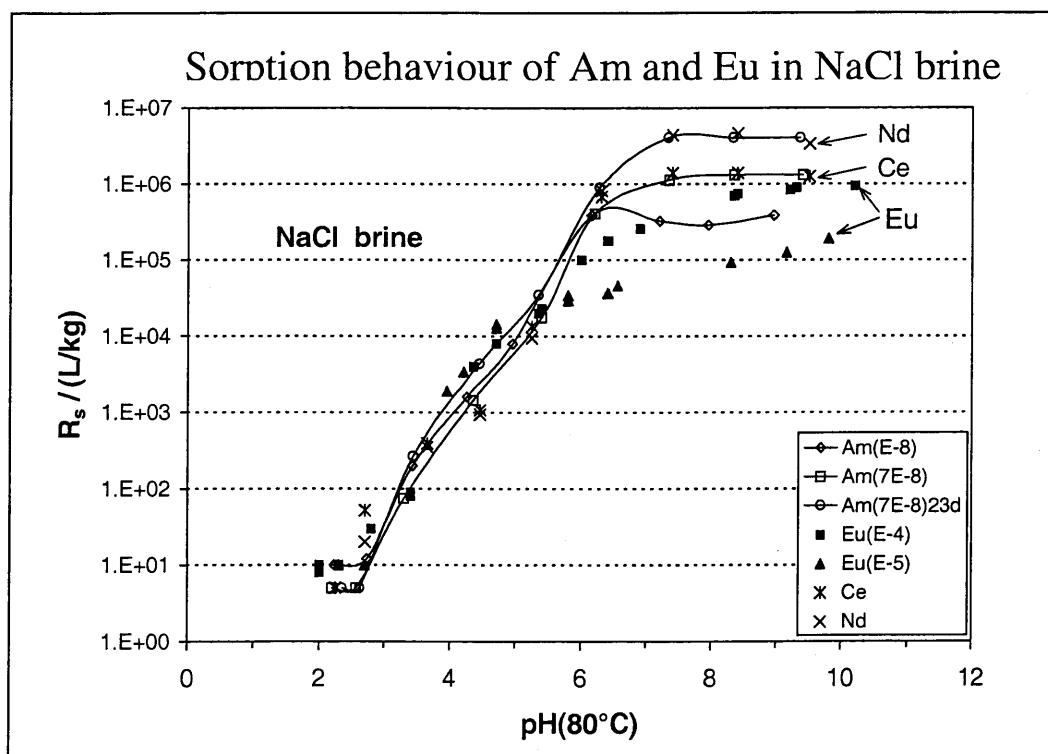
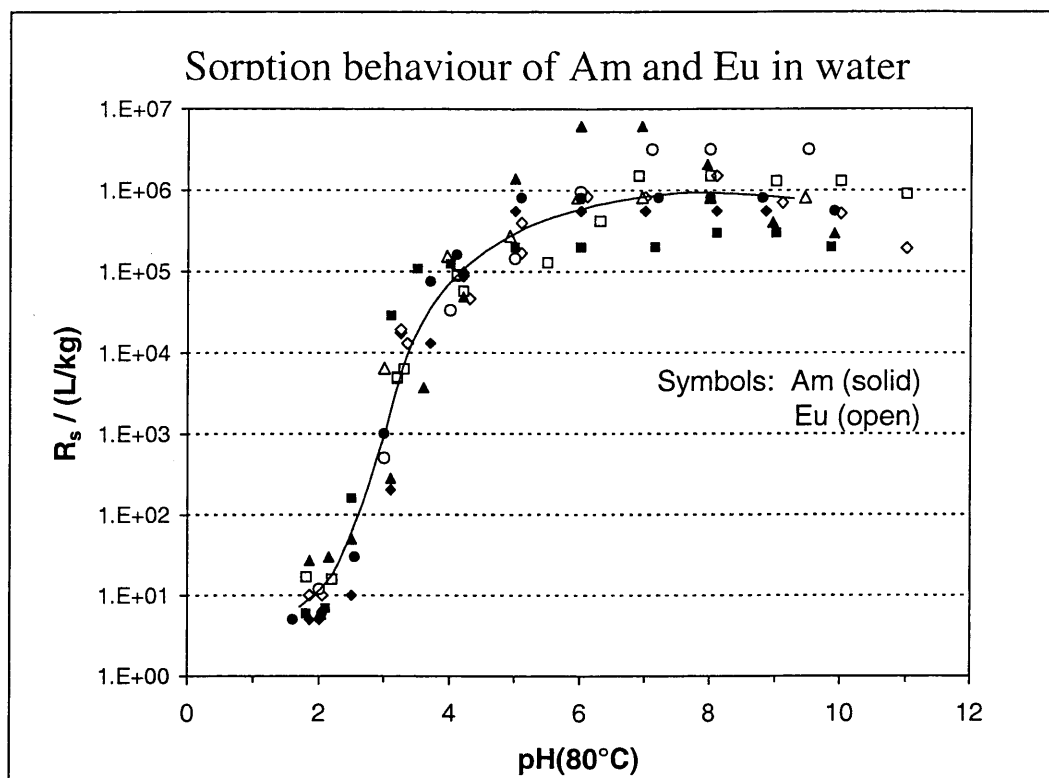
WP1-7-2: Sorption experiments: retention factors of Am in brines

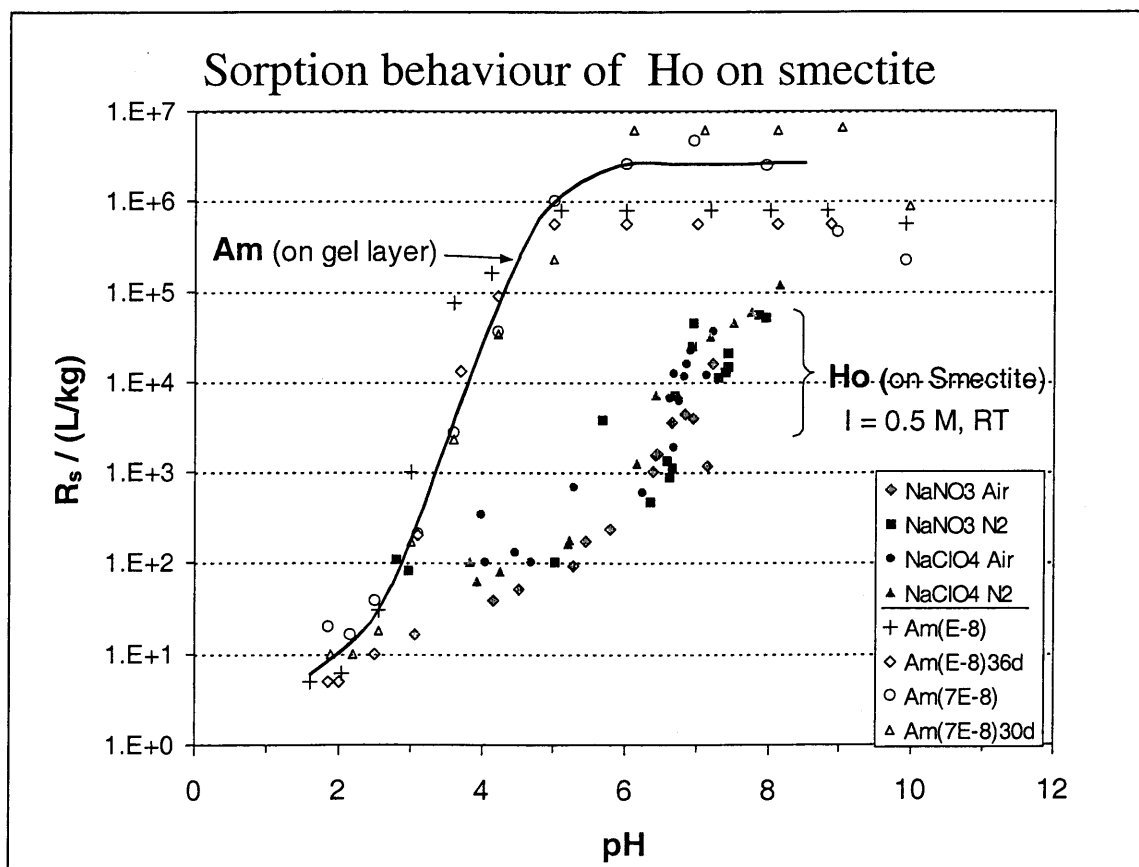
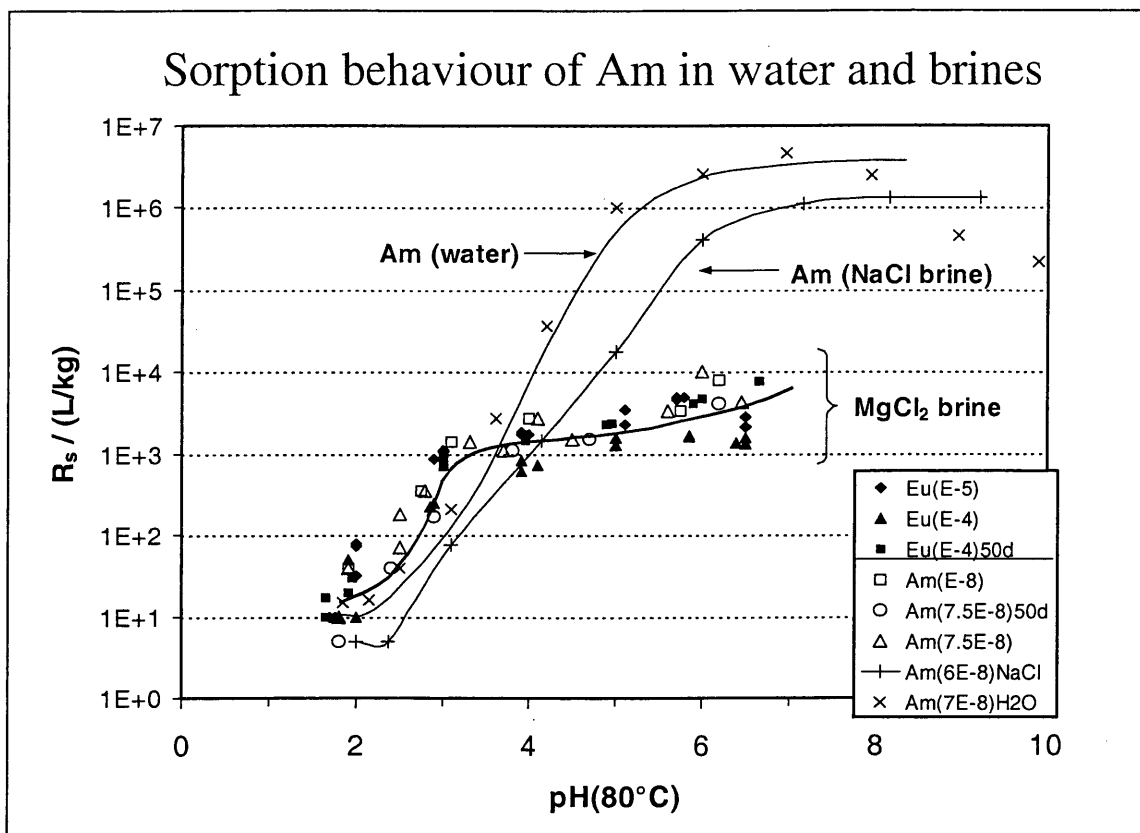
EXPERIMENTAL:

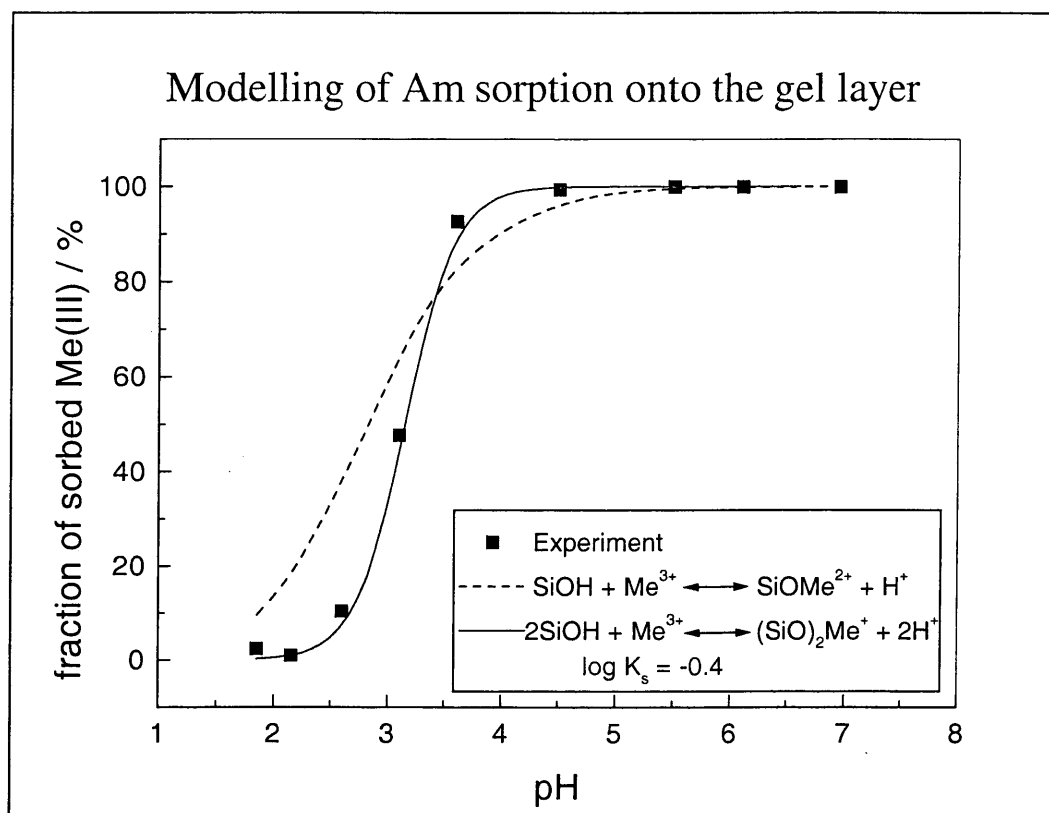
Sorption experiments with Am were performed in a similar way as the experiments from previous EU project with Eu, Th and U:

Precorrosion of glass powder:	40 days in water at 80°C, $S/V = 1000 \text{ m}^{-1}$
pH- values in H_2O and NaCl:	between 2 and 10
in 5 M MgCl_2 :	" 1.5 and 7
Concentration of Am^{241} :	10^{-9} and 10^{-7} mol/L
Solution sampling:	after 10 days (30 days)
Analysis of Am^{241} :	γ - spectrometry

$$R_s = \frac{C(\text{Me}_{\text{sorbed}})}{C(\text{Me}_{\text{dissolv.}})} \cdot \frac{V}{m} \quad (\text{L/kg})$$









Purpose of **WP4-7** and **WP4-8**: Study of the leaching behaviour of specific waste components

- **Objective:** determination of the RN solubility which is a critical parameter for PA
 - Near-field versus Far-field
 - Leach tests with doped glass in near-field conditions
 - To simulate the near-field conditions, as backfill materials
 - FoCa-clay + pyrite + metallic Fe (WP4-7)
 - Boom Clay + backfill mixture + Fe_3O_4 (WP4-8)

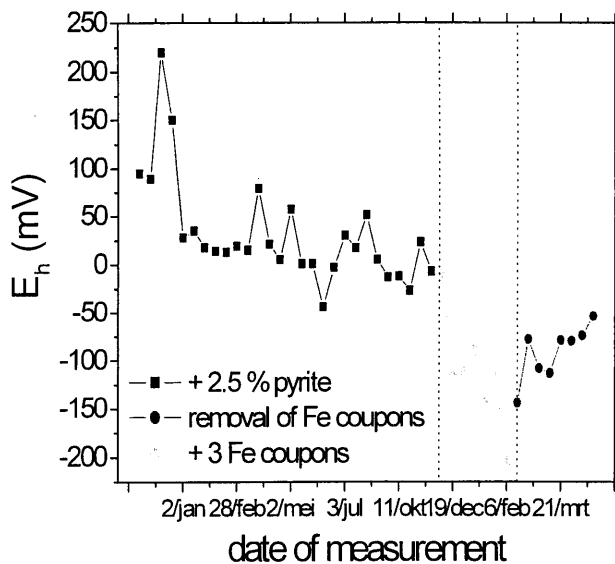
RN: radionuclide



WP4-7: Leach tests with SON68 glass doped with ^{237}Np and ^{99}Tc in FoCa-clay (under reducing conditions)

- **Objective:** Determination of the steady-state [Np] and [Tc] in the near-field under reducing conditions
 - To compare with the previous programme (importance of E_h on [Np] and [Tc] in FoCa-clay)
- **Experimental programme**
 - static tests at 40°C with SON68 glass (0.34% Np / 0.12% Tc)
 - $S/V = 50 \text{ m}^{-1}$
 - 1000 g FoCa/ liter real clay water
- **Interpretation**
 - [Np] and [Tc] in the leachates after ultrafiltration (100,000 MWCO)
 - Activity of Np and Tc sorbed or precipitated on clay

WP4-7: how to obtain reducing conditions?



- Addition of $\neq$ percentages of FeS_2

➤ Not efficient (oxidation)

- Addition of Fe coupons

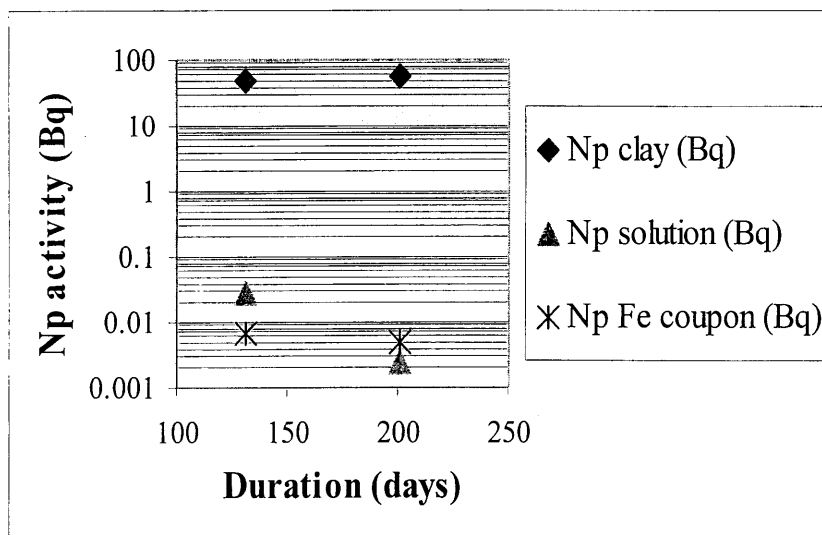
➤ Decrease of E_h

➤ Removal of Fe $\longrightarrow E_h \nearrow$



Fe coupon in every test container
(vertically and parallel to the glass plate)

WP4-7: Np activity (Bq) in the clay water, sorbed on the Fe coupon and clay



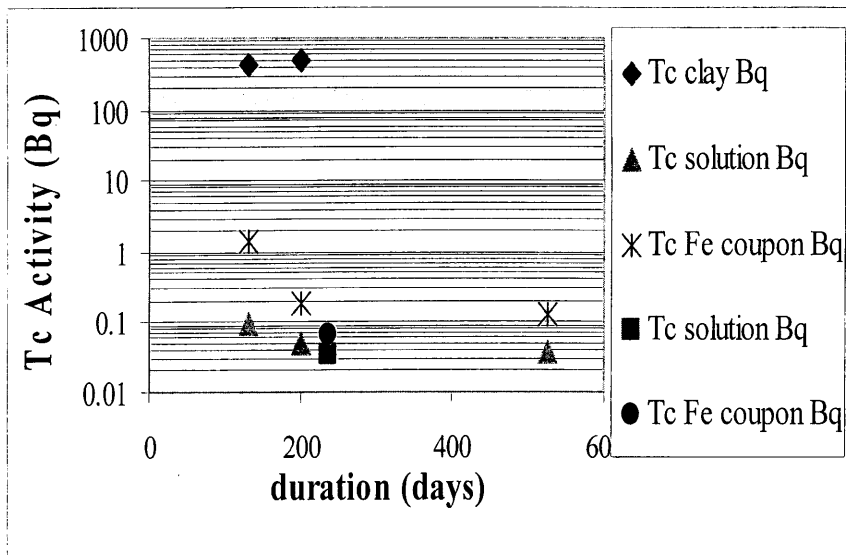
- Weight % Np
 - Theory: 0.34%
 - Measured: 0.33%

(dissolution of the glass using $\text{HNO}_3 + \text{HCl}$)

➡ Most of Np activity (99.95%) found on the clay



WP4-7: Tc activity (Bq) in the clay water, sorbed on the Fe coupon and clay



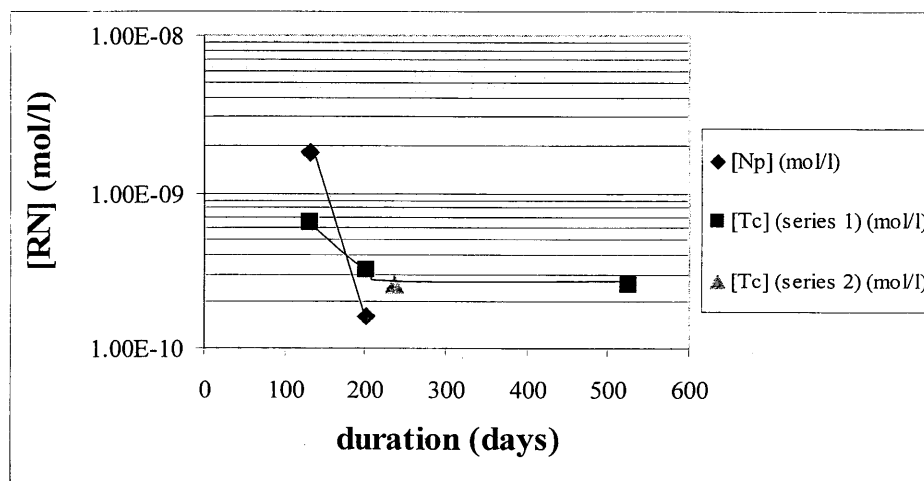
- Weight % Tc
 - Theory: 0.048%
 - Measured: 0.12%

(Dissolution of the glass using $\text{HNO}_3 + \text{HCl}$)

➡ Most of Tc activity (99.5%) found on the clay



WP4-7: [Np] and [Tc] in the leachates after ultrafiltration



[Np] and [Tc] in the clay water very low (lower than the solubility of the expected solid phases: $\text{Np}(\text{OH})_4 = 5 \times 10^{-9} \text{ M}$ and $\text{TcO}(\text{OH})_2 = 10^{-8} \text{ M}$)

$$[\text{Np}] = 1.6 \times 10^{-10} \text{ M} \quad [\text{Tc}] = 2.6 \times 10^{-10} \text{ M}$$



WP4-7: Comparison of the near-field with the far-field concentrations

(mol/l)	[RN] (near-field)	[RN] (far-field) ^a	Solubility limiting solid phase	[RN] best estimate PA	[RN] PSI ^b calculations
Np-237	1.6x10 ⁻¹⁰	6.7x10 ⁻¹⁰	Np(OH) ₄	10 ⁻⁶	5.4x10 ⁻⁹
Tc-99	2.6x10 ⁻¹⁰	10 ⁻⁸	TcO(OH) ₂	3x10 ⁻⁸	4.4x10 ⁻⁹

^A Migration data (SCK)

^B PSI: "Project Opalinus clay: [RN] limits in the near-field of a repository for spent fuel and vitrified HLW (report dec 2002)



WP4-7: Conclusion of these tests

- Comparison with the results of the previous programme

	FoCa-clay (ox. Cond.)	FoCa-clay + Fe coupon (reducing cond.)
[Np] (mol/l)	10 ⁻⁸ M	1.6x10 ⁻¹⁰ M
[Tc] (mol/l)	10 ⁻⁶ M	3.25x10 ⁻¹⁰ M

- State of progress: series 1: 365, 720d, series 2: 90 to 720d
- The redox potential is the main parameter affecting [Np] and [Tc].
 - Fe coupons induce very low Np and Tc concentrations
- Most of Np and Tc are found precipitated on the clay.



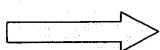
WP4-8: Leach tests with SON68 glass doped with Zr, Pd, Se, Sn in a backfill mixture

- **Objective:** Determination of the mobile steady-state concentrations of Zr, Pd, Se, Sn in near-field conditions
 - No attention given in previous programme
- **Experimental programme**
 - Static tests at 40°C with SON68 glass (inactive Zr, Pd, Se, Sn)
 - $S/V = 2500 \text{ m}^{-1}$
 - Medium: Int-RIC (1500 g of Boom Clay + FoCa-clay + sand + graphite + Fe_3O_4 + stainless steel / liter real clay water)
- **Interpretation**
 - Concentrations of Zr, Pd, Se, Sn in the leachates after ultrafiltration over 100,000 and 10,000 MWCO



WP4-8: Why inactive isotopes?

	LSC	γ -spectrometry	ICP-MS	remarks
1) Isotopes of interest				
Zr-93	Not possible	Difficult	OK	
Se-79	Could be possible	Not possible	OK	
Pd-107	Not possible	Not possible	OK	
Sn-126	Not possible	difficult	OK	
2) alternatives				
Zr-95				$T_{1/2} = 64 \text{ d}$
Se-75		Possible		$T_{1/2} = 120 \text{ d}$
Sn-113		possible		



Use of inactive isotopes measured by ICP-MS

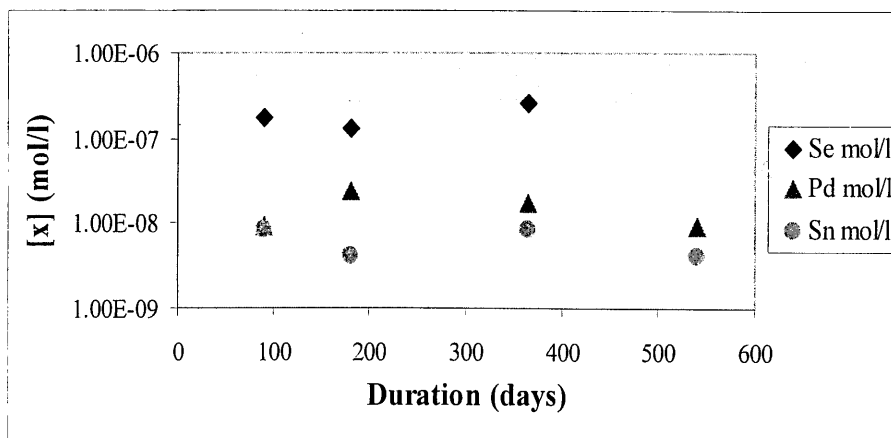
WP4-8: Weight percentages of the elements in the SON68 glass

	% in the active glass	% in SON68 as received	% in SON68 as doped	% in SON68 measured
Zr	1.7 (+0.54% inactive)	2.65	2.65	1.96
Sn	0.02	0.02	0.02	0.016
Se	0.03	trace	0.038	0.02
Pd	0.33	trace	0.35	0.033

Smaller % values compared to theoretical ones, especially for Pd
(Pd not homogeneously incorporated, precipitation?)

WP4-8: Concentrations of Sn, Se and Pd in the leachates

- No difference in concentration after ultrafiltration through 10,000 or 100,000 MWCO



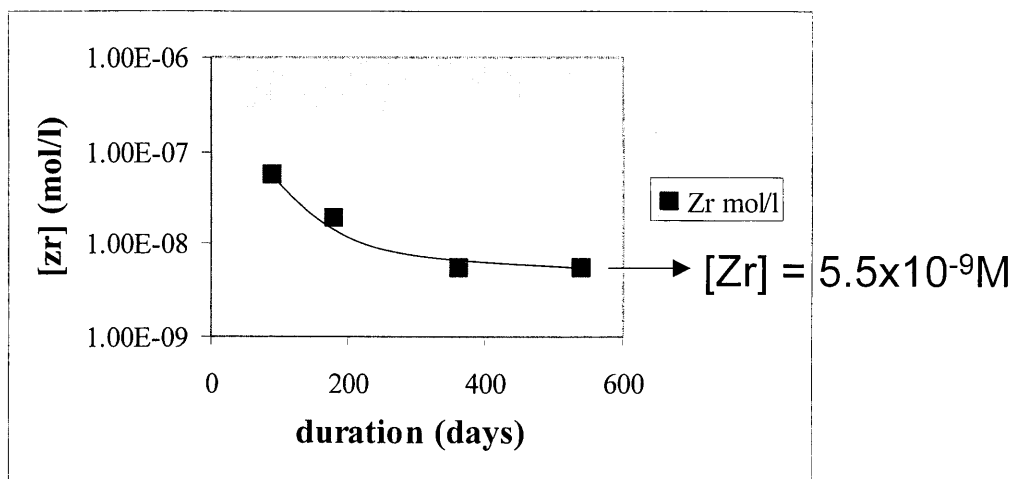
$[Se] = 2.5 \times 10^{-7} M$

$[Pd] = 9.4 \times 10^{-9} M$

$[Sn] = 4.2 \times 10^{-9} M$

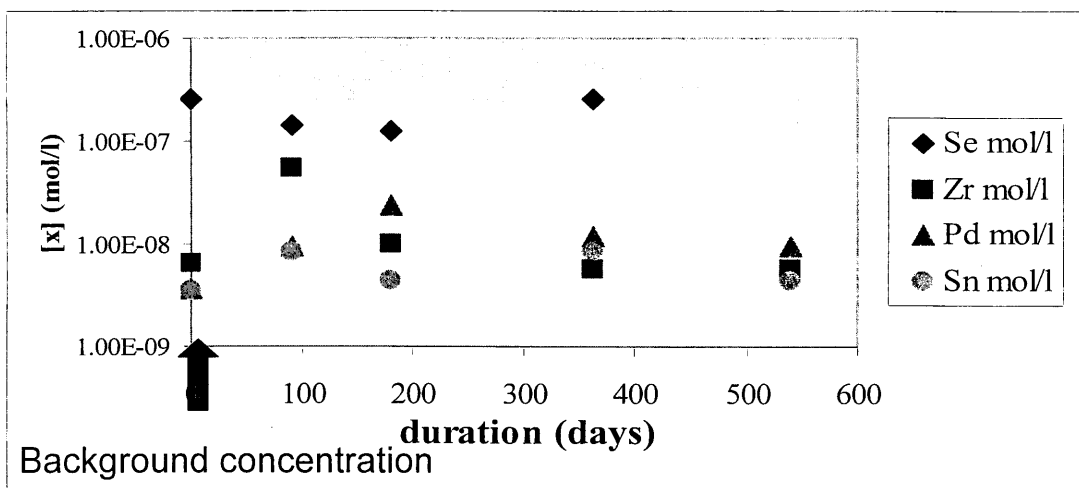
- $[Se]$, $[Pd]$, $[Sn]$ are stable with time

WP4-8: Concentrations of Zr in the leachates



- [Zr] decreases as a function of time (steady-state after 365 days)
 - Formation of Zr colloids!?

WP4-8: Comparison of [Zr], [Sn], [Se], [Pd] in the leachates with the background concentration (starting medium)



- [Se], [Sn], [Pd] are not higher than their background concentration
- [Zr] first increases and then decreases to come back to its background concentration
- [Se] relatively high (would expect SeO_4^{2-} to be present)



WP4-8: Comparison of the near-field with far-field concentrations

Element	[RN] (near-field)	[RN] (far-field) ^a	Solubility limiting solid phase	[RN] best estimate PA	[RN] PSI ^b calculations (near-field)
Se	2.5×10^{-7}	5×10^{-9} (2.4×10^{-8} in the Boom clay water)	Se (cr)	5.5×10^{-8}	5.3×10^{-9}
Zr	5.5×10^{-9}		ZrO ₂ , ZrSiO ₄	6×10^{-7}	2.2×10^{-9}
Pd	9.4×10^{-9}	2×10^{-8}	Pd(OH) ₂ , Pd	10^{-7}	Very low
Sn	4.2×10^{-9}		SnO ₂ , Sn(OH) ₄	3×10^{-5}	1.2×10^{-8}

^A Migration data SCK

^B PSI: "Project Opalinus clay: [RN] limits in the near-field of a repository for spent fuel and vitrified HLW (report dec 2002)



WP4-8: Conclusions of these tests

- State of progress: Last tests (720 days) finished, waiting for the results
- [Zr], [Pd] and [Sn] are very low and have reached a steady-state concentration in the near-field

Zr	$5.5 \times 10^{-9} \text{M}$
Pd	$9.4 \times 10^{-9} \text{M}$
Sn	$4.2 \times 10^{-9} \text{M}$

- [Se] are quite high ([Se] = $2.5 \times 10^{-7} \text{M}$) (probably selenate)
- The dissolution of the glass does not increase the overall concentrations of these elements (not higher than their background concentrations).

GLASTAB Meeting, 29/30 October 2003

PA exercise

- **Sensitivity analysis on glass dissolution rate**
- **Barrier function of gel**

Bernhard Schwyn (Nagra)

Gerhard Mayer (Colenco)

Enzo Curti (PSI)

Jürg Schneider (Nagra)

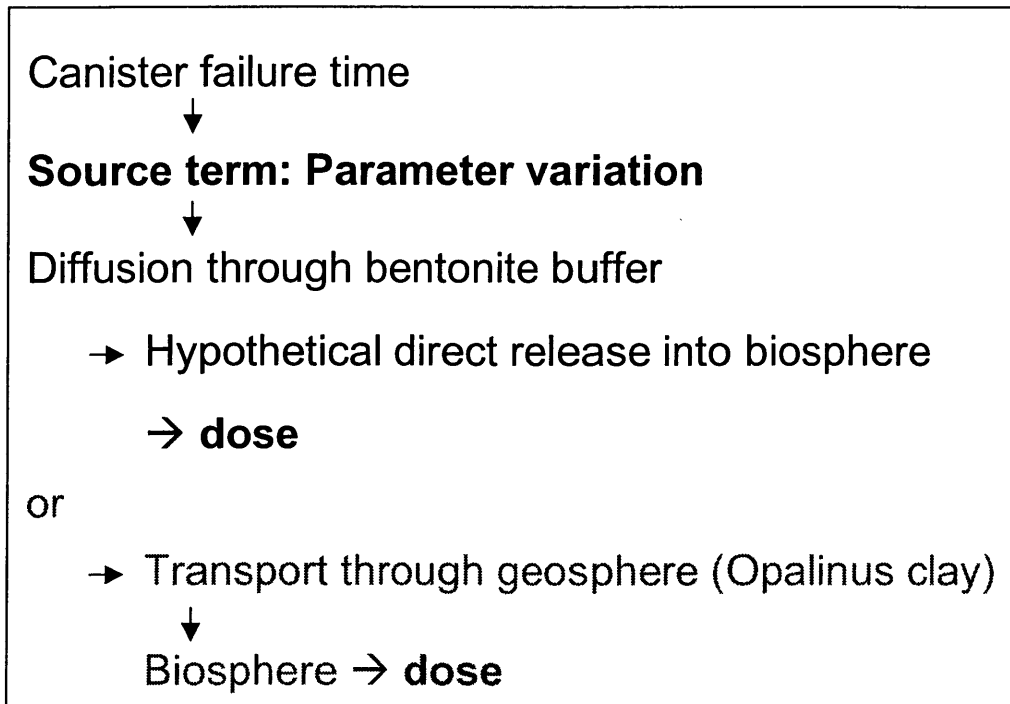


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PA calculations

- Model chain:



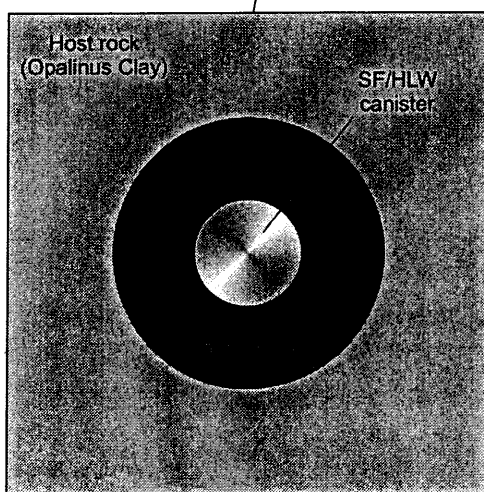
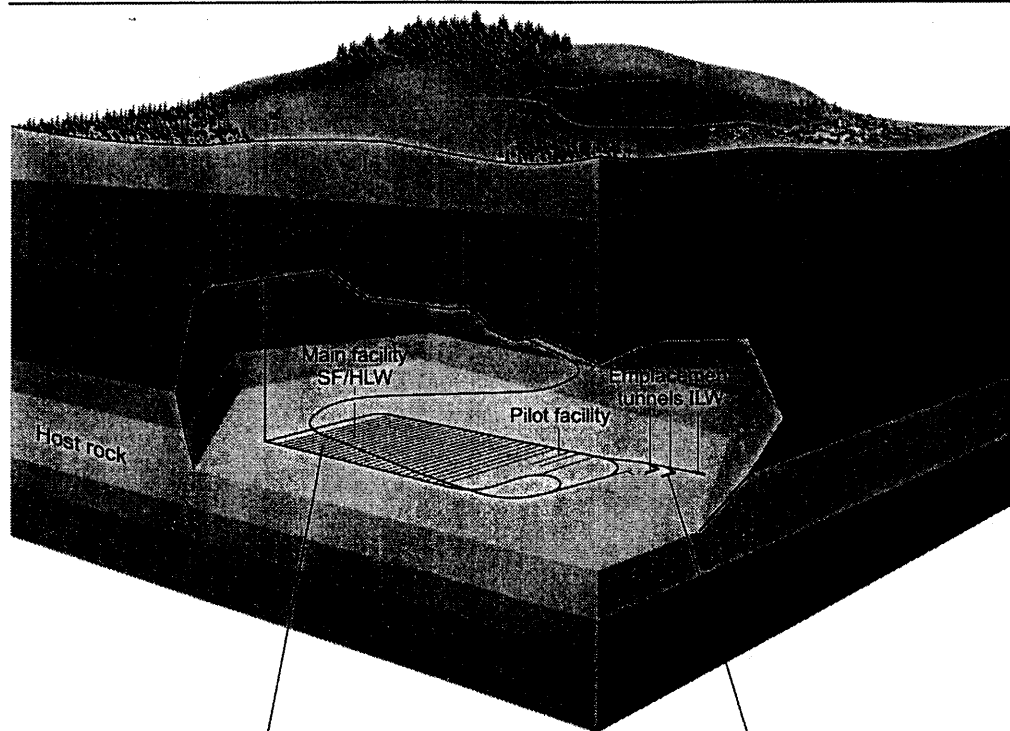
- Sensitivity analysis on
 - Glass dissolution rate → relative barrier efficiency
 - Glass surface area: particle form and size distribution
- Retention in glass corrosion products (gel)
 - Radionuclide solubility in the gel (Precipitations, solid solutions)
 - Radionuclide sorption on gel



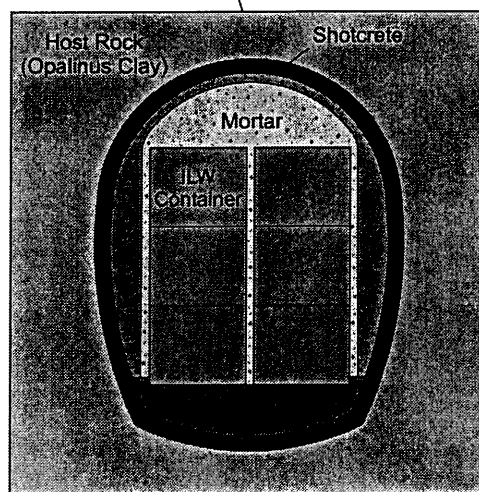
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Possible layout for a deep geological repository for SF / HLW / ILW in Opalinus Clay



Emplacement tunnel SF/HLW



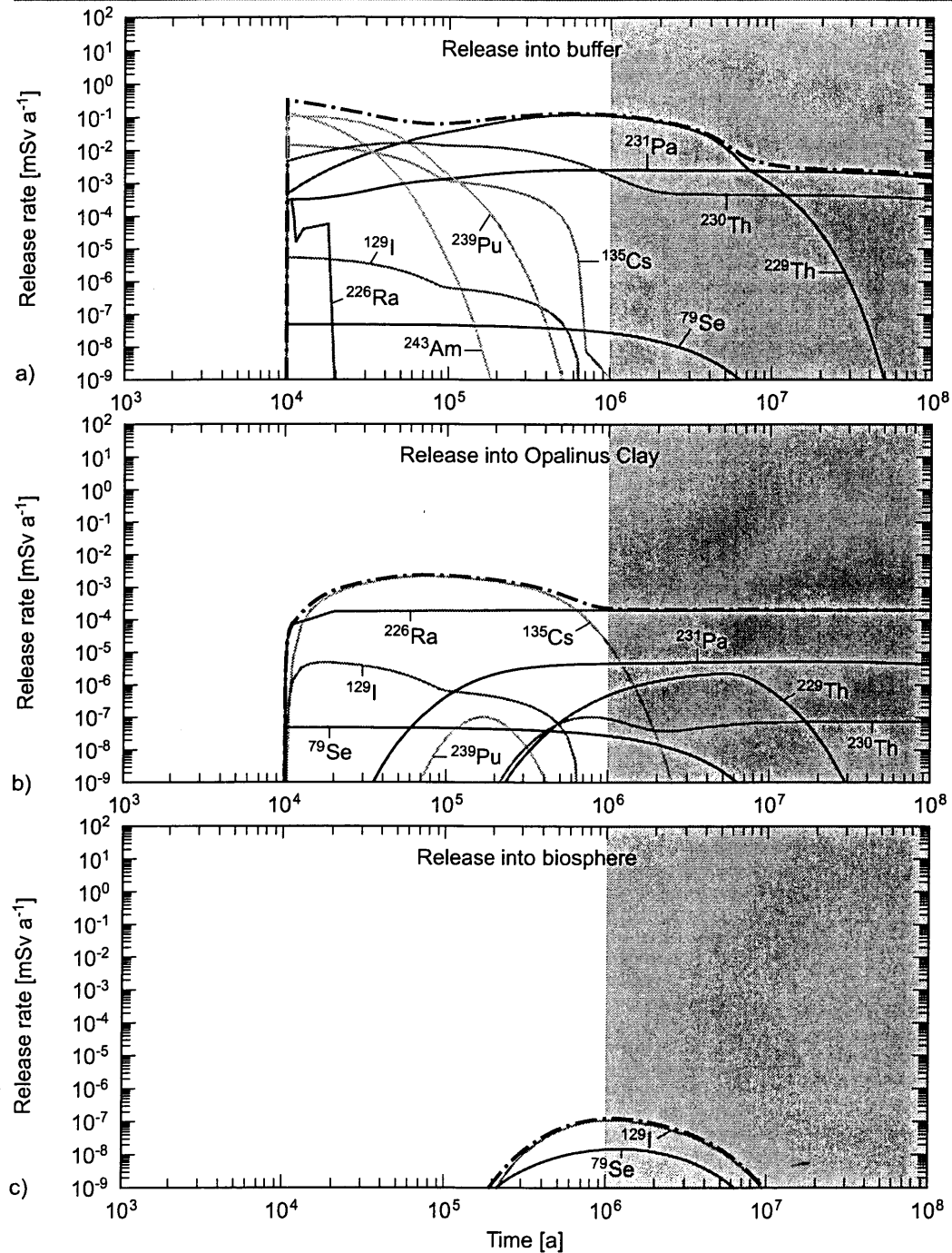
Emplacement Tunnel ILW



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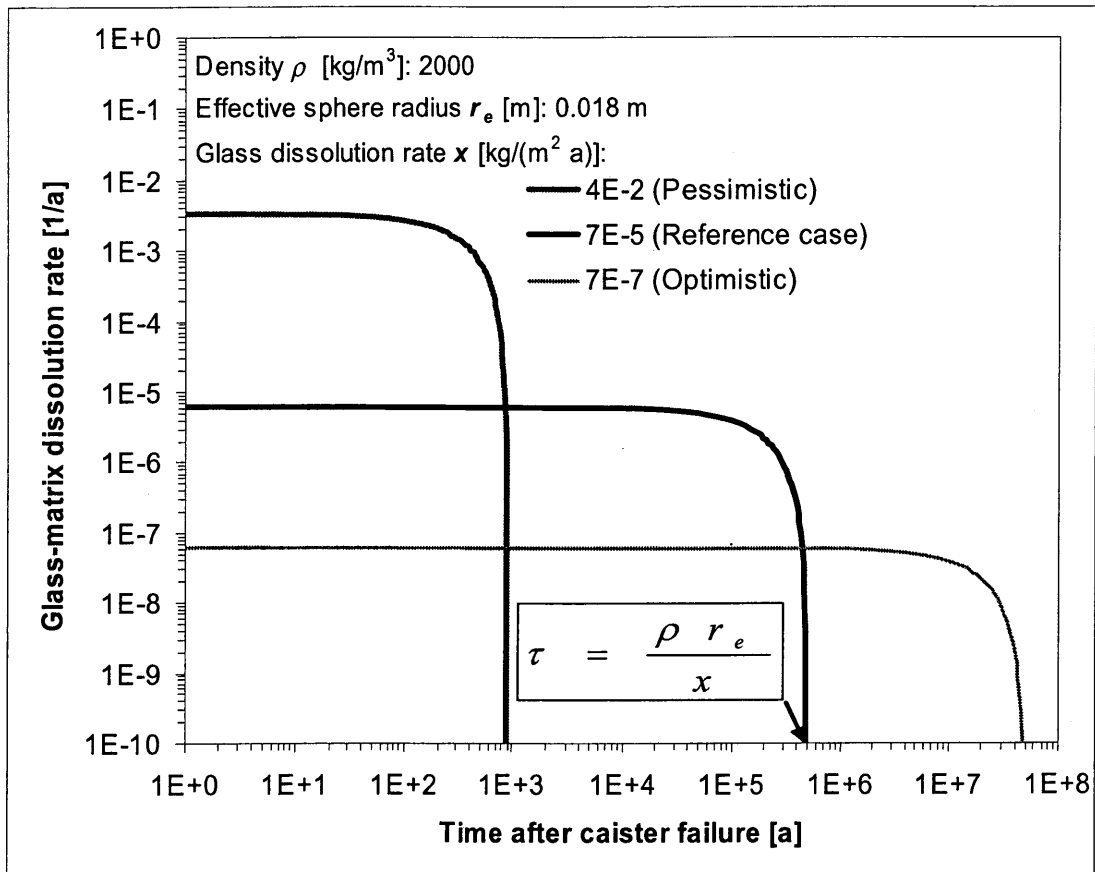
Releases of radionuclides from vitrified waste: Reference case (ca. 700 canisters)



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Glass matrix dissolution rate as a function of time after canister failure.



τ denotes the time of complete dissolution

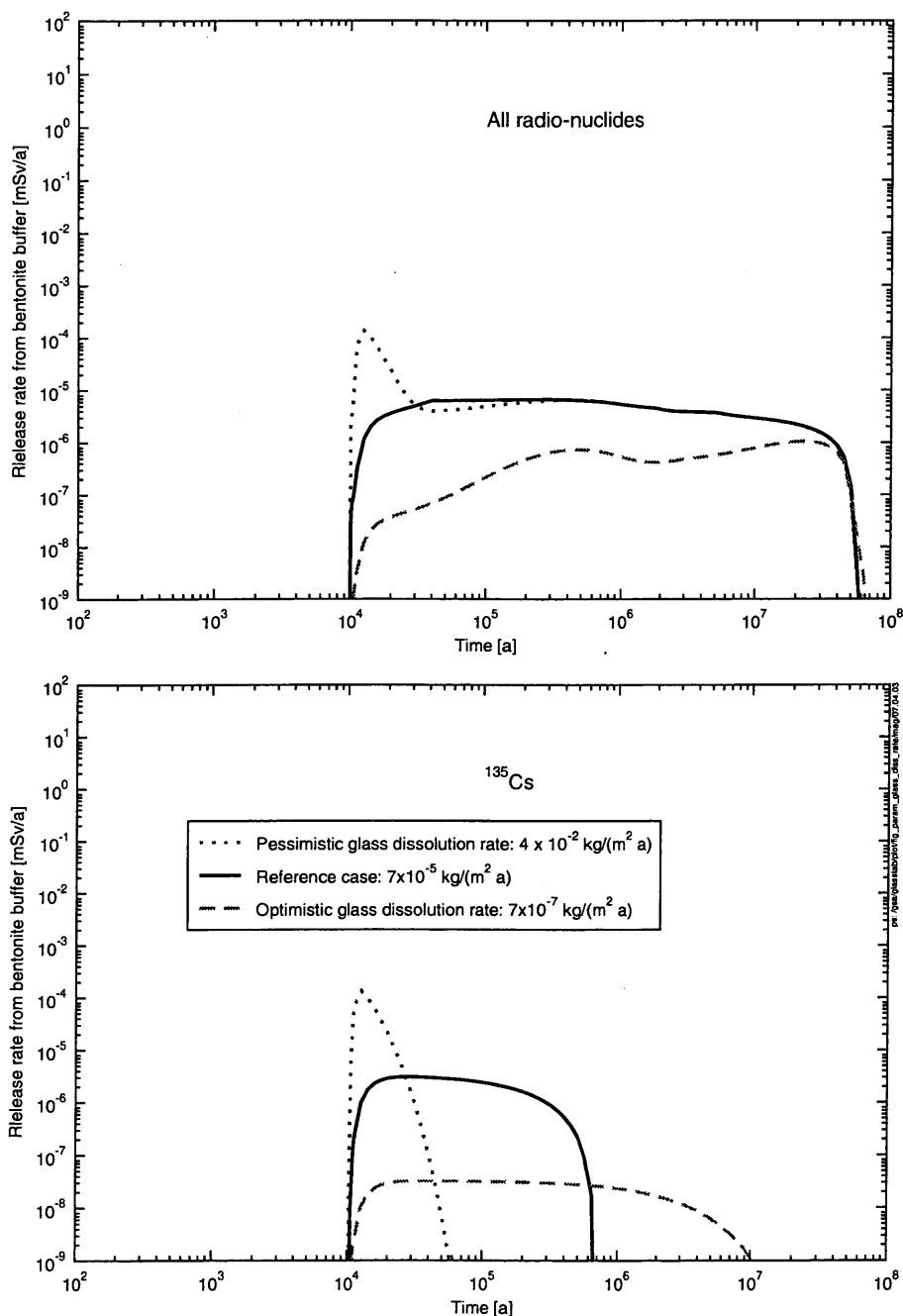
Factor of glass surface area increase due to fracturing: 15



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Release rate from bentonite buffer as function of glass dissolution rate (1 canister)



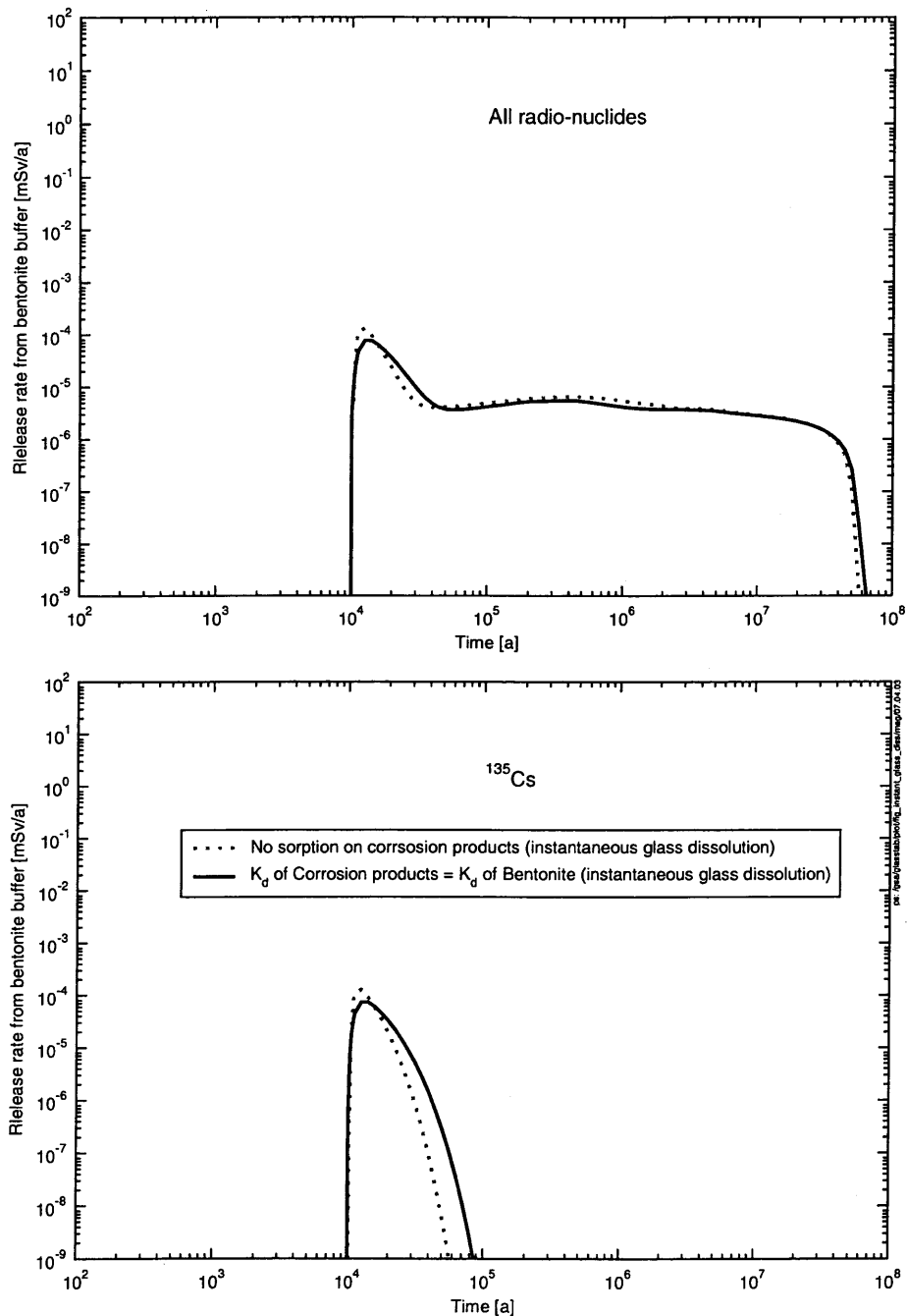
Release rate from bentonite buffer scaled with BDCFs (Biosphere Dose Conversion Factors) of OPA reference case



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Release rate from bentonite buffer, instant glass dissolution assumed (1 canister)



Release rate from bentonite buffer scaled with BDCFs of OPA reference case



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Evaluation of PSI glass dissolution experiment SON-68 glass

- Evaluation of incongruent release of elements (Li assumed to be congruently released)
- Results interpreted as:
 - Solubility limits
 - or
 - Sorption ($\rightarrow K_d$ values)

Element	SON-68 glass			Bentonite	
	f_e mol/g glass	dissolved aver.calc. [mol/l] 12 y	K_d [m ³ /kg] 12 y	Solubility [mol/l]	K_d [m ³ /kg]
Cs	1.0E-04	3.2E-05	4	high	0.1
Mo	1.3E-04	1.6E-04	0.6	1.0E-06	0
Ni	9.9E-05	1.4E-06	100	3.0E-05	0.2
Sr	3.2E-05	4.5E-07	90	2.0E-05	0.003
Zr	2.2E-04	4.2E-07	700	2.0E-09	80
La	5.5E-05	1.3E-07	600		
Ce	5.7E-05	1.5E-07	500		
Pr	2.6E-05	1.2E-07	300		
Nd	9.5E-05	1.5E-07	900		
Sm				5.0E-07	4



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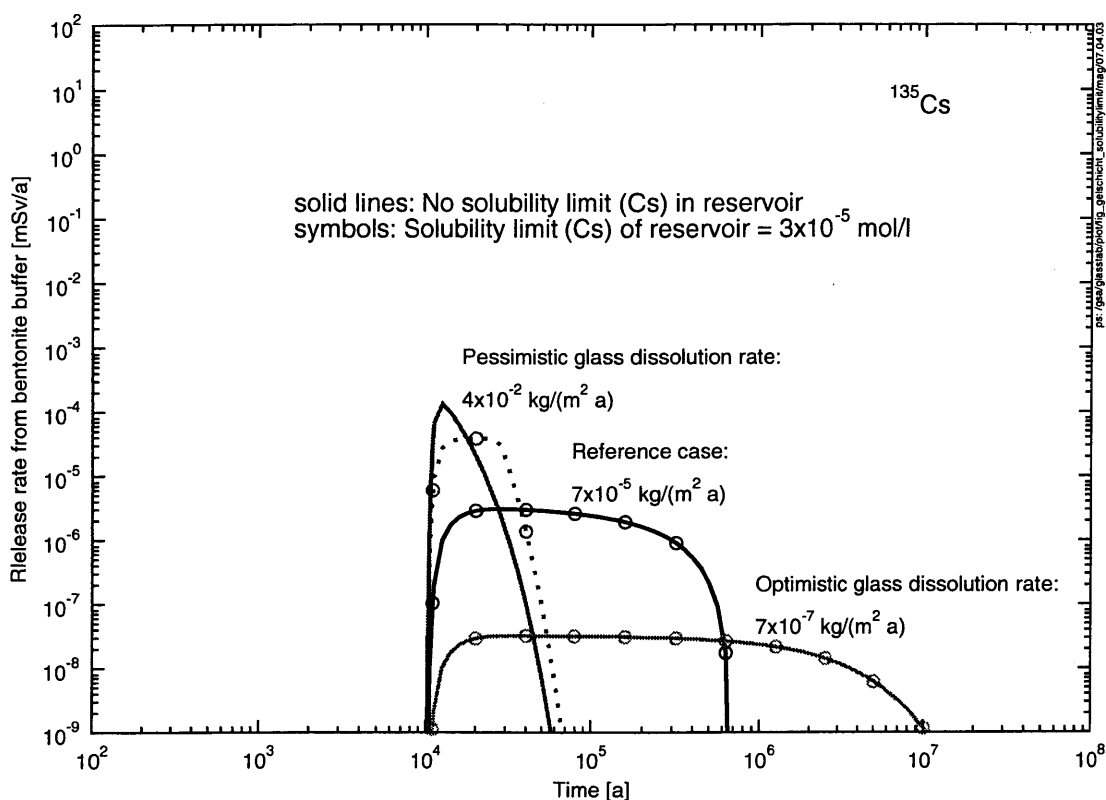
Assumption for the PA calculations

- Cesium concentration in solution assumed to be fixed by a solid or solid solution:
 - Cesium concentration in solution used as solubility limit
 - Shared solubility of Cs isotopes
- Results interpreted as cesium sorption on gel:
 - K_d value of 4 kg m^{-3} calculated from PSI glass dissolution experiments
 - Porosity = 0.27: calculated from the density difference between glass and gel
 - Diffusivity assumed to be high (free water)
 - gel = mixing tank
 - Gel layer of constant thickness: 20 cm (ca. radius of original glass cylinder; no coupling between glass dissolution gel layer growth)



Cs solubility limited in gel:

Release rate of Cs-135 from bentonite buffer as a function of glass dissolution rate (1 canister)



- Release rate of Cs-135 from bentonite buffer scaled with BDCF of OPA reference case

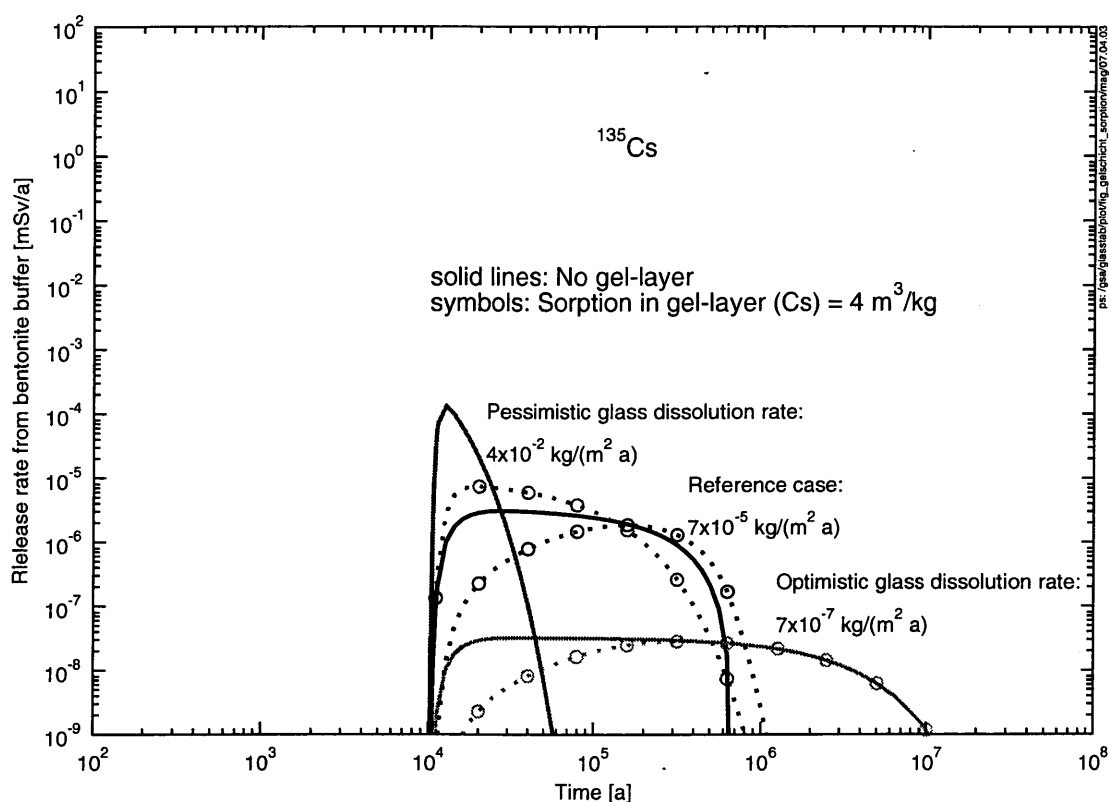


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Sorption of Cs in the gel:

Release rate of Cs-135 from bentonite buffer as a function of glass dissolution rate (1 canister)



- Release rate of Cs-135 from bentonite buffer scaled with BTK of OPA reference case
- The thickness of the gel layer is assumed to be 20 cm.



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Summary

- Sensitivity analysis on glass dissolution rate:
 - Within the near-field barrier system the glass dissolution rate starts to get significant around the Nagra reference value of $7 \cdot 10^{-5} \text{ kg m}^{-2} \text{ a}^{-1}$ (SON-68)
 - Below $7 \cdot 10^{-5} \text{ kg m}^{-2} \text{ a}^{-1}$: insignificant
 - Above $7 \cdot 10^{-5} \text{ kg m}^{-2} \text{ a}^{-1}$: increasing significance
- Retention capability of the gel for cesium:
 - Interpretation of cesium concentration in solution as solubility limit:
 - No additional retention
 - Interpretation of retained cesium as sorbed
 - good retention; sorption on gel compensates for high glass dissolution rates
- Sensitivity analysis on glass surface area (particle form and size distribution): work in progress.



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Long-term kinetics and alteration of two reference borosilicate glasses (MW, SON68) for radioactive waste disposal in Switzerland

GLASTAB WP 1-6 + WP 5-5

E. Curti

**PAUL SCHERRER INSTITUT
WASTE MANAGEMENT LABORATORY
VILLIGEN (CH)**

&

J.L. Crovisier

**ECOLE ET OBSERVATOIRE DES SCIENCES DE LA TERRE
CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517),
STRASBOURG (F)**



Avignon 29-31/10/03



1

Scope and motivation

(1) Provide reliable long-term dissolution rates for the Swiss reference HLW glasses

➡ source-term parameter for safety analysis

(2) Identify secondary phases formed during the alteration process:

➡ how do they correlate with solution chemistry and glass composition?

➡ in which phases are FP/actinides retained ?

COMPOSITION OF INVESTIGATED GLASSES

weight %	SON68 (COGEMA, F)	MW (BNFL, GB)
SiO ₂	45.5	46.2
B ₂ O ₃	14.0	16.7
Al ₂ O ₃	4.9	5.3
Na ₂ O	9.9	8.1
CaO	4.0	-
MgO	-	5.9
ZnO	2.5	-
Fe ₂ O ₃	2.9	2.7
Li ₂ O	2.0	3.8
MoO ₂	1.7	1.8
FP+ Actinides *	10.4	8.6
other minor els.	2.2	1.3

PSI - long term glass leaching tests

Experimental setup:

Corrosion time:
now ~ 13 years

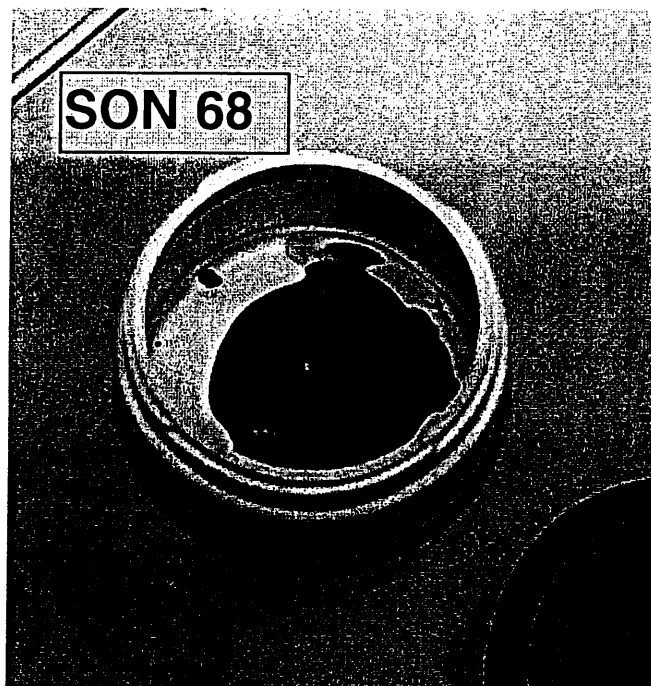
600 ml distilled
 H_2O + 24 g glass

SON68 (5 X)
MW (5 X)

- $S/V = 1200 \text{ m}^{-1}$
- $T = 90 \text{ }^\circ\text{C}$
- static conditions
- CO_2 exclusion
- 10 ml samples
(drawn after 28, 91, 365,
548, 730 then yearly)
- no refill



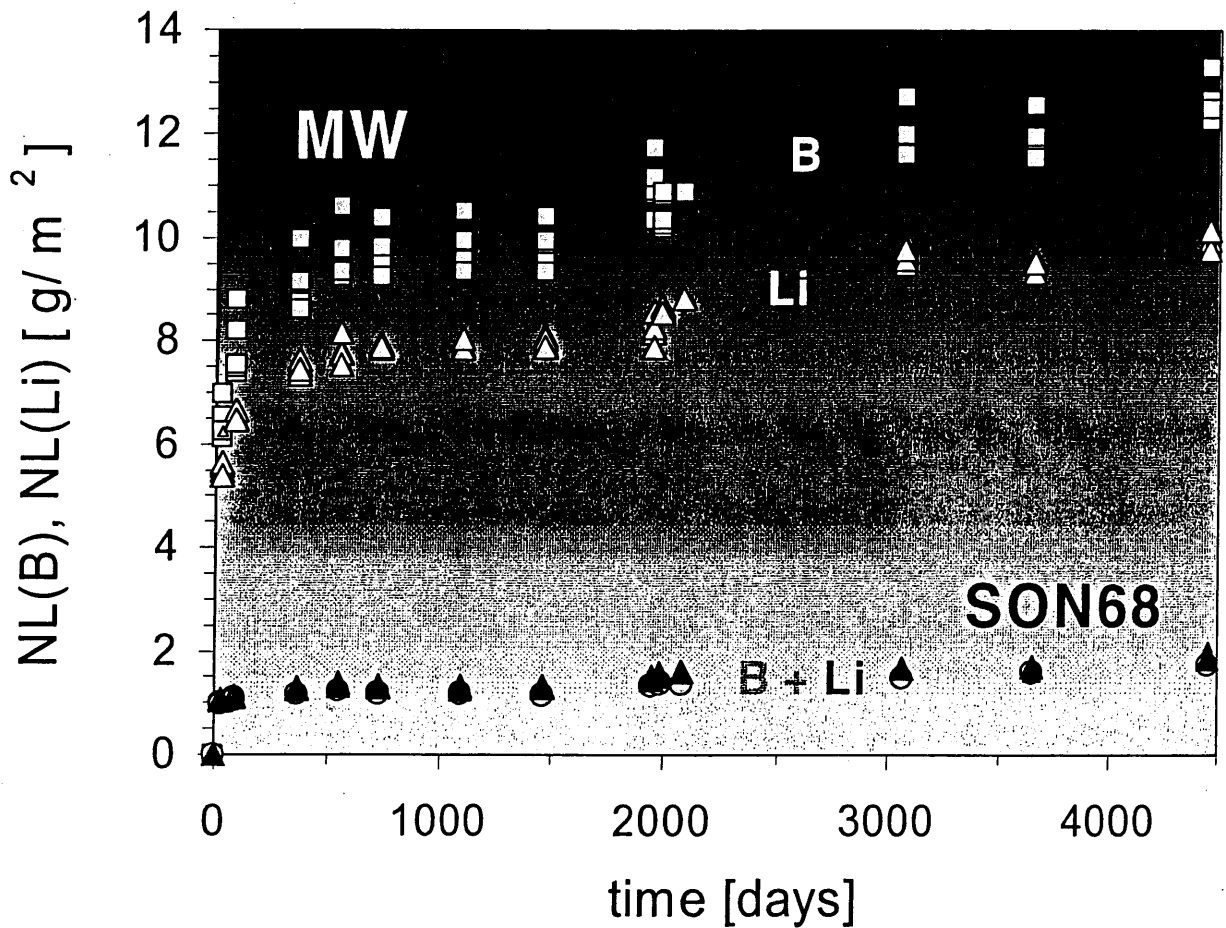
PSI - long term glass leaching experiments: Wet glass samples after 5 y reaction



Crust of
secondary
precipitates

Overview of kinetic data

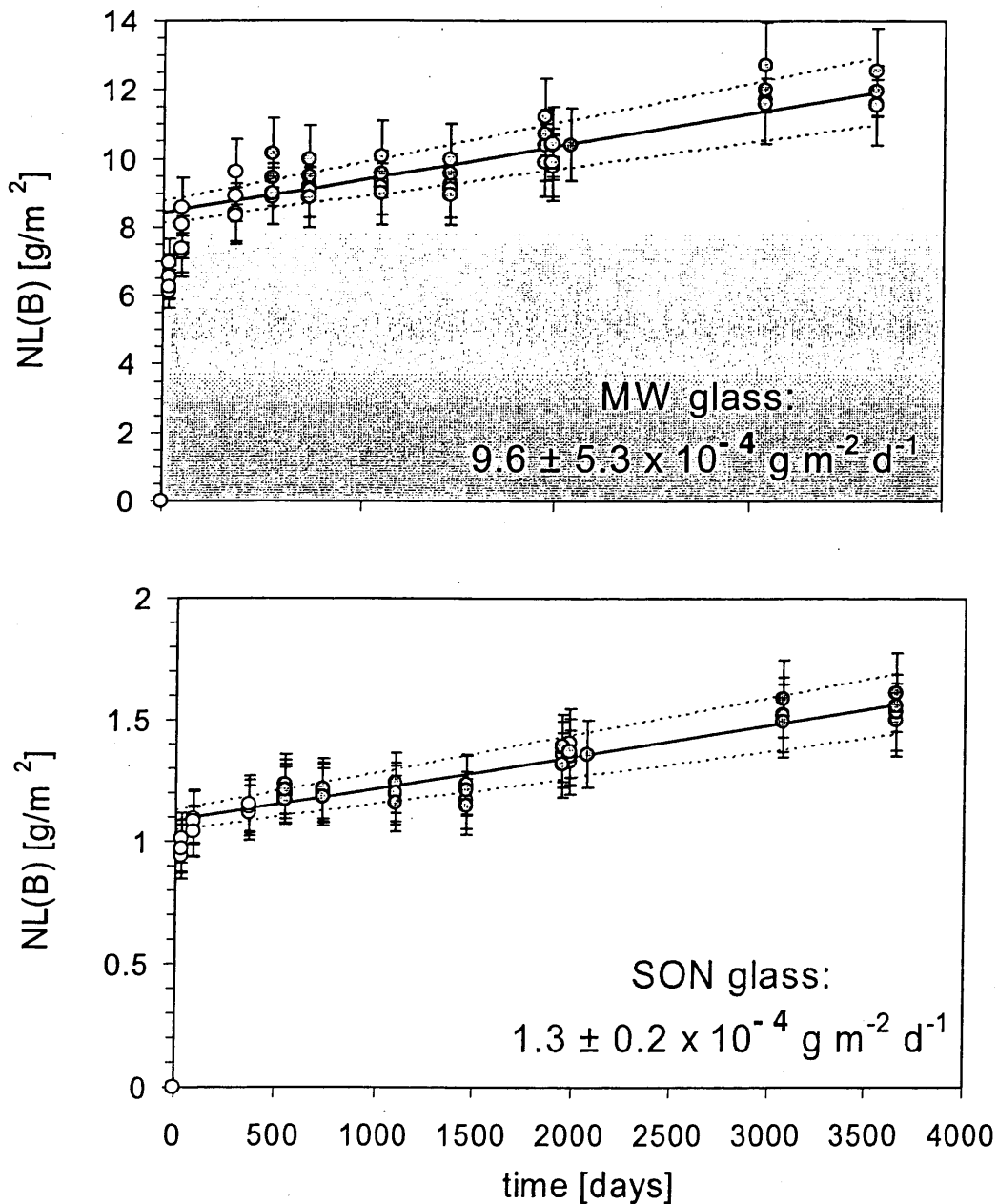
Normalised mass loss:
$$NL(B) = \frac{[B]}{f_B(S/V)}$$



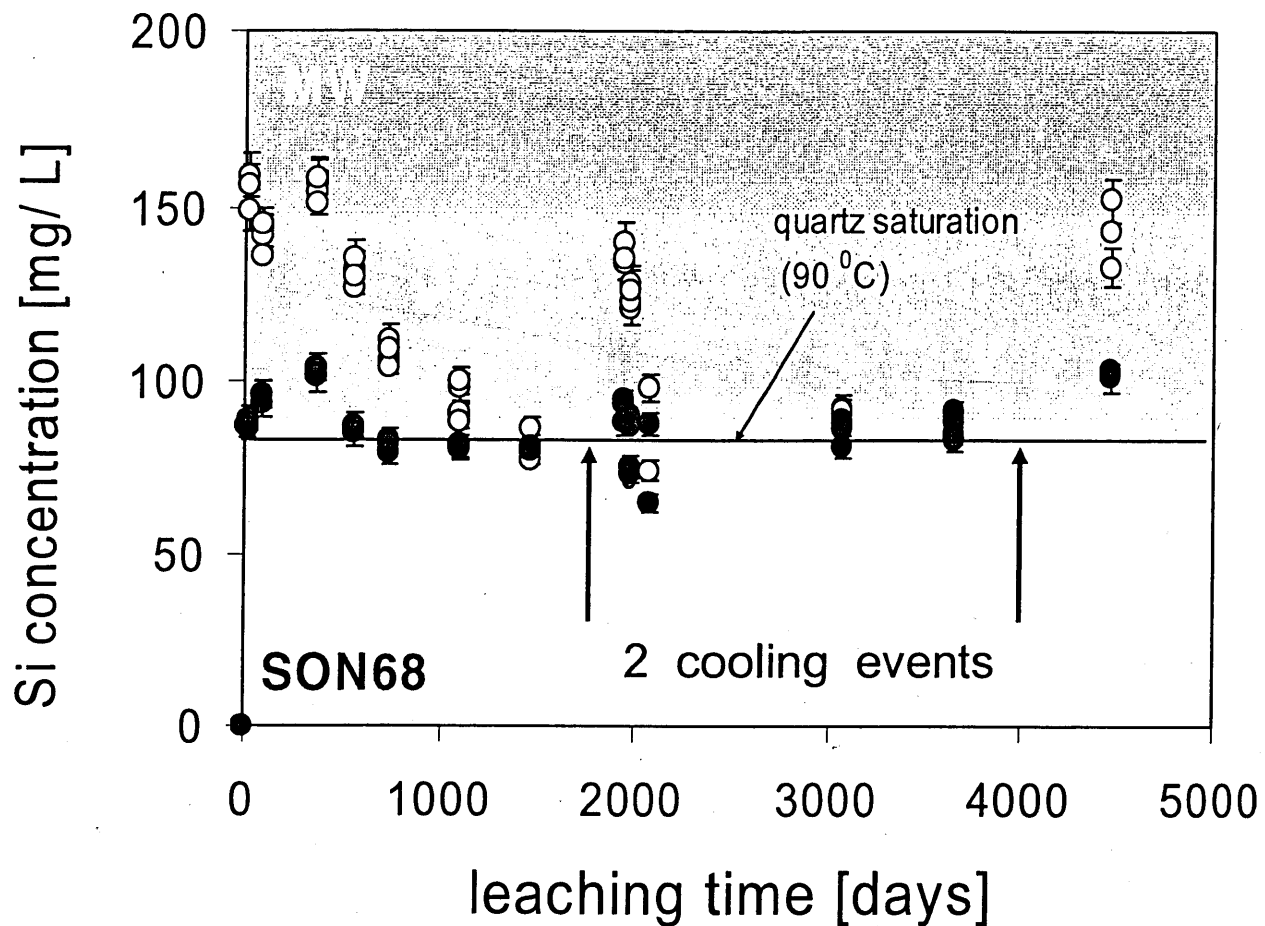
- MW corrosion >> SON68 corrosion
- $NL(Li) < NL(B)$ for MW,
 $NL(Li) = NL(B)$ for SON68

Determination of corrosion rates

- Only data > 500 days considered
- Each single point weighted $\sigma = \pm 10\%$



Silica concentrations



1. fast increase to [Si] ~150 g/L in 1st year
2. Slow decrease to ~ 90 g/L up to 3rd year
3. Renewed [Si] increase correlates with 2 unwanted cooling events (oven malfunction)

Alteration after 5.7 years (SEM)

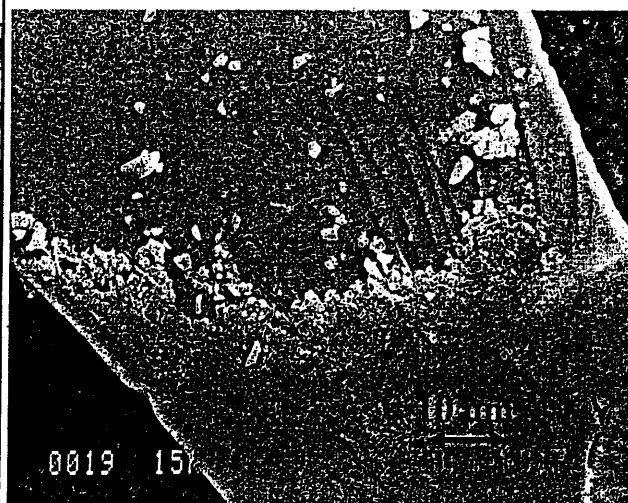
MW

rich in alteration products
coalesced grains (crust)

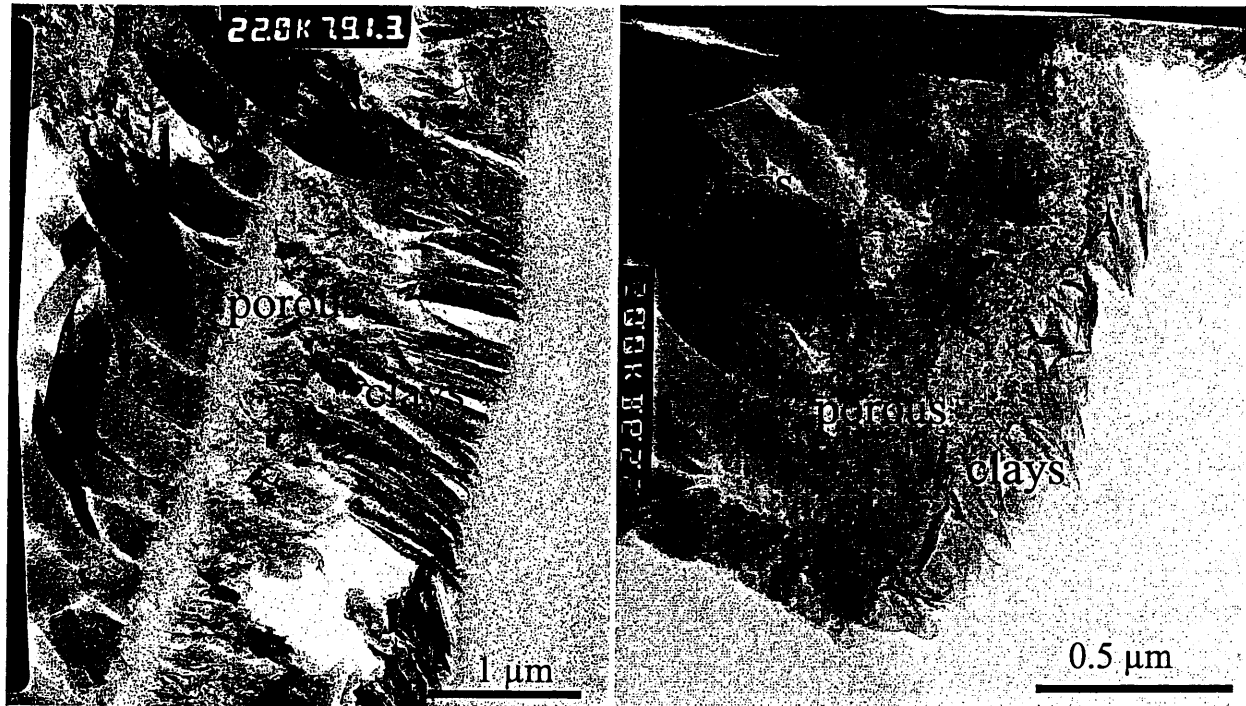


SON 68

less alteration products
loose grains



Alteration (TEM sections)



MW alteration zones:

well-differentiated

thick coatings

SON 68 alteration zones:

poorly differentiated

thin coatings

Overview TEM (MW glass)

Cross section through grain

Ln phosphate particle

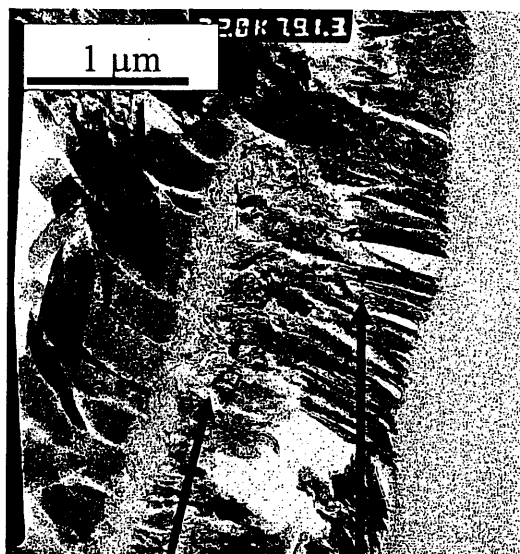


Weight % (12.7 y)	Glass	Porous zone	Clay zone	Ln-P Particle
Na ₂ O	1.6	0.7	1.0	0.4
MgO	6.0	13.1	14.7	7.1
Al ₂ O ₃	11.3	8.8	11.5	7.5
SiO ₂	70.0	64.6	66.7	42.6
P ₂ O ₅	1.5	1.7	0.0	12.9
CaO	0.1	0.9	0.6	1.0
Fe ₂ O ₃	3.2	3.2	3.4	0.0
NiO	0.0	0.3	0.0	0.0
ZrO ₂	1.2	1.8	0.3	0.0
Cs ₂ O	1.1	0.2	0.2	0.2
Ln ₂ O ₃	3.3	4.6	0.8	28.1

ALTERATION IN "POROUS ZONE" (MW)

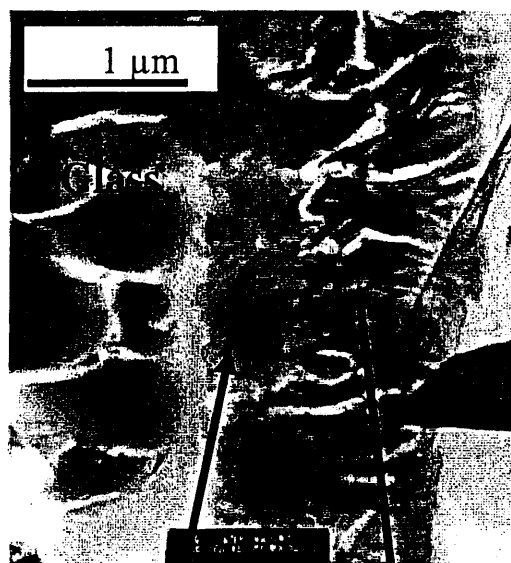
5.7 years

12.2 years



Porous zone

Clay zone



Porous zone

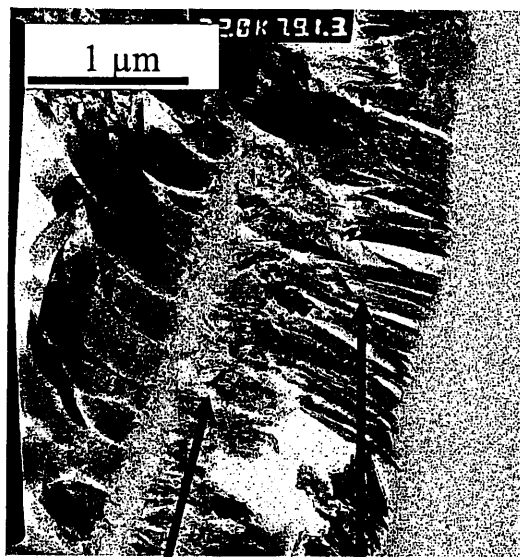
Clay zone

Little
compositional
changes over
time

	Glass	Porous zone	
		5.7 y	12.2 y
Na ₂ O	1.6	0.2	0.7
MgO	6.0	13.1	13.1
Al ₂ O ₃	11.3	6.2	8.8
SiO ₂	70.0	65.9	64.6
P ₂ O ₅	1.5	0.0	1.7
K ₂ O	0.7	0.8	0.2
CaO	0.1	1.7	0.9
Fe ₂ O ₃	3.2	6.2	3.2
NiO	0.0	0.0	0.3
ZrO ₂	1.2	0.8	1.8
Cs ₂ O	1.1	1.9	0.2
Ln ₂ O ₃	3.3	3.1	4.7
sum	100.0	100.0	100.0

ALTERATION IN "CLAY ZONE" (MW)

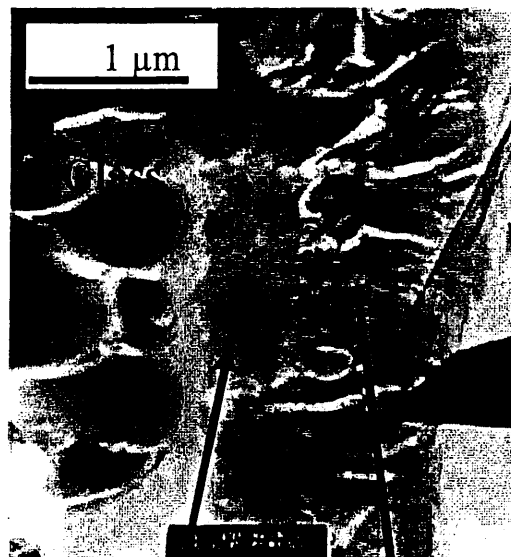
5.7 years



Porous zone

Clay zone

12.2 years



Porous zone

Clay zone

Little
compositional
changes over
time

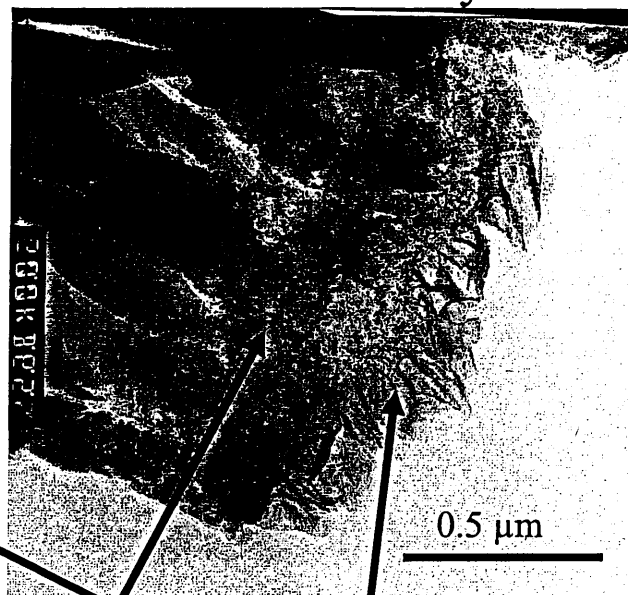
Weight %	Glass	Clay zone	
		5 y	12 y
Na ₂ O	1.6	0.2	1.0
MgO	6.0	13.2	14.7
Al ₂ O ₃	11.3	9.8	11.5
SiO ₂	70.0	68.2	66.7
P ₂ O ₅	1.5	0.0	0.8
K ₂ O	0.7	0.7	0.1
CaO	0.1	1.7	0.6
Fe ₂ O ₃	3.2	3.8	3.4
ZrO ₂	1.2	0.3	0.3
Cs ₂ O	1.1	1.2	0.2
Ln ₂ O ₃	3.3	0.9	0.8
sum	100.0	100.0	100.0

ALTERATION IN "POROUS ZONE" (SON68)

SON68 5.7 years



SON68 12.2 years



	Glass 12.2 y	Porous 5.7 y	zone 12.2 y	Clay 5.7 y	zone 12.2 y
Na ₂ O	5.5	0.8	0.4	3.5	2.9
Al ₂ O ₃	7.9	9.4	8.8	8.0	6.4
SiO ₂	70.7	71.5	70.5	61.9	61.9
CaO	4.5	4.8	3.3	0.9	0.7
Fe ₂ O ₃	3.4	3.2	7.8	7.8	8.7
ZnO	2.8	0.7	0.9	8.9	11.1
NiO	0.8	n.d.	0.3	3.8	3.7
ZrO ₂	2.8	1.8	5.3	1.4	0.0
Cs ₂ O	1.2	1.9	0.6	0.0	0.1
Ln ₂ O ₃	4.2	3.4	5.4	n.d.	2.8

CONCENTRATIONS IN LEACHANT & RETENTION FACTORS

(MW glass)

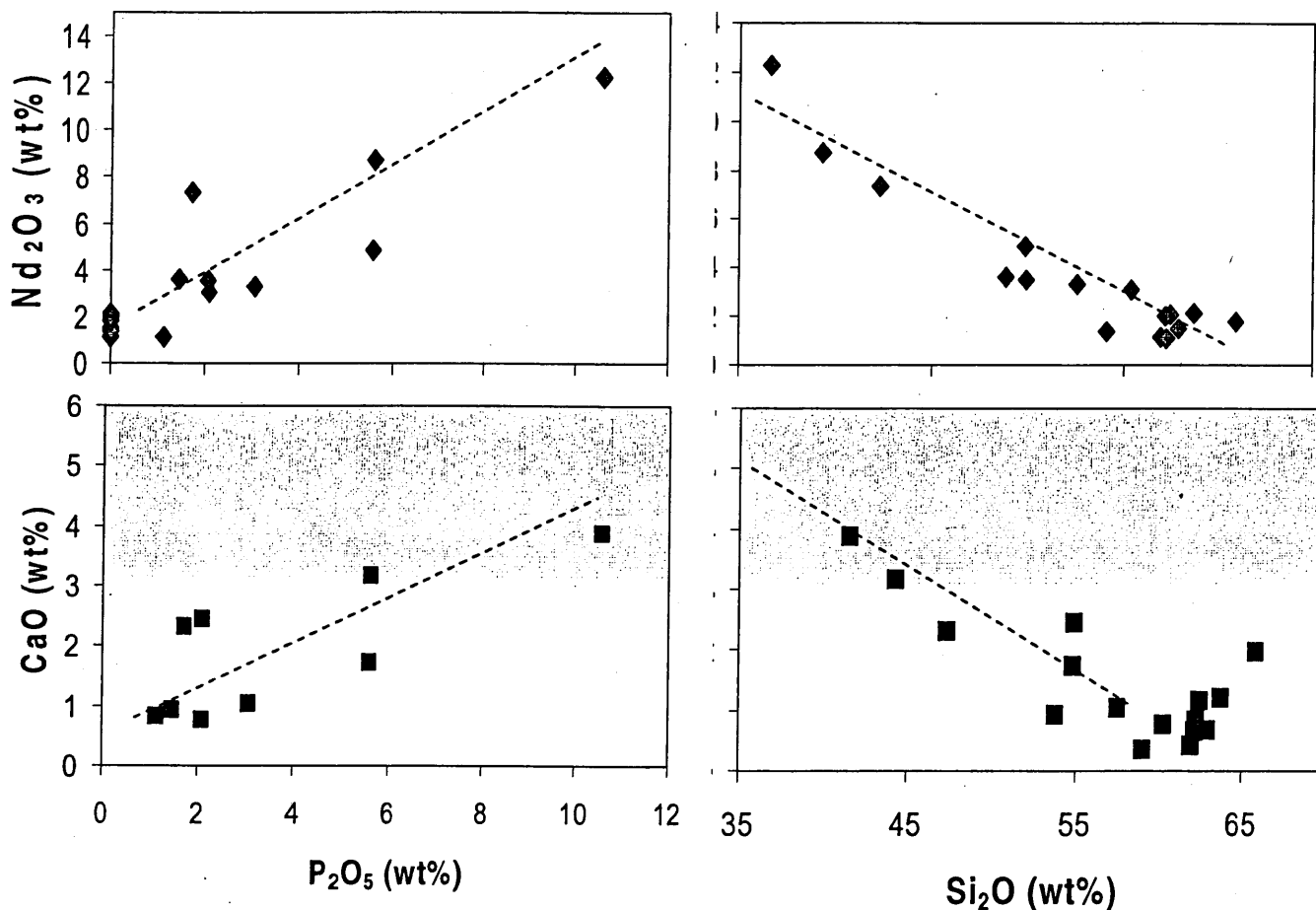
	5.7 years		12.2 years	
	C (mol / L)	RF %	C (mol / L)	RF %
Cs ⁺	5.3×10^{-5}	94.6	4.9×10^{-5}	95.7
Ni ²⁺	6.3×10^{-7}	99.9	1.7×10^{-6}	99.7
Sr ²⁺	1.3×10^{-6}	99.7	1.5×10^{-6}	99.7
Nd ³⁺	7.0×10^{-6}	99.4	6.2×10^{-6}	99.5
Zr ⁴⁺	4.7×10^{-6}	99.7	4.7×10^{-6}	99.8

- High retention factors for FP (and actinides)
- Conc. stable over time (solubility limits?)
- Similar picture for SON68 glass

ELEMENT CORRELATIONS IN PHASE MIXTURES (TEM ANALYSES)

SON 68, 12.2 y, clay zone

LnPO_4 ?



Apatite? $\text{Ca}_5\text{OH}(\text{PO}_4)_3$

Correlations suggest presence of Ca, Ln phosphates also in SON68 (nanophases)

CONCLUSIONS

- (1) Our 12 – years kinetic experiments allowed us to determine precise long-term rates for HLW safety assessment in Switzerland
- (2) A considerable number of safety-relevant fission products have been shown to be immobilised in secondary alteration phases (clays, phosphates)
- (3) The mineralogy of the alteration products AND the kinetics depend on glass composition: Mg favors clay formation and speeds up corrosion
- (4) Therefore, prediction of RN release and migration has no generic solution, but is site and glass-specific

Corrosion under Irradiation

Summary

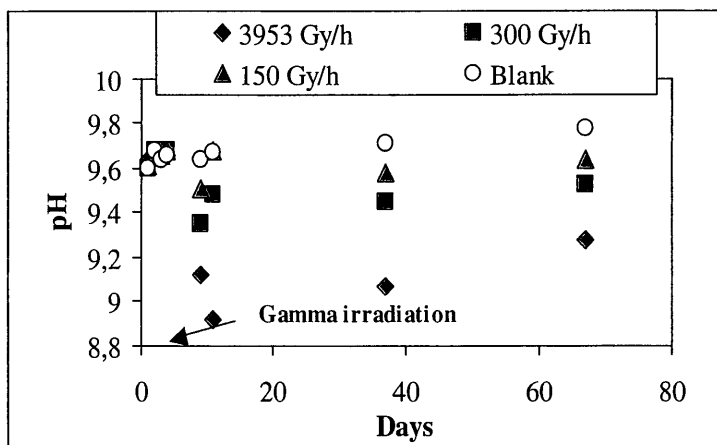
- Gamma experiments
- Alpha experiments

Gamma irradiation experiments

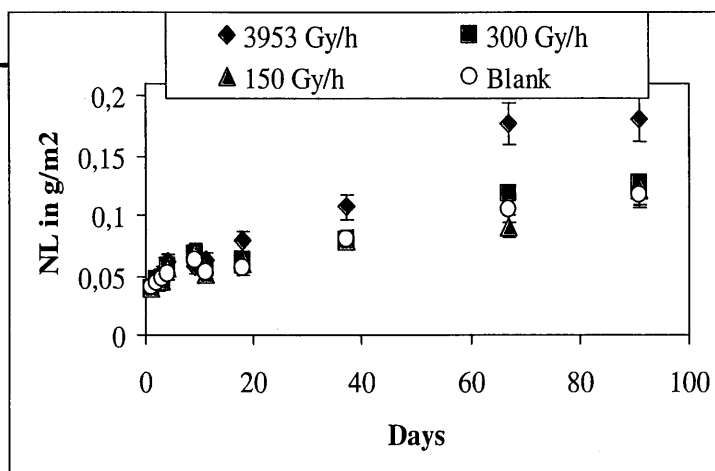
Experimental conditions

- Static experiments at 90°C during one week
 $S/V = 3970 \text{ m}^{-1}$ (SON 68 powder $S = 1.39 \text{ m}^2/\text{g}$).
- Corrosion solution : synthetic solution saturated in silicon, boron and sodium.
- Initial pH = 9.7 (pH in equilibrium with atmosphere).
- Irradiation at Orsay University with ^{60}Co .
time of irradiation = 14.6 hours with three dose rates :
3953 Gy/h, 300 Gy/h and 150 Gy/h.

pH evolution



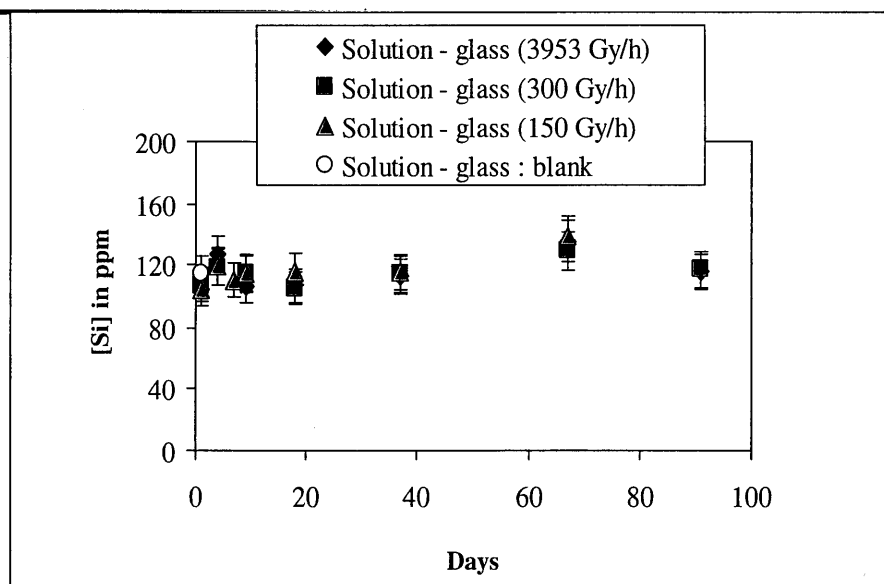
Li-mass loss



93 days	Blank	150 Gy/h	300 Gy/h	3953 Gy/h
NL(Li)	0.13	0.14	0.13	0.2
NL(Mo)	0.014	0.014	0.013	0.014

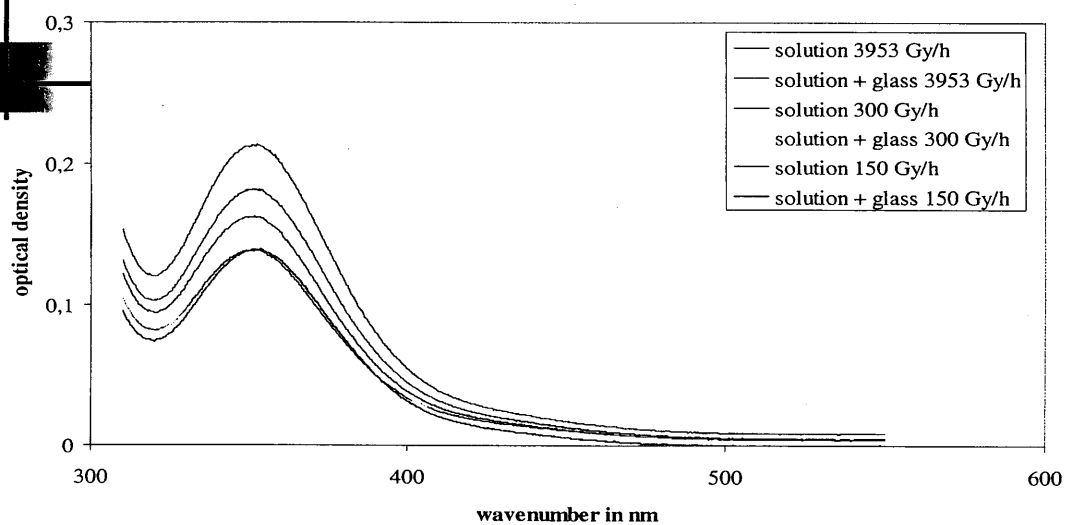
- Increase of ionic exchange

Si-concentration



- No matrix hydrolysis

H₂O₂ concentration



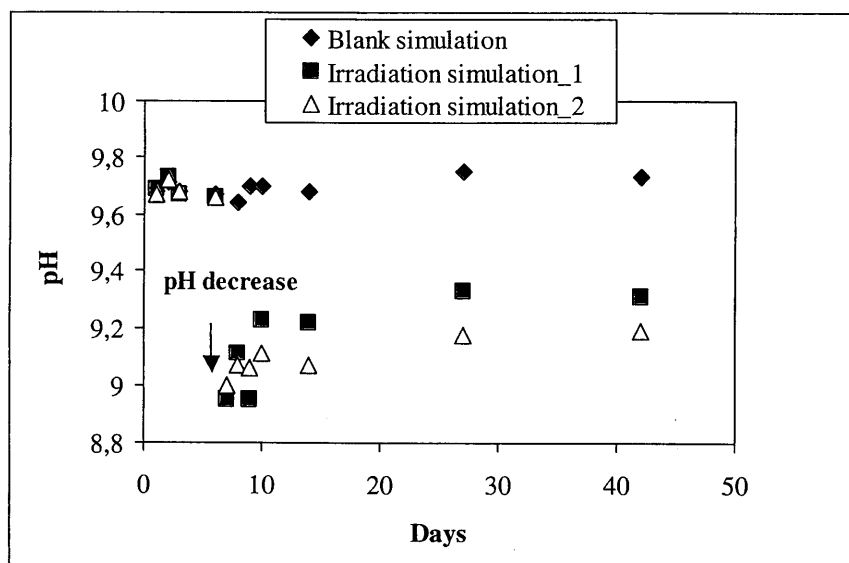
Dose rate Gy.h ⁻¹	150	300	3953
Dose Gy	2190	4380	57714
Glass + Solution	1,59.10 ⁻⁵	1,70.10 ⁻⁵	2,38.10 ⁻⁵
Solution	2,04.10 ⁻⁵	1,59.10 ⁻⁵	1,82.10 ⁻⁵

Simulation of gamma irradiation : pH decrease

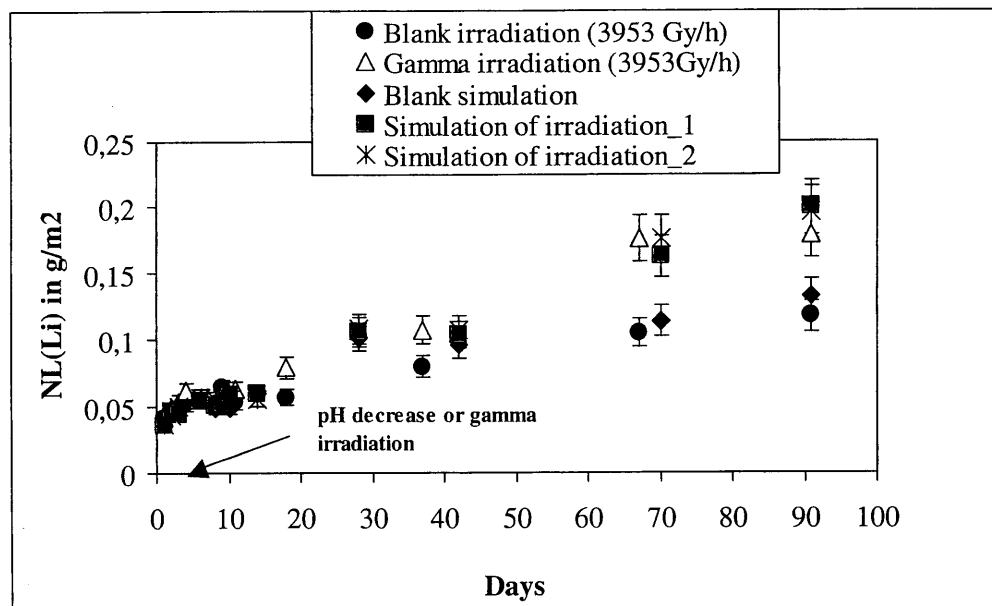
Experimental conditions

- Experiments in static conditions at 90°C during one week
S/V = 3970 m⁻¹ (SON 68 powder SA = 1.39 m²/g).
- Corrosion solution : synthetic solution enriched in silicon, boron and sodium.
- Initial pH = 9.6.
- Decrease of pH to 9 with HNO₃ (observed with a gamma irradiation of about 58 000 Gy):
 - ◆ One reactor directly at 90°C after the decrease.
 - ◆ The other, one day at room temperature then 90°C.

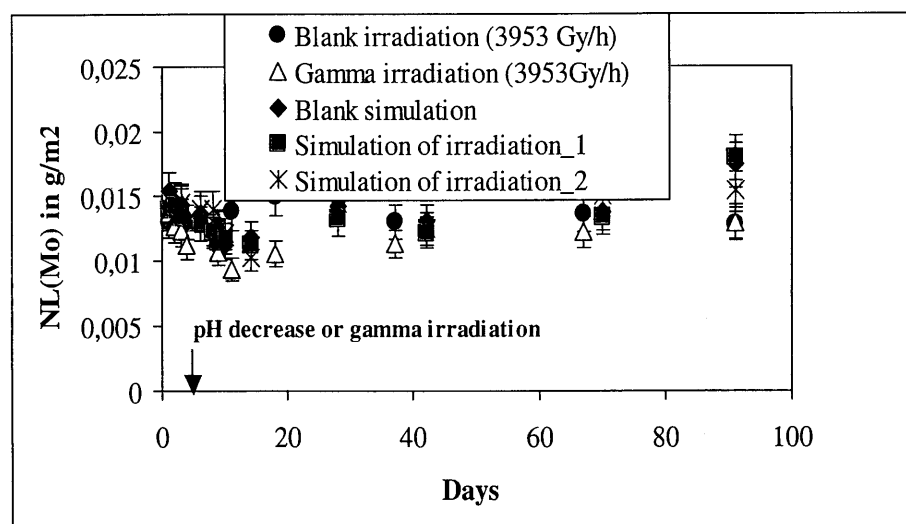
pH evolution



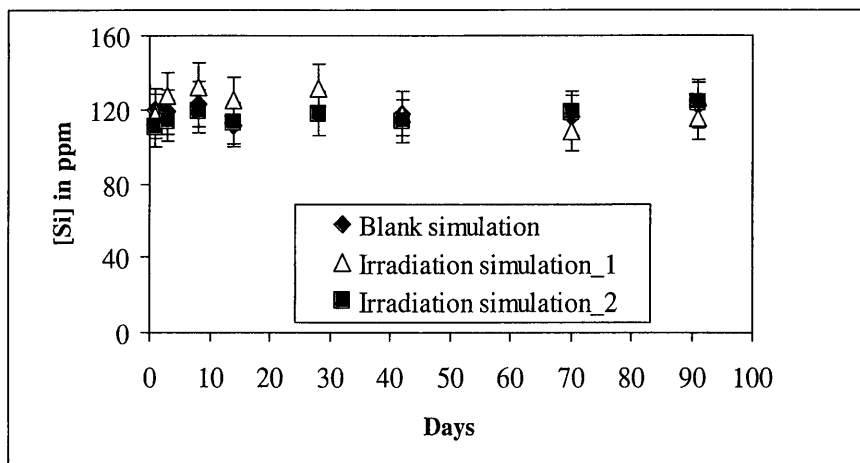
Li-mass loss



Mo-mass loss



Si-concentration



Gamma irradiation

Conclusions

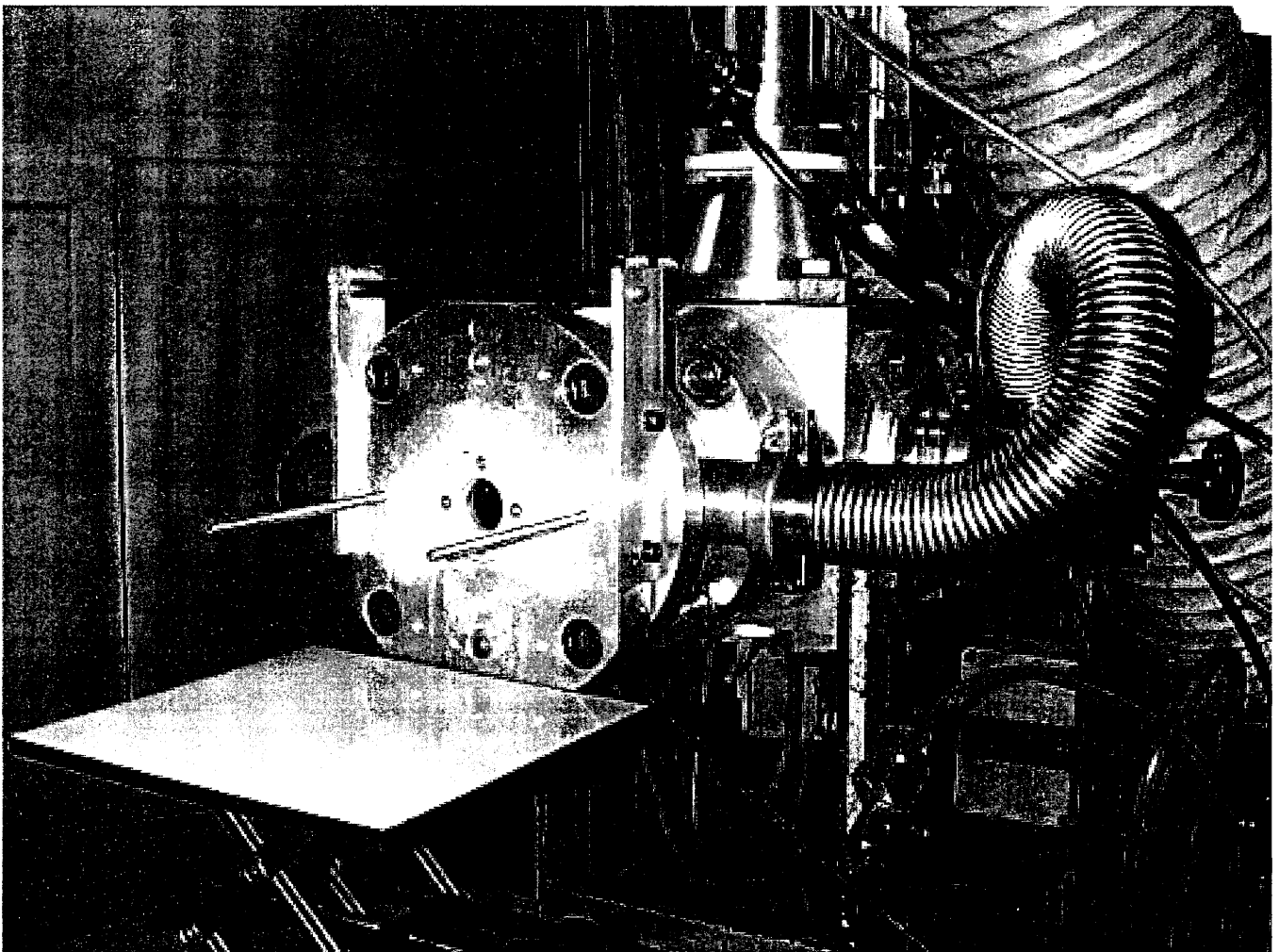
High gamma irradiation doses can enhance the ionic exchange process via a decrease of pH.

Alpha irradiation experiments

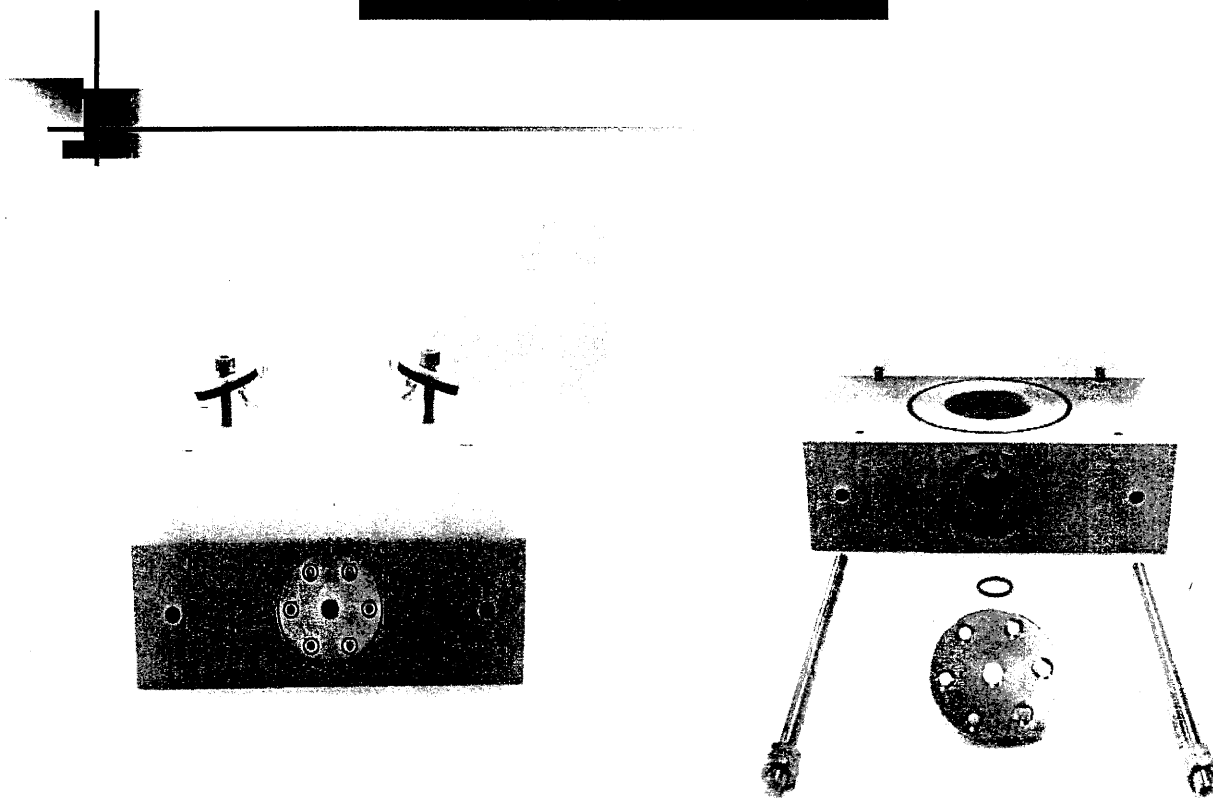
Alpha Irradiation : cyclotron at CERI/CNRS (Orléans).

Time of irradiation : 30 minutes under mixing.

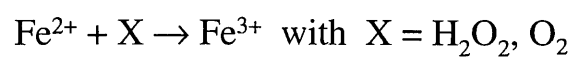
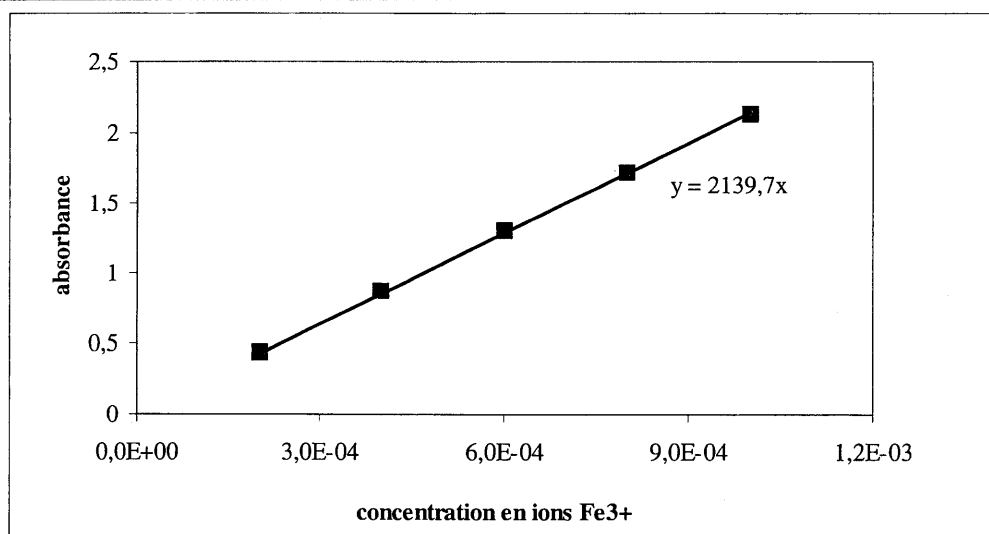
$E_{\text{incident}} = 28 \text{ MeV} \rightarrow$ between 5 et 10 MeV due to interaction with titanium sheets, air and cell window (SRIM calculation)



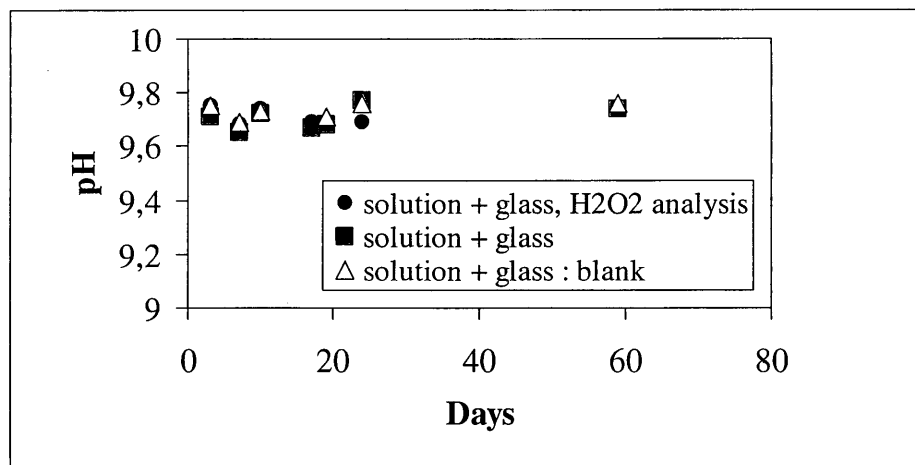
Electrochemical cell



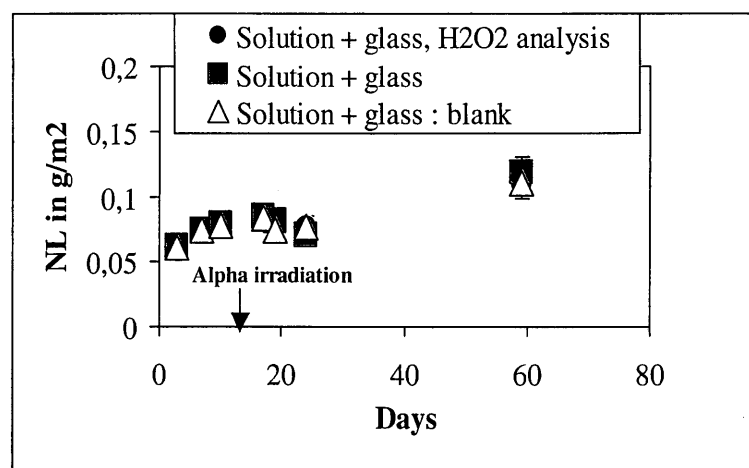
Fricke dosimeter



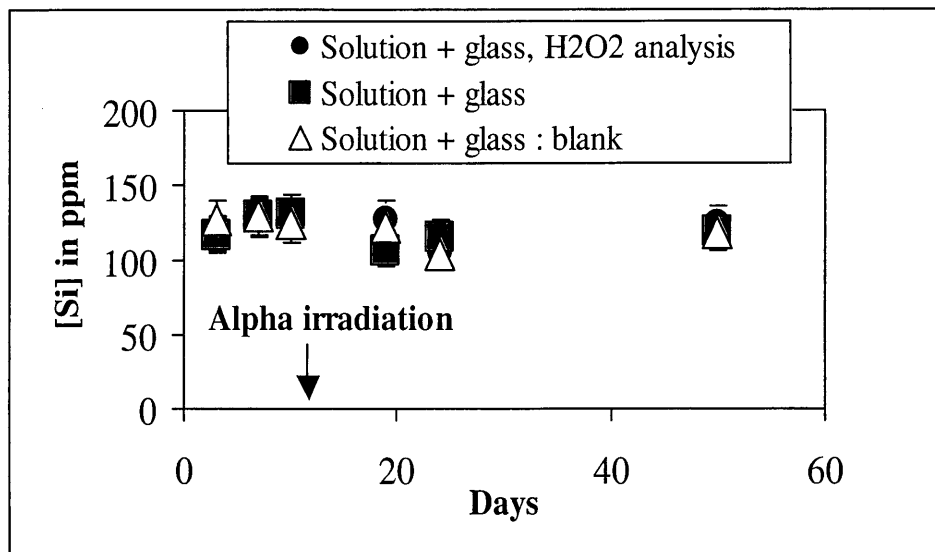
pH evolution



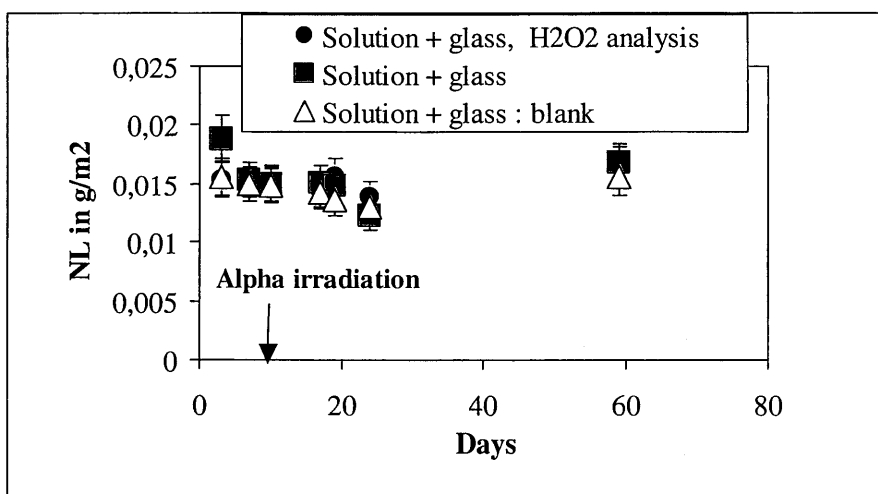
Li-mass loss



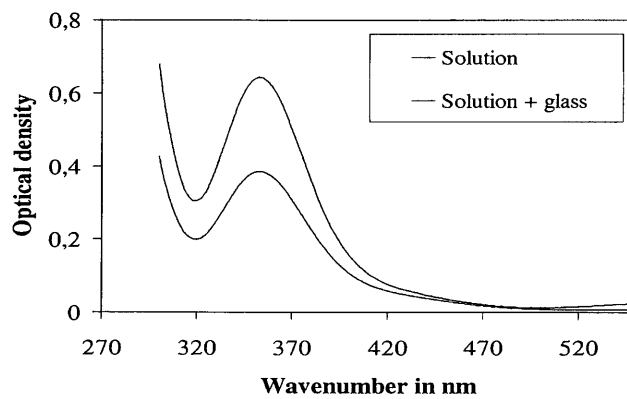
Si-concentration



Mo-mass loss



H_2O_2 concentration



Experiment	Solution	Solution + Glass
pH	9.83	9.79
[H_2O_2] en mol/L	$4,3 \cdot 10^{-5}$	$7,27 \cdot 10^{-5}$



α -DOPED GELS LEACHING UNDER OXIDIZING AND REDUCING CONDITIONS

P. JOLLIVET, G. PARISOT

CEA Marcoule

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1



GELS PREPARATION

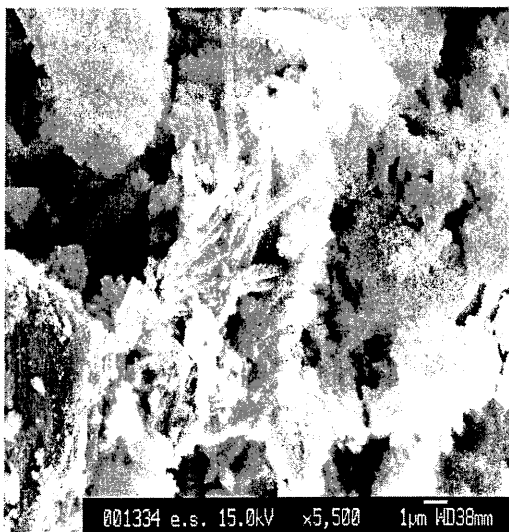
- Gels have been obtained by static hydrothermal glass alteration in stainless steel reactors with gold joints
- Glasses doped with $^{237}\text{NpO}_2$ (0.85w%), $^{239+240}\text{PuO}_2$ (0.74w%) and $^{241}\text{Am}_2\text{O}_3$ (0.79 w%)
 - glass monoliths : $25 \times 25 \times 3 \text{ mm}^3$
 - $V \approx 40 \text{ cm}^3$
 - $S = 45 \text{ cm}^2$ $\Rightarrow S/V \approx 1.1 \text{ cm}^{-1}$
 - $T = 300^\circ\text{C}$ and $P = 100 \text{ bars}$
- Glasses were fully altered (≈ 70 days)
- After alteration, monoliths volume x2 and many cracks
- After drying, gels became hard
- The gel monoliths were ground with a mortar and a pestle
- $S_g = 4.4 \text{ m}^2.\text{g}^{-1}$

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SEM OBSERVATIONS OF GELS BEFORE LEACHING

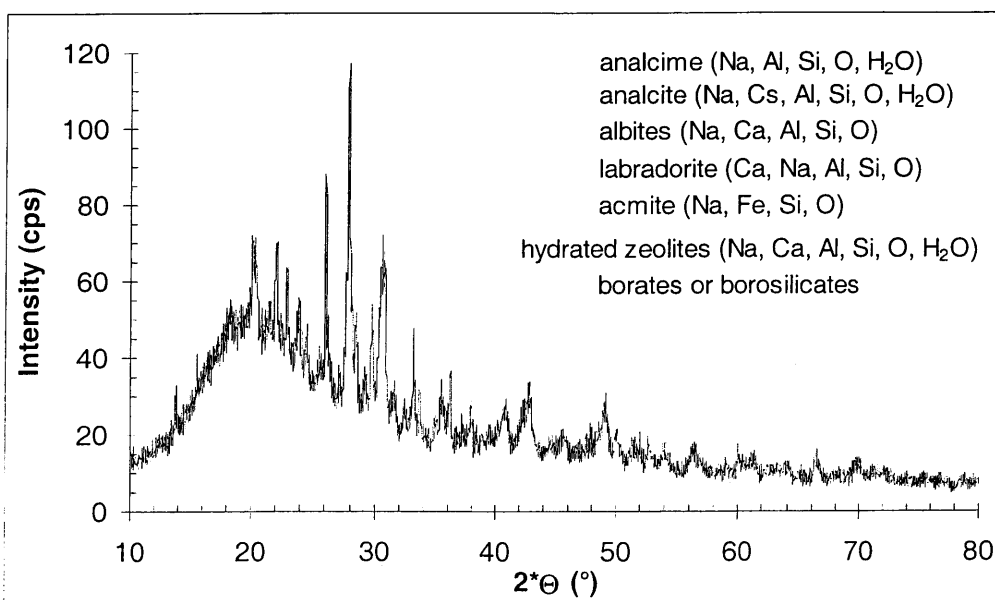


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XRD analysis on a non-radioactive gel



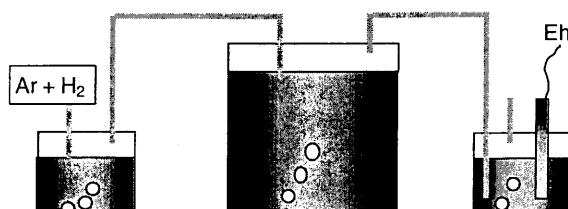
XRD analysis on α -doped gels in progress
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GELS LEACHING CONDITIONS

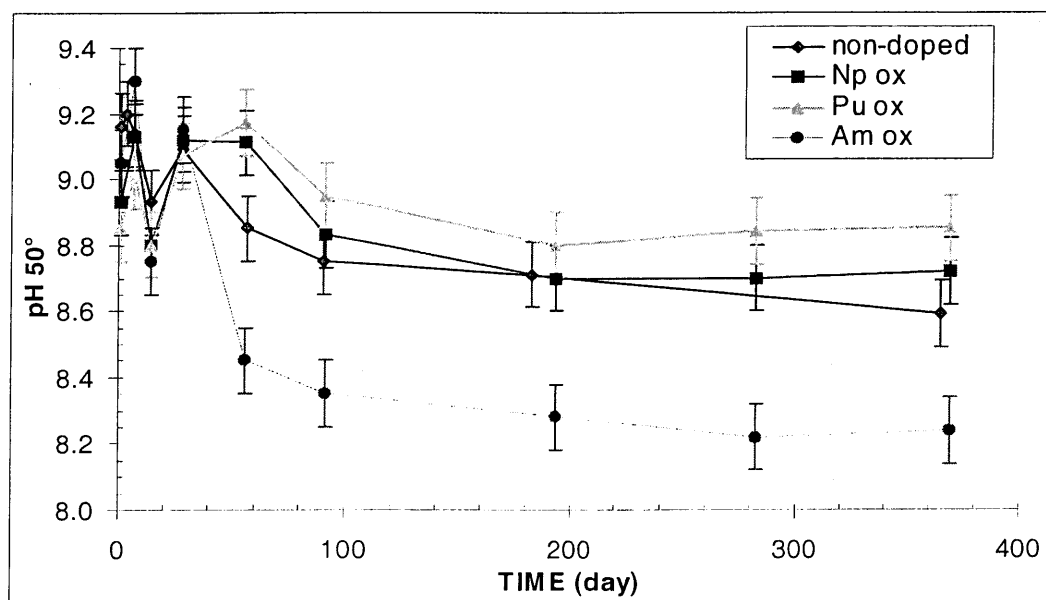
- Gels have been leached at 50°C
- $S/V \approx 44 \text{ cm}^{-1}$
- Oxidizing atmosphere: PTFE reactors, $V = 1000 \text{ cm}^3$
- Reducing atmosphere: stainless steel reactors, $V = 500 \text{ cm}^3$
- Reducing atmosphere obtained by $\text{Ar} + \text{H}_2$ bubbling after each samplings



- Ox : $E_{\text{HNE}}^{50^\circ} \approx +150 \text{ mV}$ Red : $E_{\text{HNE}}^{50^\circ} \approx -280 \text{ mV}$
 - Direct and UF 10 000 Daltons samplings (+ filtered $0.45 \mu\text{m}$ for An) 5
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pH measured at 50°C

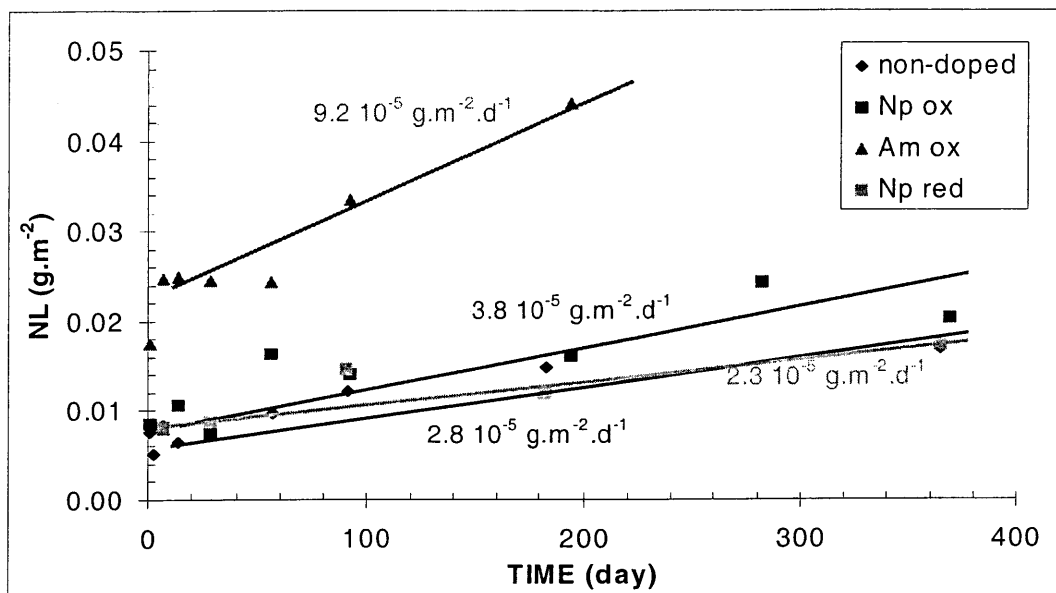


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NL(Si) - UF Sampling

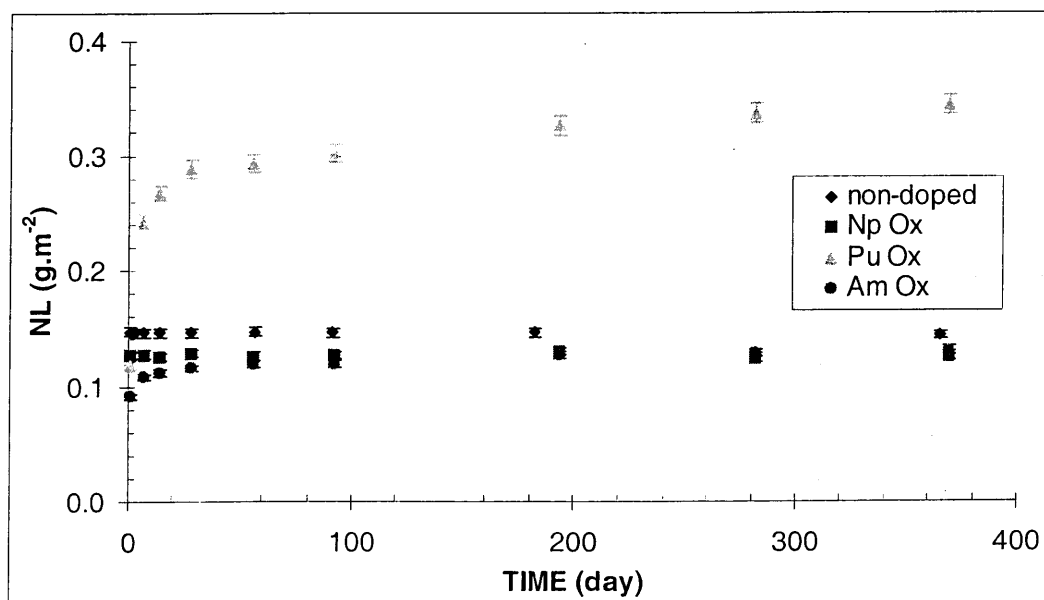
[Si] $\approx$ 40 to 60 ppm

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NL(B) ox - UF Sampling

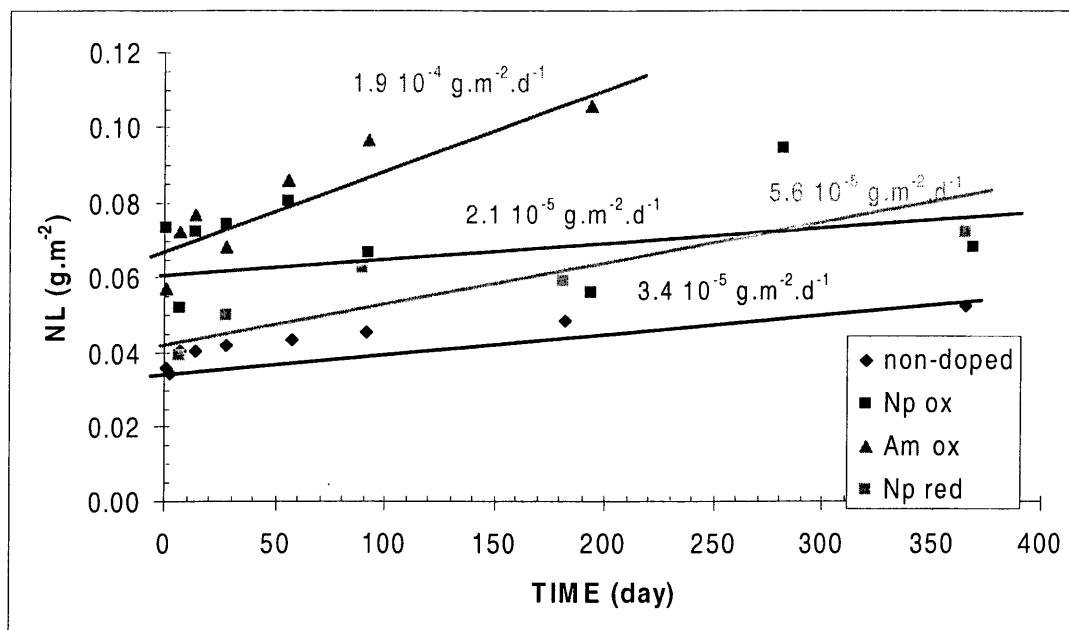


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NL(Na) - UF Sampling

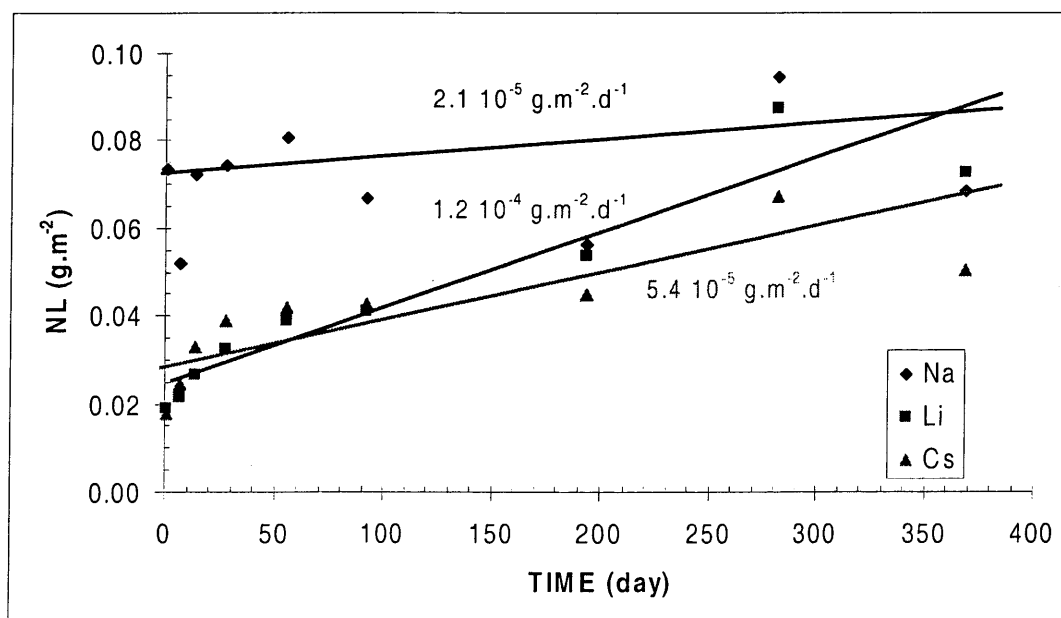


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NL(Na,Li,Cs) Np ox - UF Sampling

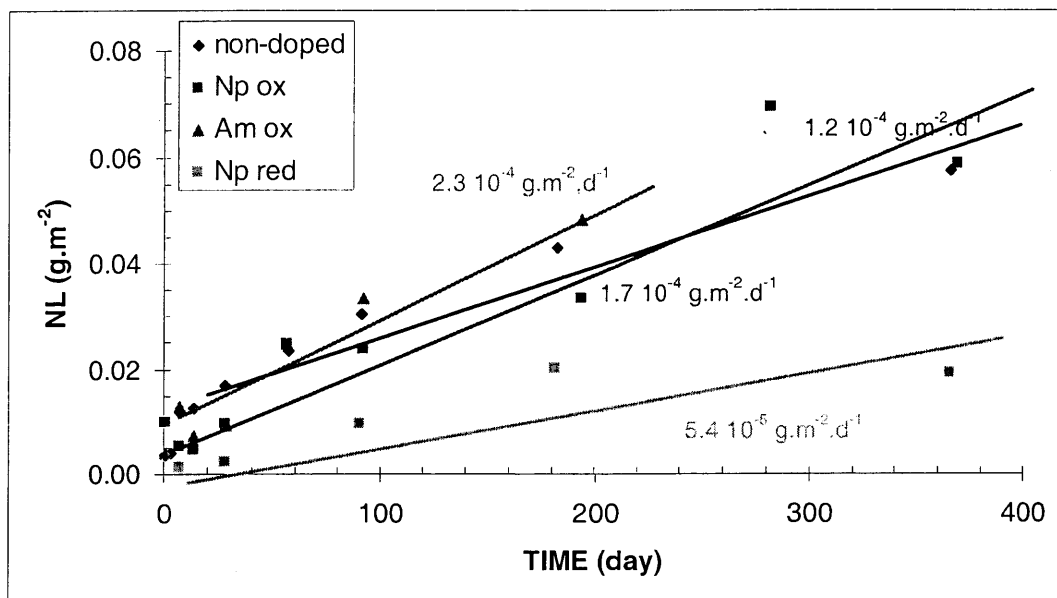


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NL(Ca) - UF Sampling



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Dissolution rates

GEL	RATE (g.m ⁻² .d ⁻¹)						
	Si	Na	Li	Cs	Ca	Sr	Al
Inactif	2.8 ± 0.6 10 ⁻⁵	3.4 ± 0.4 10 ⁻⁵	1.7 ± 0.1 10 ⁻⁴	-	1.2 ± 0.1 10 ⁻⁴	3.8 ± 0.8 10 ⁻⁵	-
Np ox	3.8 ± 0.9 10 ⁻⁵	2.1 ± 3.4 10 ⁻⁵	1.2 ± 0.3 10 ⁻⁴	5.4 ± 2.7 10 ⁻⁵	1.7 ± 0.2 10 ⁻⁴	-	3.7 ± 1.2 10 ⁻⁶
Pu ox	2.9 ± 0.8 10 ⁻⁵	-	1.3 ± 0.4 10 ⁻⁴	4.4 ± 0.7 10 ⁻⁶	2.3 ± 0.3 10 ⁻⁵	-	-
Am ox	9.2 ± 1.6 10 ⁻⁵	1.9 ± 0.4 10 ⁻⁴	5.2 ± 0.3 10 ⁻⁴	5.4 ± 0.6 10 ⁻⁵	2.3 ± 0.3 10 ⁻⁴	1.1 ± 0.1 10 ⁻⁴	-
Np red	2.3 ± 0.8 10 ⁻⁵	5.6 ± 2.0 10 ⁻⁵	1.0 ± 0.3 10 ⁻⁴	5.1 ± 2.3 10 ⁻⁵	5.4 ± 1.8 10 ⁻⁵	-	3.6 ± 0.8 10 ⁻⁶
Pu red	5.4 ± 0.7 10 ⁻⁵	4.5 ± 0.7 10 ⁻⁴	4.7 ± 1.5 10 ⁻⁵	-	8.8 ± 1.2 10 ⁻⁵	-	8.1 ± 1.9 10 ⁻⁶

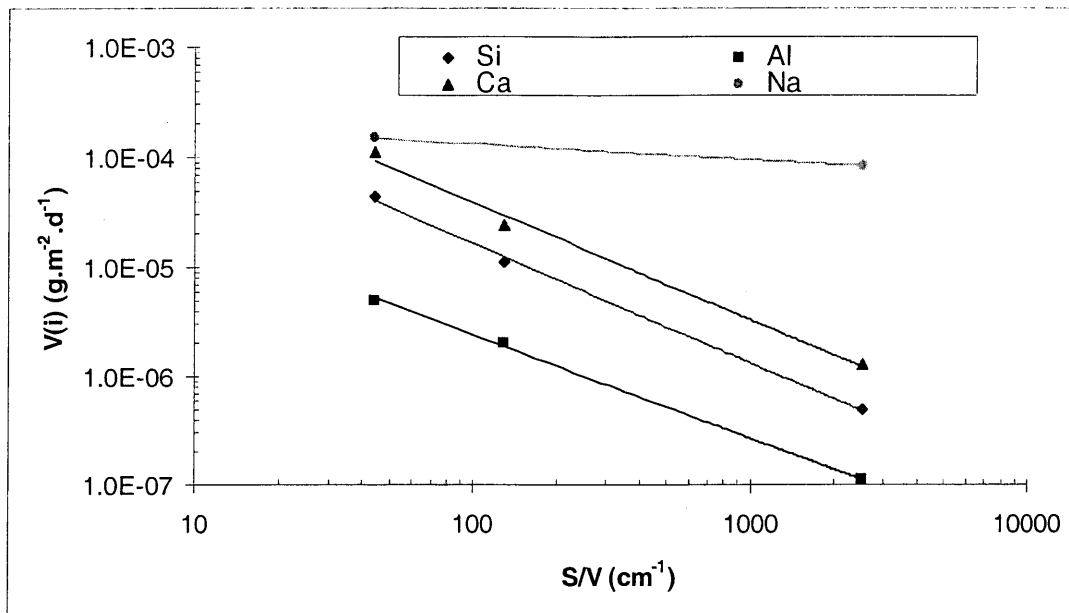
- [Al]_{uf} ≈ 0.2 ppm
- [Fe]_{uf} ≈ 0.8 ppm

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Dissolution rates vs S/V

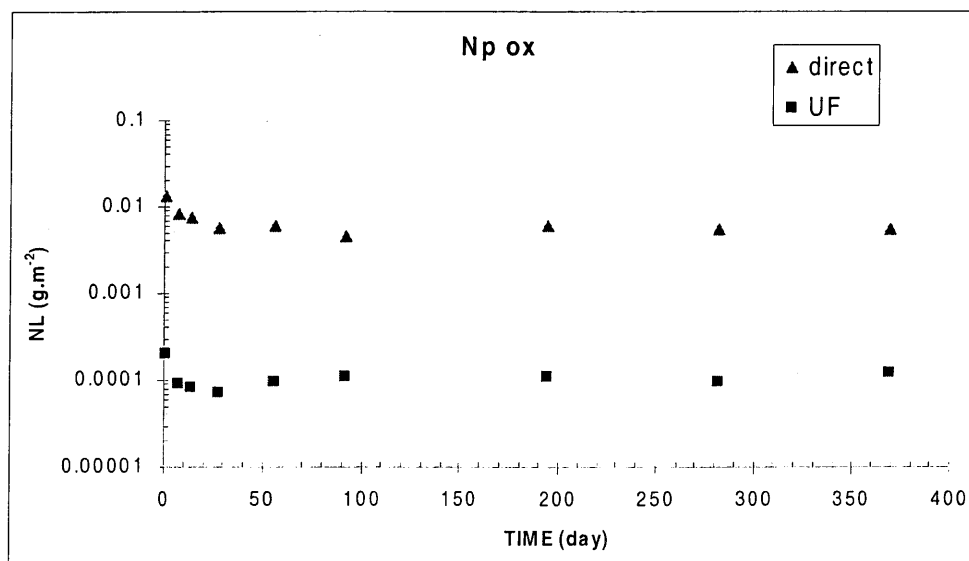


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NL(Zr) - Direct and UF Sampling

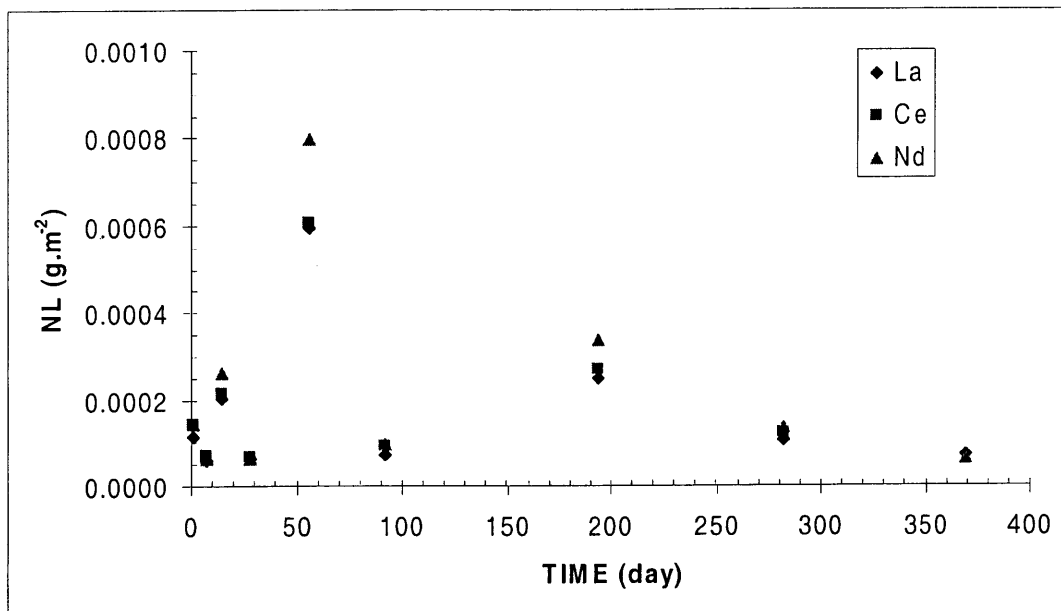
 $[Zr]_d \approx 400$ ppb $[Zr]_{uf} \approx 15$ ppb

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NL(La, Nd, Ce) Np ox - UF Sampling

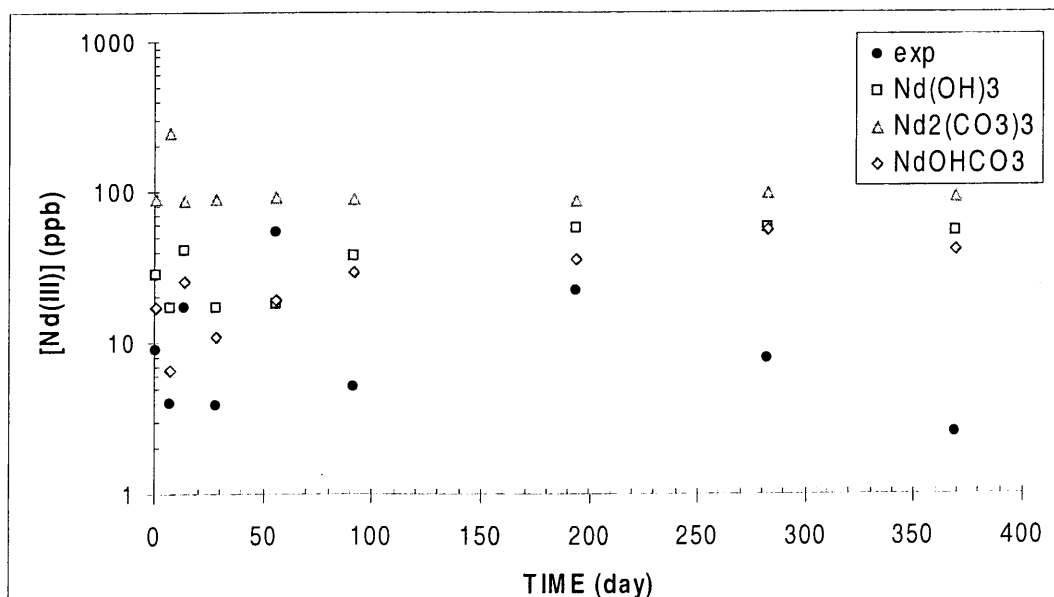


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[Nd] Np ox - UF Sampling

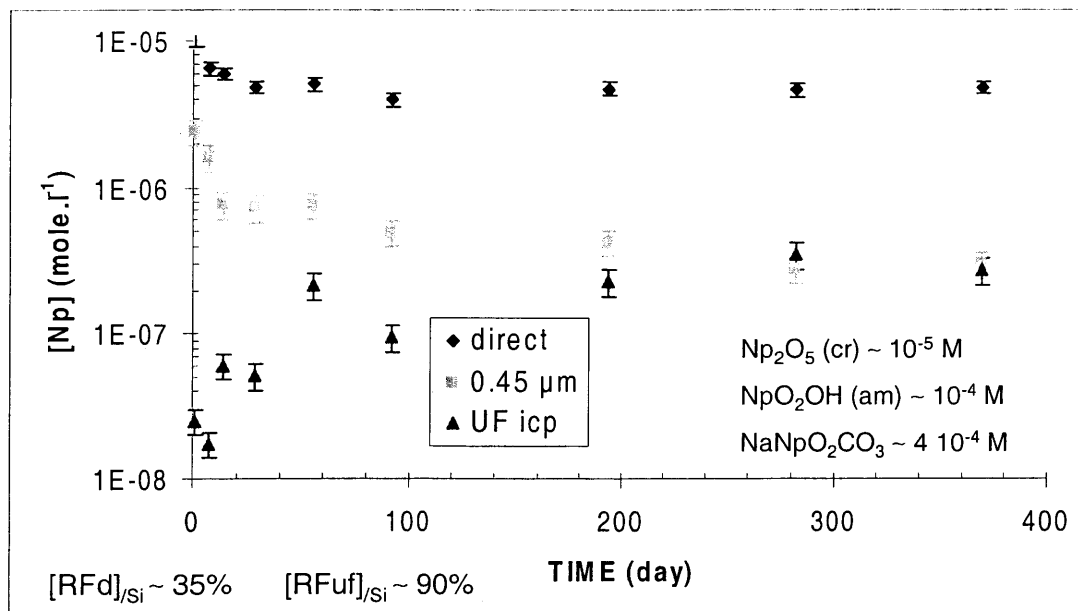


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Np concentrations - oxidizing medium

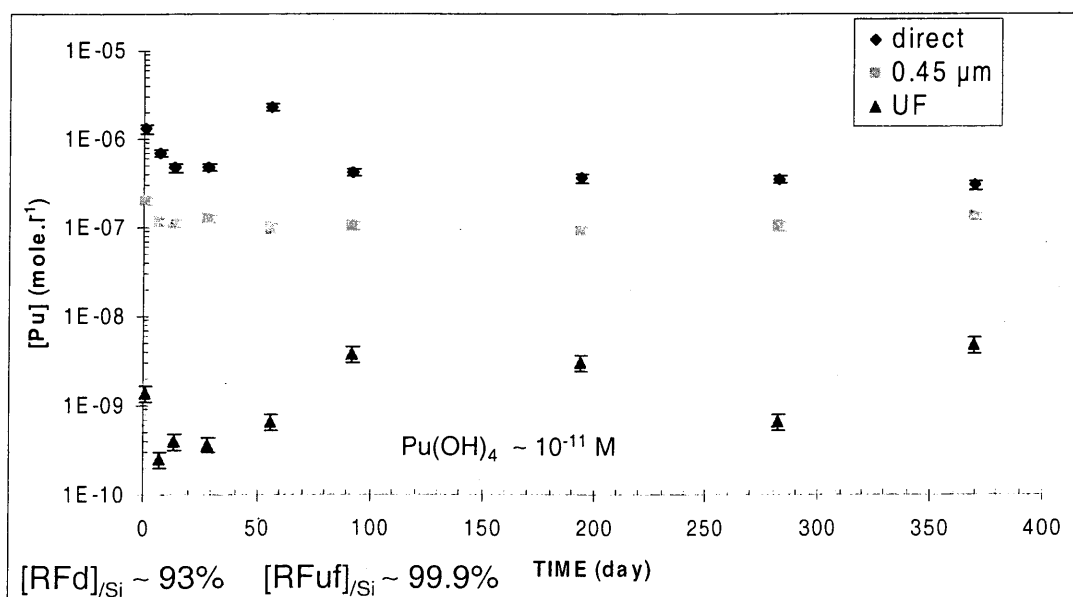


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Pu concentrations - oxidizing medium

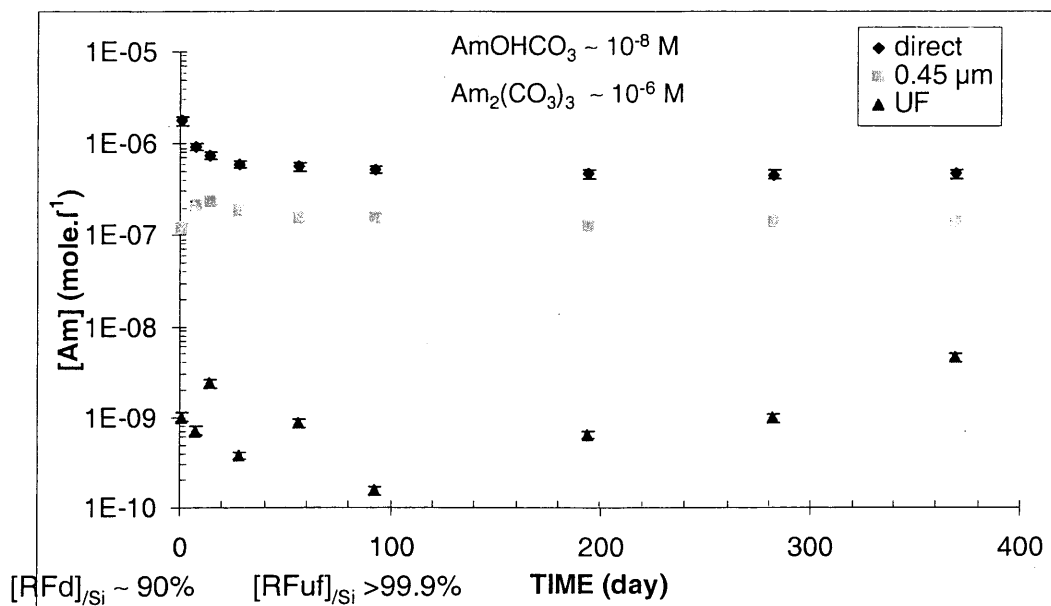


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Am concentrations - oxidizing medium

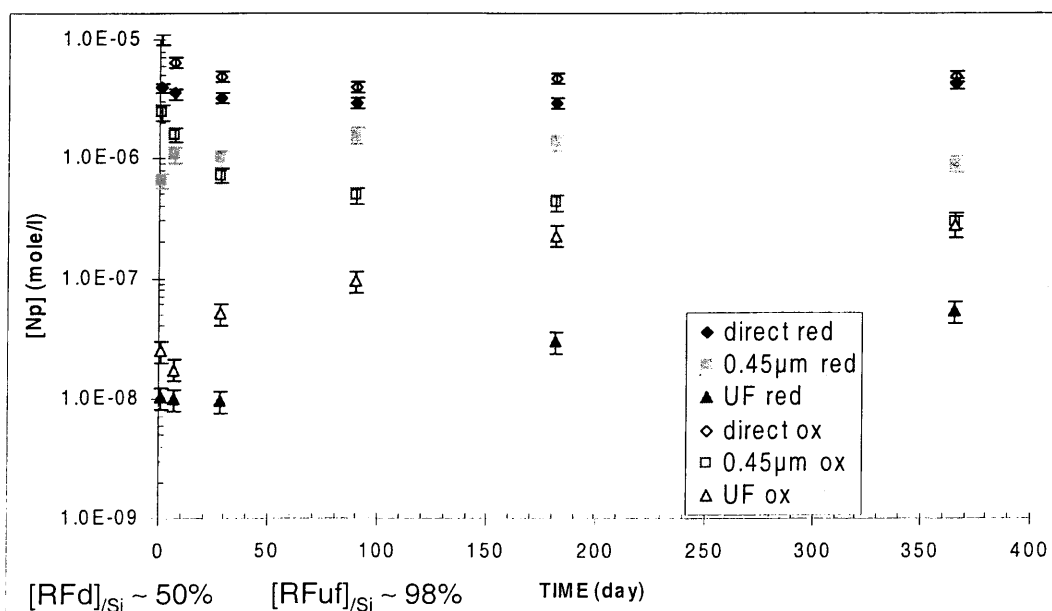


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Np concentrations - reducing medium

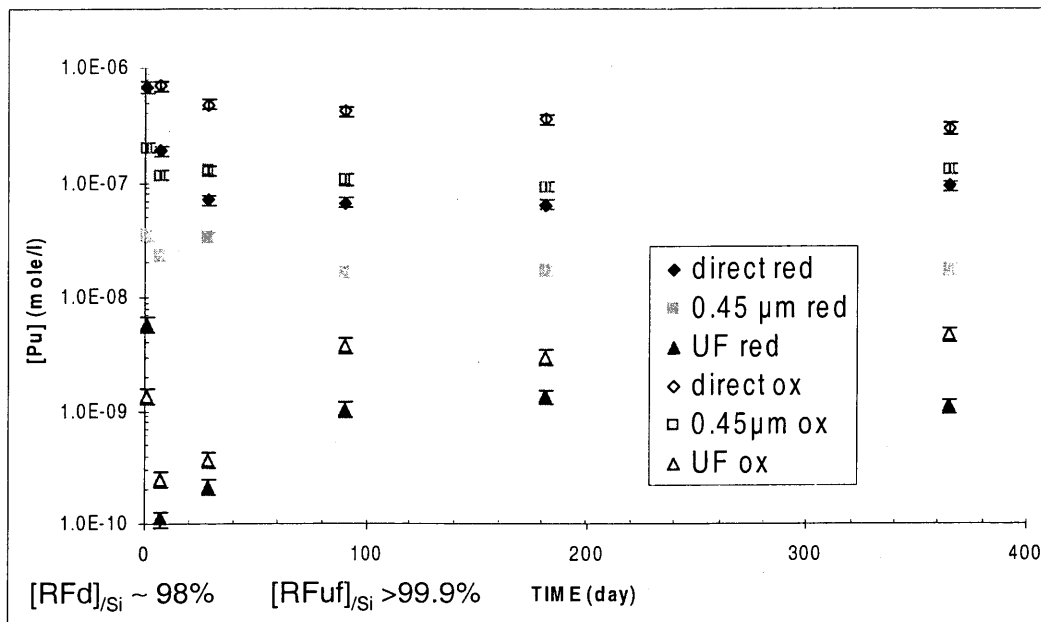


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Pu concentrations - reducing medium



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CONCLUSION

- ~ 50% of the amount of elements are released since 1 day
- Since 3 days, gels dissolution highly not congruent
- $r(\text{Li}) \approx 2 \text{ to } 5 \text{ } r(\text{Na})$ $r(\text{Cs}) \approx r(\text{Na})$
- $r(\text{Li}) \approx r(\text{Ca}) \approx 1 \text{ to } 10 \text{ } r(\text{Si})$ $r(\text{Na}) \approx r(\text{Si}) \approx 3 \cdot 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$
- dissolution rates of Am-doped gel greater than for other gels
- Gel formed at 90°C and altered at 50°C: $r(\text{Si}) \approx 10^{-5} \text{ g.m}^{-2}.\text{d}^{-1}$
- Crystallized phases dissolution and gel dissolution
- same behavior for La, Ce and Nd
- $\text{RF}(\text{Np}) < \text{RF}(\text{Pu}) < \text{RF}(\text{Am})$
- $[\text{Np}]_{\text{ox}} \approx 6 [\text{Np}]_{\text{red}}$
- $[\text{Pu}]_{\text{ox}} \approx 4 [\text{Pu}]_{\text{red}}$

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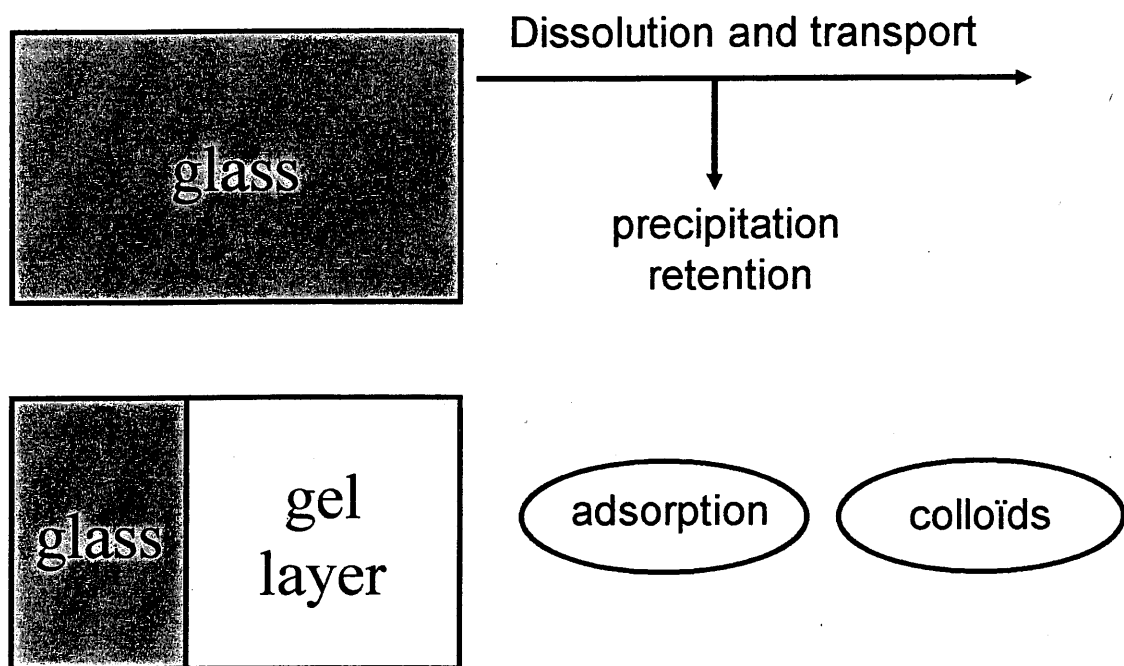
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Characterising the gels



Why is the characterization of these gels so important ?



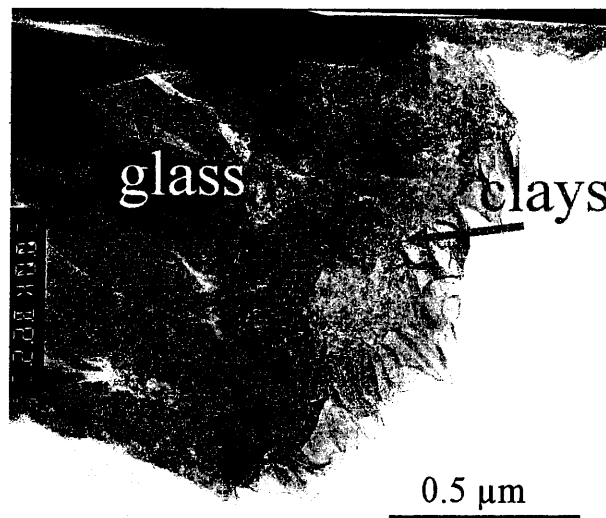
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2) Retention of radio elements





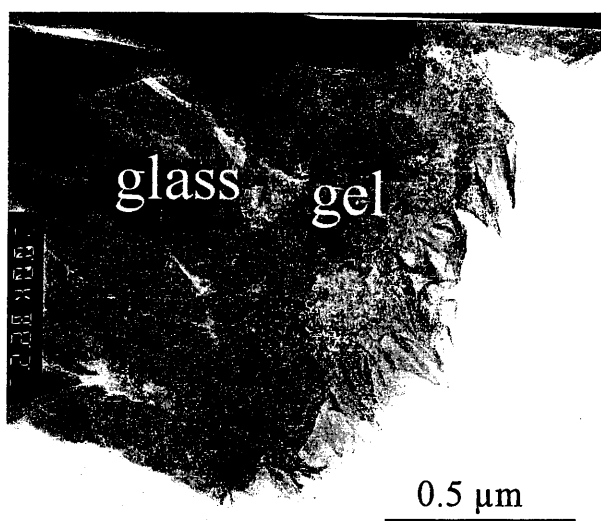
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1) Protective effect





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Study of alteration layers from basaltic glasses
CGS

WP1-1-2 WP1-2 (J.L. Crovisier)

Study of alteration layers from nuclear glasses
PSI – CGS

WP1-6 (E. Curti, J.L. Crovisier)

Diffusion through the layer

Basaltic glass WP1-1 (CEA, P. Berne)

Nuclear glass WP3-3 (SUBATECH, K. Ferrand)

In-situ irradiation

WP2-7-5 (SUBATECH, A. Abdelouas)

Gel stability

WP4-2 (CEA, S. Gin)



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WP1-2 Bibliographic survey of the effects of natural gels...

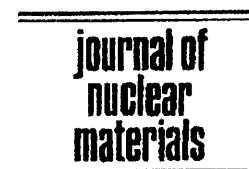


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Journal of Nuclear Materials 321 (2003) 91–109



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Review

Nature and role of natural alteration gels formed on the surface of ancient volcanic glasses (Natural analogs of waste containment glasses)

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^b CEA/VRH/DIEC, Service de Confinement des Déchets et Vitrification, Marcoule BP 17 171, 30207 Bagnol-sur-Cèze cedex, France

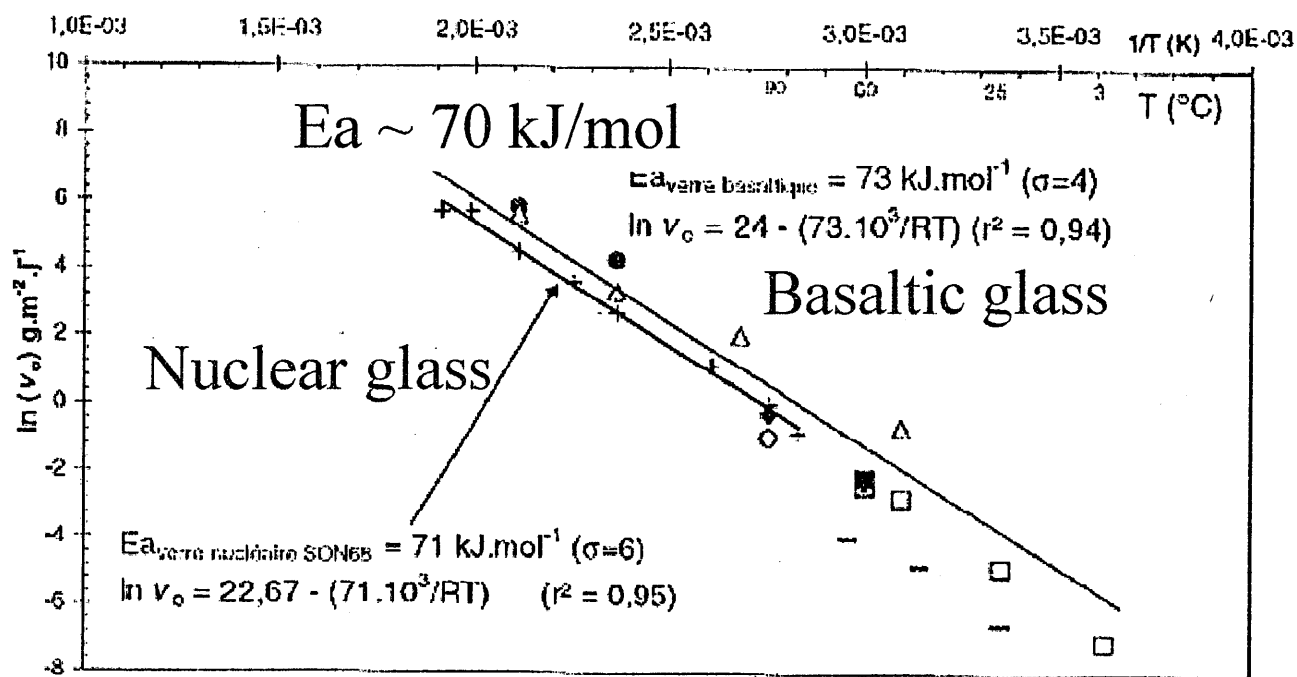
Received 22 July 2002; accepted 28 March 2003



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Techer, 1999

Verre basaltique	Verre SON
□ Crovisier <i>et al.</i> (1985)	± Delage and Dussossoy (1991)
x Alais (1989)	
○ Daux <i>et al.</i> (1997)	
— Gislason and Eugster (1987)	
△ Guy and Schott (1989)	
● Berger <i>et al.</i> (1994)	
■ Crovisier <i>et al.</i> (1989a)	
◆ Cette étude	



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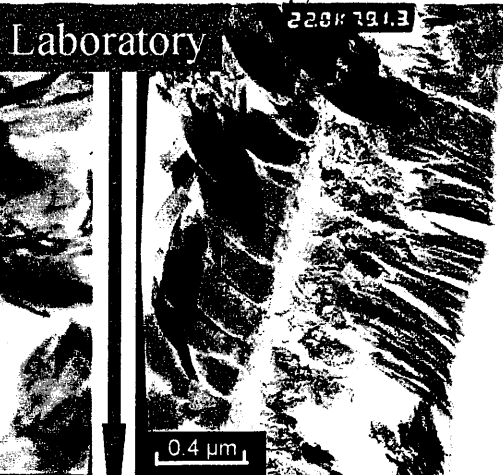


Basaltic glass

Nuclear glass

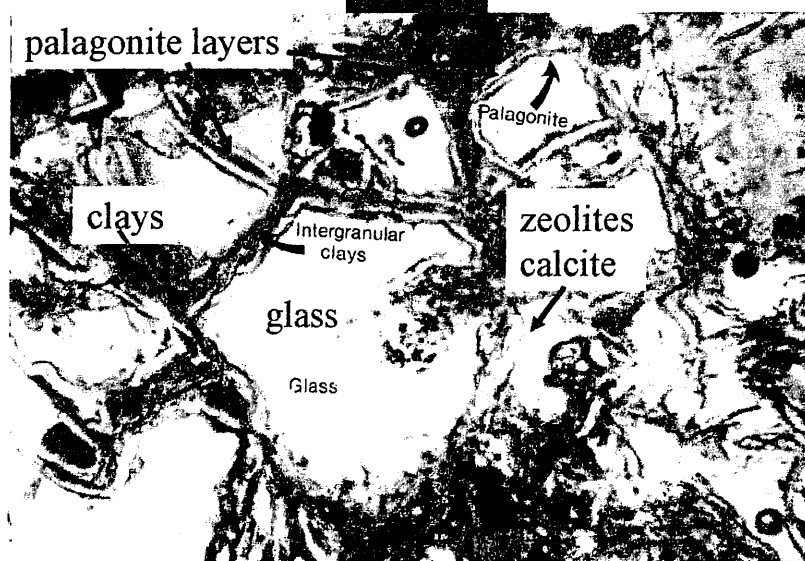


Crovisier 1985, 60°C, 120 days



Curti, 2001 MW glass

Field



GLASTAB Avignon, 29 & 30 octobre 2003

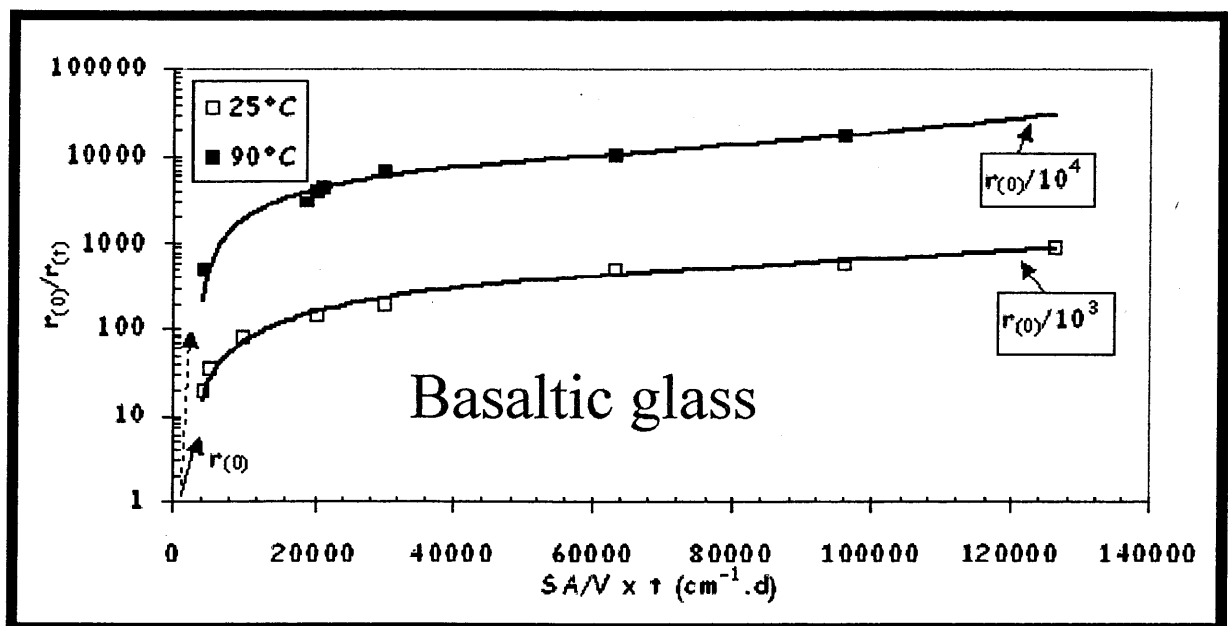
7



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Techer, 1999

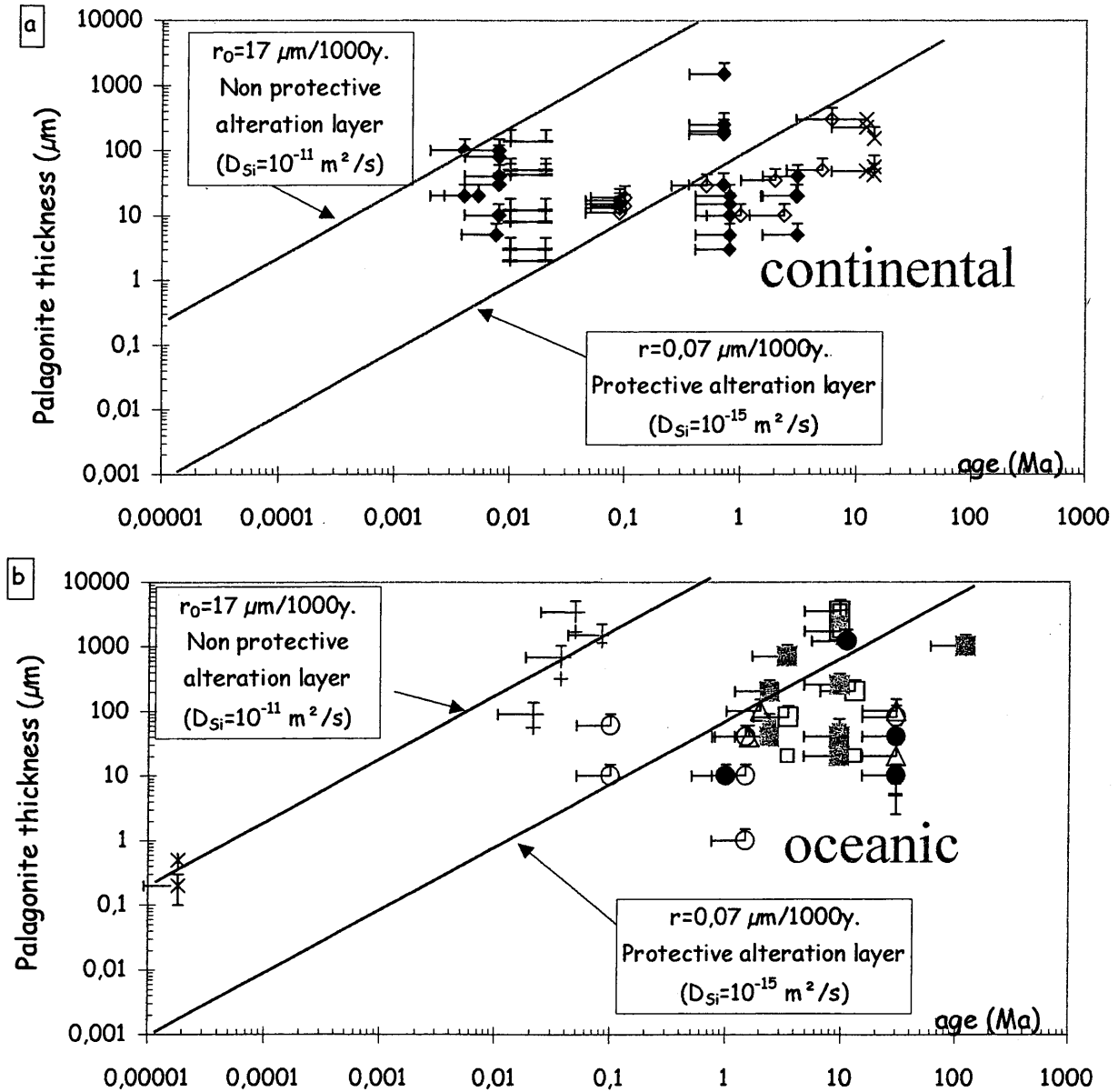


ECOLE ET OBSERVATOIRE DES SCIENCES DE LA TERRE

CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517)



STRASBOURG, FRANCE



Techer, 1999



ECOLE ET OBSERVATOIRE DES SCIENCES DE LA TERRE

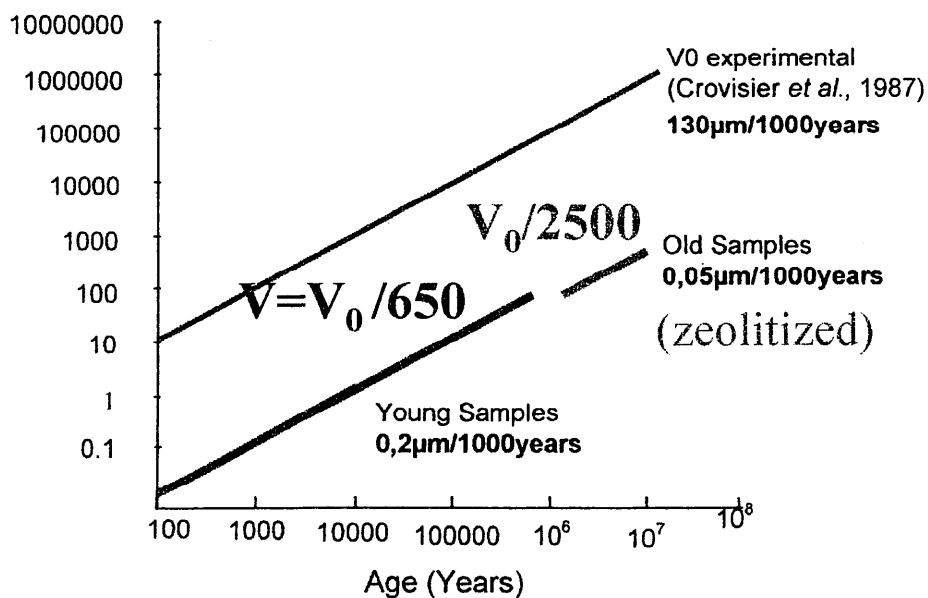
CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517)

STRASBOURG, FRANCE



Iceland (sub-glacial)

Thickness of alteration layer (μm)



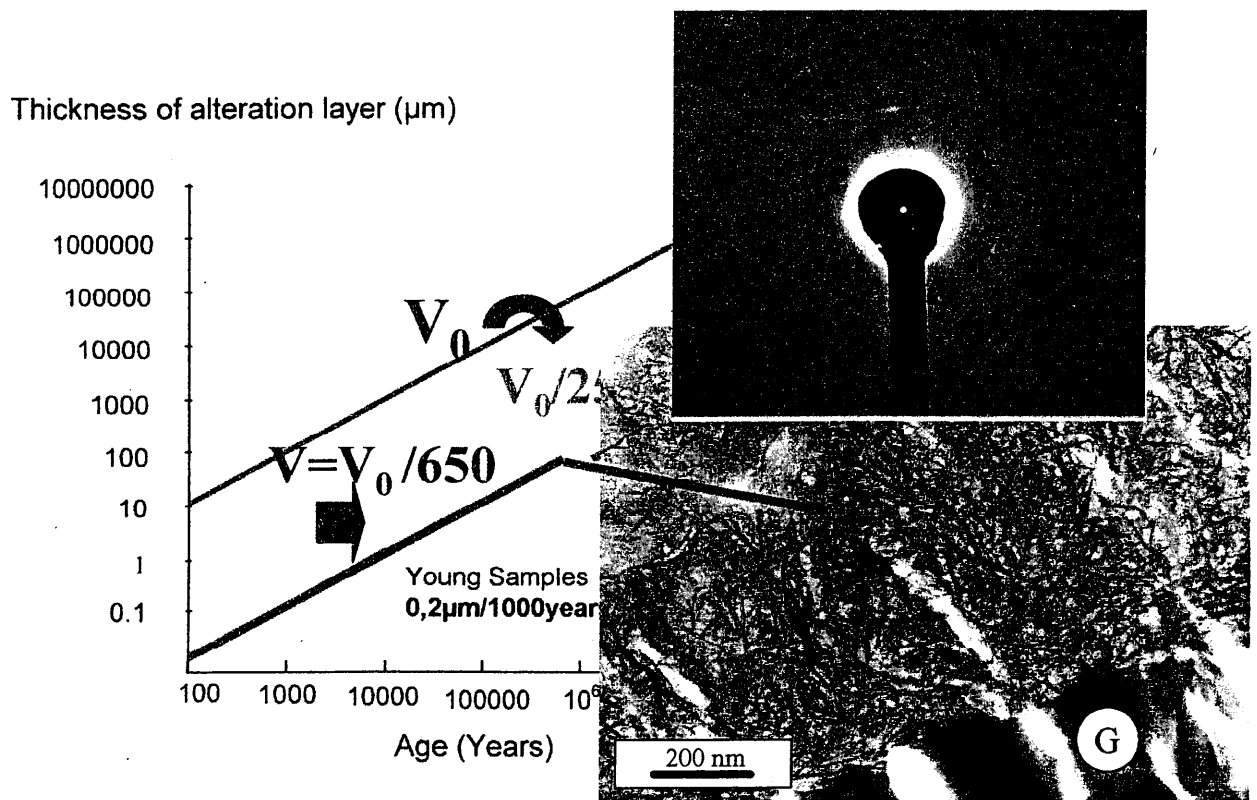
Le Gal, 1999



ECOLE ET OBSERVATOIRE DES SCIENCES DE LA TERRE

CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517)

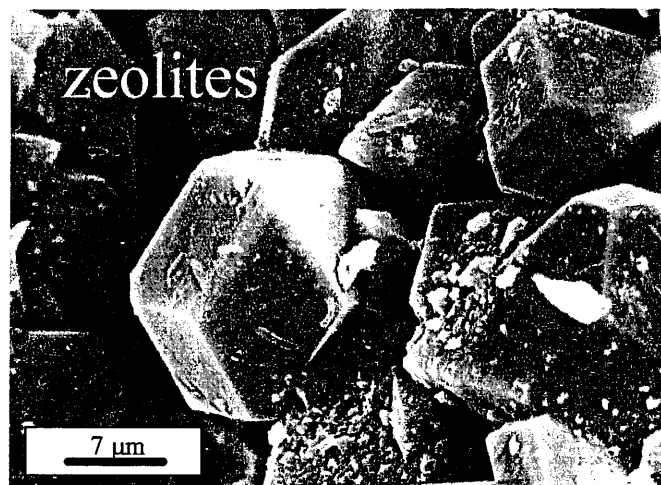
STRASBOURG, FRANCE



Le Gal, 1999

WP1-1 and 2

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E LA SURFACE (UMR 7517)

RG, FRANCE

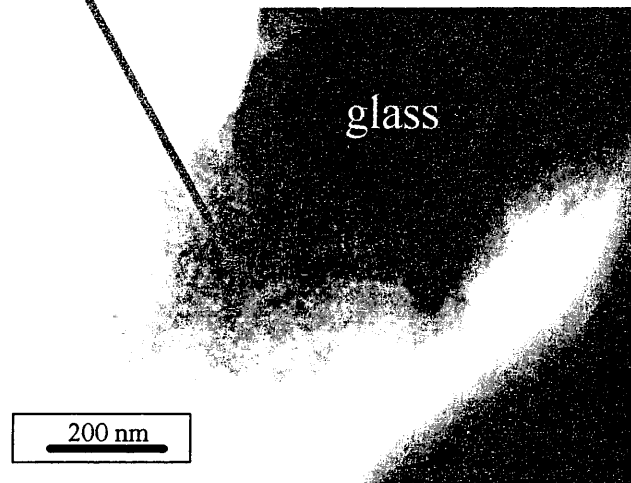
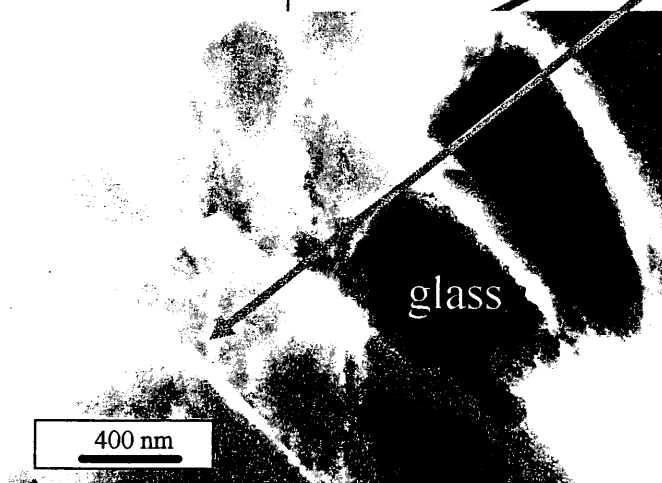
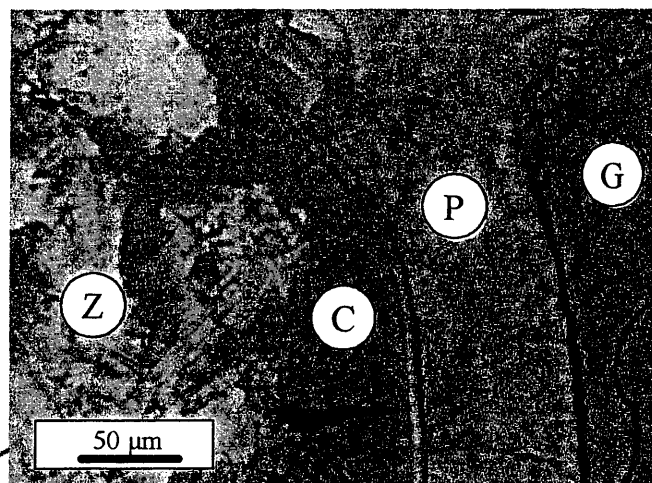
CNRS

Thickness of alteration layer (μm)

10000000
1000000
100000
10000
1000
100
10

$V_0/2500$

Old Samples
0,05 μm/1000 years
(zeolitized)



WP1-1 and 2

GLASTAB Avignon, 29 & 30 octobre 2003

12



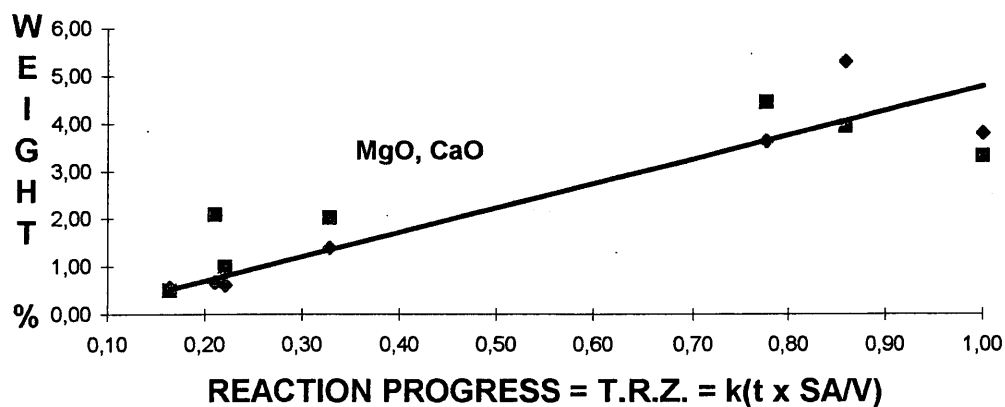
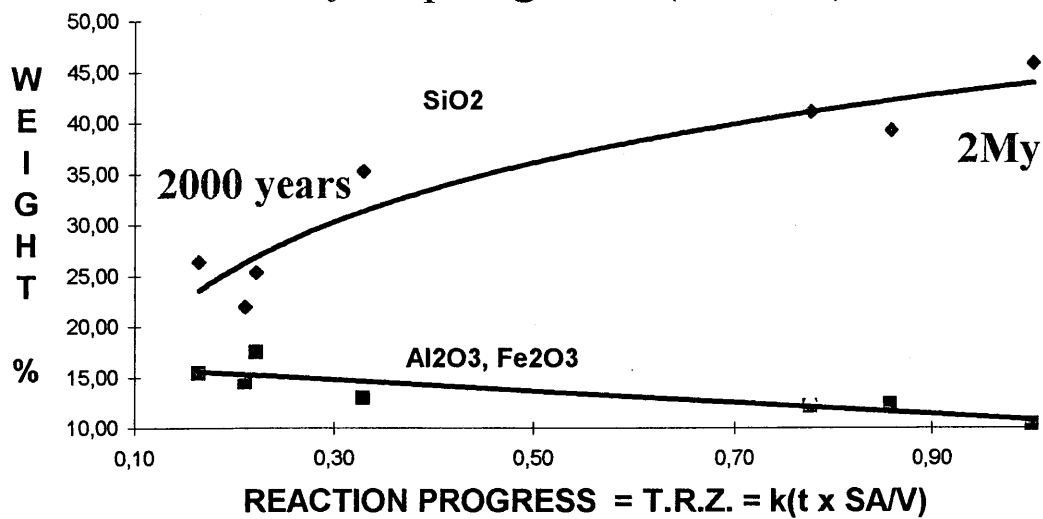
ECOLE ET OBSERVATOIRE DES SCIENCES DE LA TERRE

CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517)

STRASBOURG, FRANCE



Chemistry of palagonite (Iceland)





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CENTRE DE GEOCHIMIE DE LA SURFACE (UMR 7517)

STRASBOURG, FRANCE



Conclusions

1) Basaltic and nuclear glasses
have the same activation energy

2) Alteration layers are observed on the surface
of both glasses

➡ the composition and properties of palagonite
vary with time

➡ palagonite has an effect on the long term rate
(natural glasses may survive for millions of years
under subsurface conditions)

3) Palagonite may form
by coprecipitation of solubilized elements
or by interdiffusion processes



5.4 サイクル機構が実施した核種移行モデリング評価結果

Predictive Modelling of the Alteration of Alpha-doped SON68 Glass and the Radionuclide Leaching and Migration in the CORALUS In-situ Test

M.Yui, H.Makino, Y.Yoshida,
T.Jintoku and T.Ebina

JNC-Tokai, Japan



Objectives

- Blind prediction before dismantling and analyses
- Application of Japanese models and database used for H12 report
- glass : 1st order reaction rate + Si sorption on bentonite
- porewater chemistry : ion-exchange, surface complexation and dissolution of accessory minerals
- solubility : thermodynamic model by JNC-TDB
- sorption : minimum, maximum, mechanistic modelling
- diffusion : effective diffusivity
- transport model : diffusion, sorption and decay in 1D cylindrical geometry



Case for Analysis for CORALUS Experiments

Case1(Module A) : reference case (25°C, 1st order reaction rate, Boom clay porewater → solubility, sorption (minimum), diffusion from H12, Si Kd low)

Case2(↑) : Case1 except for Si Kd high

Case3(Module B) : Case1 except for Fo-Ca clay porewater → solubility

Case4(Module A) : Case1 except for 90°C → glass dissolution rate

Case5(↑) : Case1 except for sorption (maximum)

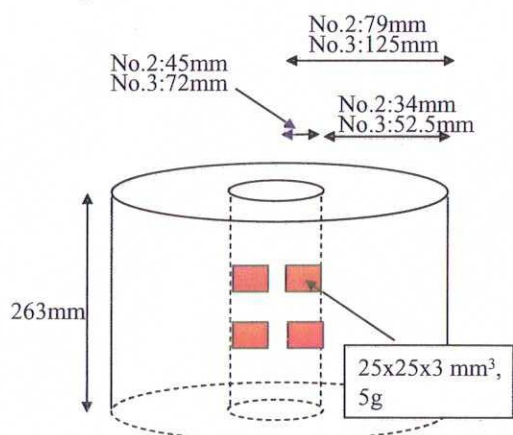
Case6(↑) : Case1 except for porewater under consideration of degassing → solubility

Case7(↑) : Case1 except for sorption (mechanistic sorption of Am)

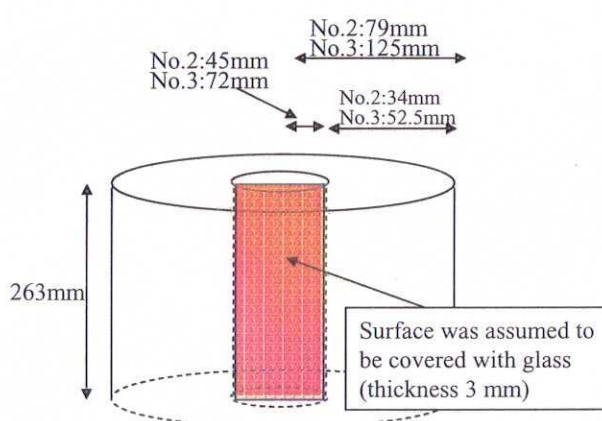


Experimental Design and Model of Geometry

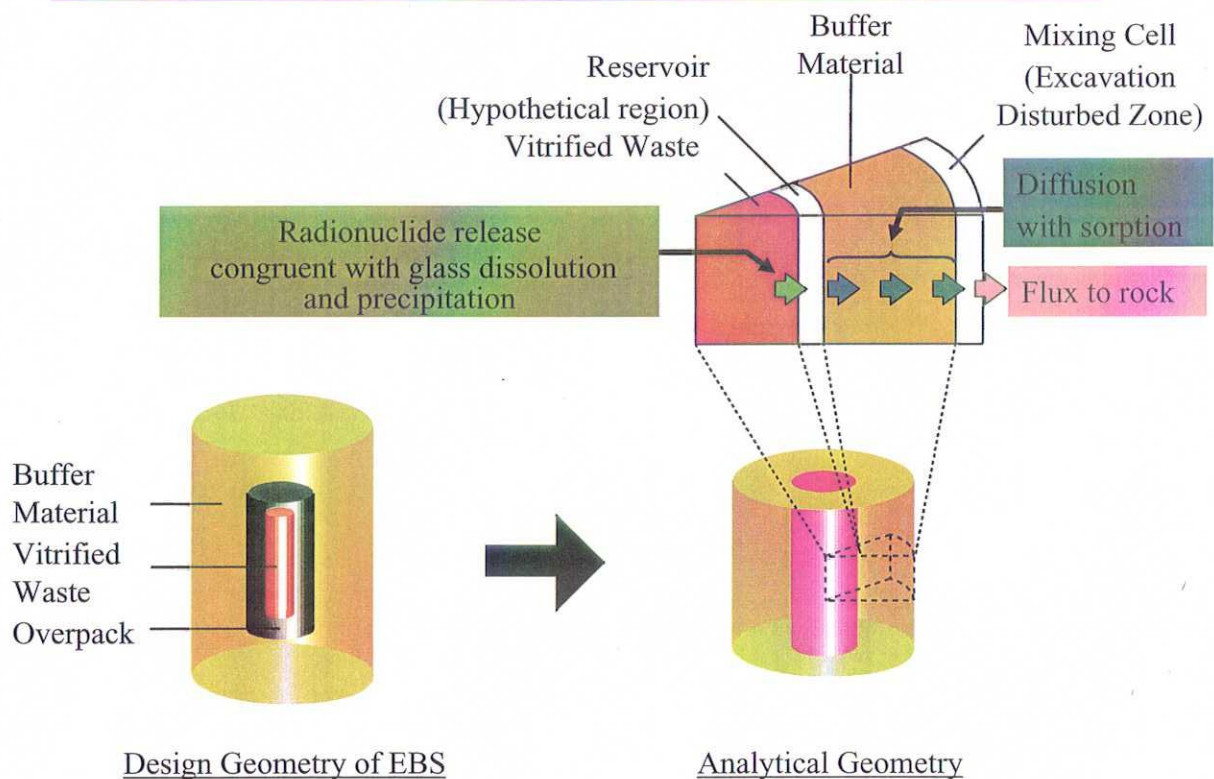
Experiment



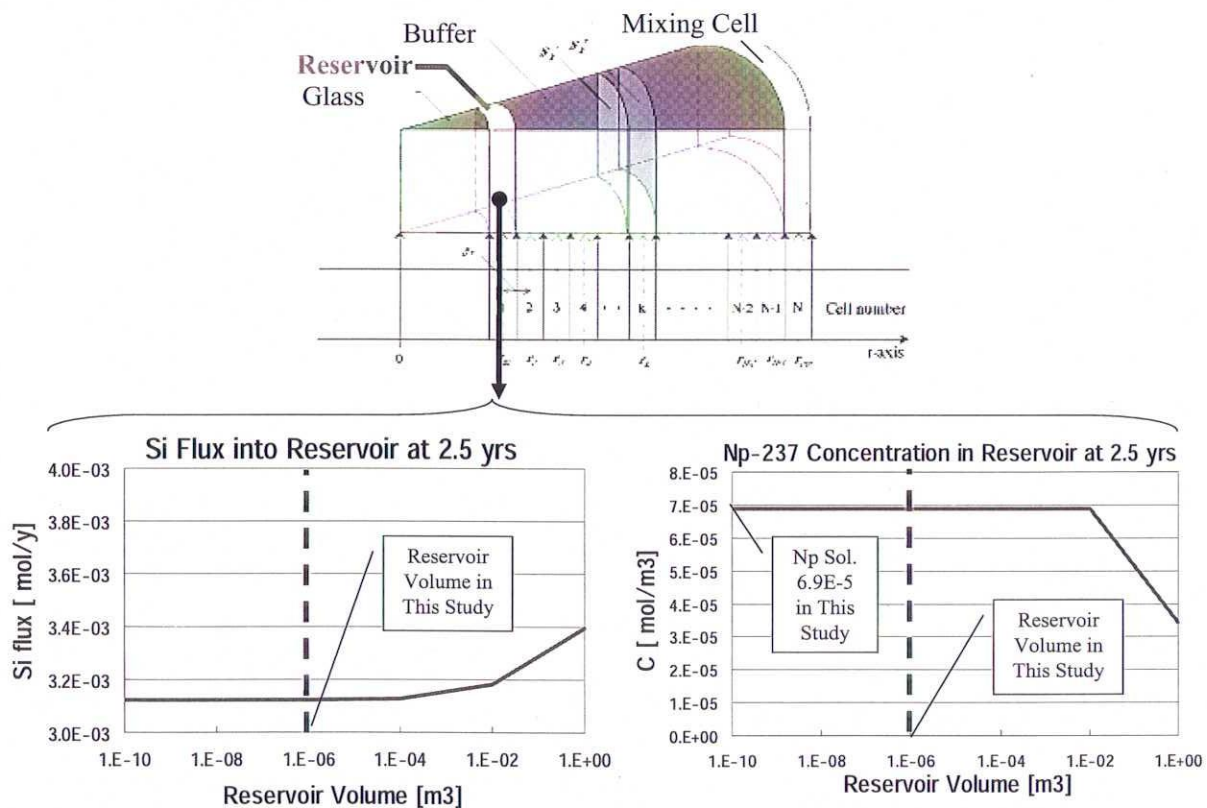
Model



Overview of Radionuclide Migration Code (MESHNOTE)

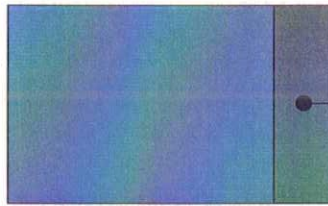


Concept and Treatment of Reservoir Cell in MESHNOTE



Glass Dissolution Models

Initial Stage



① Congruent dissolution $\propto k^+$ (constant)

② Congruent dissolution $\propto k^+(1-C/C_0)$
with Si transport in bentonite

③ Congruent dissolution $\propto k^+(1-C/C_0)$
without Si transport in bentonite

H_4SiO_4
Soluble elements
(Cs, ...)
Insoluble elements
(Actinides, ...)

Long-term

- Congruent dissolution $\propto \kappa_r$ (residual reaction rate)
- Congruent dissolution of $k^+(1-C/C_0)$ combined with diffusion in the altered layer
- Congruent dissolution of $k^+(1-C/C_0)$ for soluble elements and incongruent dissolution of $k_{RN} (1 - \frac{C_{RN}}{C_{O,RN}})$ for insoluble elements



Glass Dissolution Model and Parameters

Glass Dissolution:

+

Dissolved Silica Migration
through Clay Material

Glass Dissolution:

$$R = A \times k^+ \left(1 - \frac{C}{C^*}\right)$$

- R : Glass Dissolution Rate [g/d]
 A : Surface Area of Glass [m²]
 k⁺ : Initial Glass Dissolution Rate [g/m²/d] ($\Rightarrow$ Next Slide)
 C : Concentration of Dissolved Silica [mol/m³]
 C* : Solubility of SiO₂ (am) [mol/m³] (3.5 [mol/m³])

Dissolved Silica Migration through Clay Material

- Diffusion through Clay Material $\leftarrow D_p$ [m²/s] and Porosity
- Sorption on Clay Material $\leftarrow K_d$ [m³/kg] ($\Rightarrow$ Next Slide)

Parameters used in Glass Dissolution Model

k^+ [g/m²/d]: Initial Glass Dissolution Rate

Tube2: 0.0075 [g of SiO₂/m²/d] obtained by E-mail
 ↓ Conversion using 45.48wt% of SiO₂ in glass
 0.017 [g of glass /m²/d]

Tube3: 1.1 [g of glass /m²/d] at pH7.4
 Derivation using the equation obtained by E-mail and
 conversion using SiO₂ wt% in Glass

Kd [m³/kg] : Sorption on Clay Material

Case1 and Cases 3-7 : 0.01 [m³/kg] [1][2]

Case2 : 0.5 [m³/kg] [2]

[1]Karel Lemmens et al. (1996); The Corrosion of Nuclear Waste Glass in a Clay Environment : Mechanisms and Modelling, R-3092, Mol.

[2] Enzo Curti et al. (1993); Enhancement of the Glass Corrosion in the Presence of Clay Minerals : Testing Experimental Results with an Integrated Glass Dissolution Model, Mat. Res. Soc. Symp. Proc. Vol.294.

Porewater Chemistry

- Porewater modelling has two steps.
 - 1) EG/BS water modelling to derive Eh
 - 2) Porewater modelling
- Code and TDB

Code : PHREEQC ver. 2.3 (Parkhurst. D.L., 1995)

TDB : JNC-TDB (Yui et al., 1999)
- Constants (JNC, 2000) based on Japanese bentonite, Kunigel V1
 - Ion exchange reactions, K_{GT} : Gaines and Thomas selectivity coefficient

$2\text{ZNa} + \text{Ca}^{2+} = \text{Z}_2\text{Ca} + 2\text{Na}^+$	$\log K_{GT} = 0.69$
$\text{ZNa} + \text{K}^+ = \text{ZK} + \text{Na}^+$	$\log K_{GT} = 0.42$
$2\text{ZNa} + \text{Mg}^{2+} = \text{Z}_2\text{Mg} + 2\text{Na}^+$	$\log K_{GT} = 0.67$
$\text{ZNa} + \text{H}^+ = \text{ZH} + \text{Na}^+$	$\log K_{GT} = 1.88$
 - Surface complexation reactions

$\text{Surf_sOH} + \text{H}^+ = \text{Surf_sOH}_2^+$	$\log K(+) = 5.67$
$\text{Surf_sOH} = \text{Surf_sO}^- + \text{H}^+$	$\log K(-) = -7.92$
Site concentration	6.5e-5 mol/g
Specific surface area	29 m ² /g

Modelling of Porewater Chemistry

- Focal parameters : pH, Eh, HCO_3 , Si
- Module A (Case 1, 2, 4, 5 and 7)
 - Density : 1.88 kg/l, porosity : 0.296, CEC 2.27e-1 eq/kg (SCK-CEN, 2001)
 - Equilibrium with calcite and pyrite
 - Ion exchange and surface complexation reactions of Boom clay
- Module B (Case 3)
 - Density : 1.88 kg/l, porosity : 0.296, CEC 7.1e-1 eq/kg (SCK-CEN, 2001)
 - Equilibrium with calcite and gypsum
 - Ion exchange and surface complexation reactions of Fo-Ca clay
- Module C
 - Density : 1.62 kg/l, porosity : 0.327, CEC 7.1e-1 eq/kg (SCK-CEN, 2001)
 - Equilibrium with calcite and gypsum
 - Ion exchange and surface complexation reactions of Fo-Ca clay
 - Glass dissolution and $\text{SiO}_2(\text{am})$ precipitation (to be consistent with measured B concentration)
- Additional case (Case 6)
 - Degassing of $\text{CO}_2(\text{g})$ was additionally included for each module.

Mineral Composition of Backfill Materials

	Kunigel-V1 JNC (2000) [wt%]	Boom clay SCK-CEN (2001) [wt%]	Fo-Ca clay SCK-CEN (2001) [wt%]
Smectite	46 - 49	10 - 20	40 - 50 Montmorillonite FeMg 30 Beidellite FeMg 40 Beidellite Fe 30
Illite		20 - 30	
Chlorite		5 - 20	
Illite / smectite mixed layer		5 - 10	
Chlorite / smectite mixed layer		5 - 10	
Kaolinite		20 - 30	50 - 60
Quartz	0.5 - 0.7	20	5 - 7
Chalcedony	37 - 38		
Feldspar	2.7 - 5.5		
K-feldspar		5 - 10	
Calcite	2.1 - 2.6	present	1.2 - 1.6
Dolomite	2.0 - 2.8	present	
Siderite		present	
Ankerite		present	
Analcime	3.0 - 3.5	present	
Goethite			5 - 7
Hematite			0.2
Gypsum			0.4
Pyrite	0.5 - 0.7	1 - 5	
Organic carbon		1 - 5	0.1

CEC and Initial Cation Distribution

	Kunigel-V1 JNC (2000)	Boom clay SCK-CEN (2001)	Fo-Ca clay SCK-CEN (2001)
CEC [meq/100g]	60.1	22.7	71
Initial cation distribution [eq %]			
ZNa [eq%]	86	37	5
Z ₂ Ca	12		85
ZK	1	16	1
Z ₂ Mg	1.2	48	9

Results of Porewater Chemistry Modelling

	EG/BS water	Module A			Module B			Module C		
	Measured	Measured (average)	Calculated	Calculated (Degassing)	Measured (average)	Calculated	Calculated (Degassing)	Measured (average)	Calculated	Calculated (Degassing)
pH	8.2	7.8	7.425	8.298	8.3	6.626	7.510	7.8	6.644	7.370
Eh mV	-274	-300	-229	-293	-280	-147	-209	-60	-148	-199
C	1.4e-2	1.1e-2	3.8e-2	2.9e-3	3.0e-3	7.1e-3	5.1e-4	1.8e-3	6.8e-3	7.2e-4
Ca	1.0e-4	7.4e-3	2.5e-4	3.4e-4	6.3e-3	1.4e-2	1.8e-2	1.0e-2	1.4e-2	1.8e-2
Fe	1.6e-5	7.7e-5	1.2e-7	5.2e-8	3.1e-5	1.6e-5*	1.6e-5*	7.2e-6	1.6e-5*	1.6e-5*
K	2.9e-4	4.5e-3	8.5e-3	9.9e-3	6.1e-4	8.5e-4	1.0e-3	6.0e-4	8.5e-4	1.0e-3
Mg	1.2e-4	6.8e-3	3.6e-3	4.1e-3	6.8e-4	1.5e-3	1.9e-3	6.7e-5	1.5e-3	1.9e-3
Na	1.8e-2	8.6e-2	5.0e-2	5.7e-2	2.2e-2	1.1e-2	1.2e-2	3.5e-2	1.0e-2	1.2e-2
S	2.1e-6	4.4e-2	2.4e-7	1.0e-7	1.3e-2	1.9e-2	1.5e-2	1.8e-2	1.9e-2	1.5e-2
Si	1.8e-4	3.6e-4	1.8e-4*	1.8e-4*	4.2e-4	1.8e-4*	1.8e-4*	2.6e-3	1.9e-3	1.9e-3
Case	-	-	Case 1, 2, 4, 5 and 7	Case 6	-	Case 3	-	-	-	-

* Not modelled

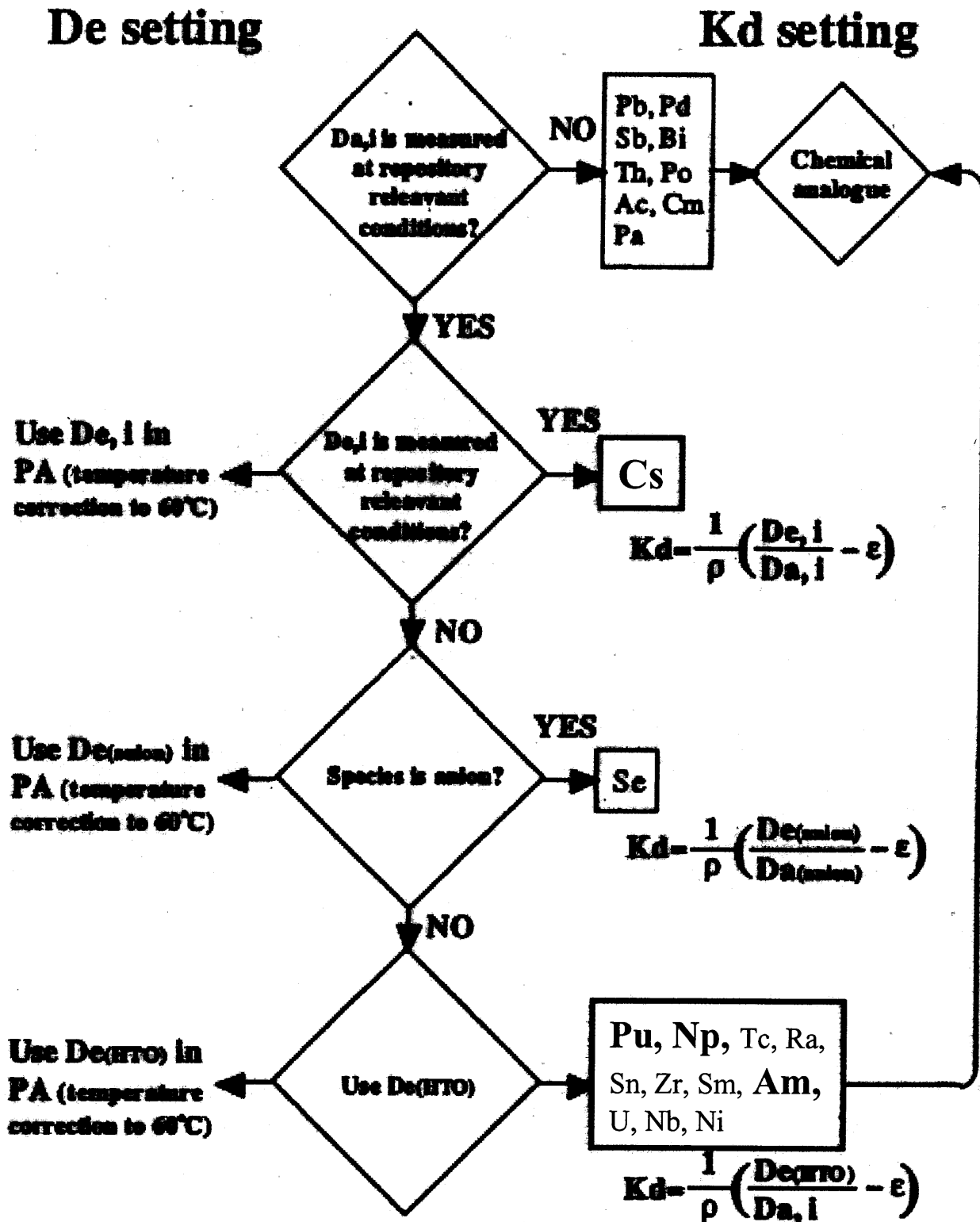
Solubility

Solubility limiting solid phases : amorphous or hydroxide

Code : PHREEQC (Parkhurst, D.L., 1995)

TDB : JNC-TDB (Yui et al., 1999)

	Module A	Module A (Degassing)	Module B	Module C
Np Solid	NpO₂(am)	NpO₂(am)	NpO₂(am)	NpO₂(am)
Dominant species	Np(OH) ₂ (CO ₃) ₂ ²⁻	Np(OH) ₂ (CO ₃) ₂ ²⁻	Np(OH) ₂ (CO ₃) ₂ ²⁻	Np(OH) ₂ (CO ₃) ₂ ²⁻
Solubility	6.9e-8	4.2e-10	1.4e-9	1.3e-9
Pu Solid	PuO₂(am)	PuO₂(am)	PuO₂(am)	PuO₂(am)
Dominant species	Pu(CO ₃) ₂ ⁻ , PuCO ₃ ⁺	Pu(CO ₃) ₂ ⁻ , PuCO ₃ ⁺ , Pu(OH) ₂ ⁺	PuCO ₃ ⁺ , Pu ³⁺	PuCO ₃ ⁺ , Pu ³⁺
Solubility	9.9e-7	2.4e-9	1.2e-7	1.2e-7
Am Solid	AmOHCO₃(cr)	AmOHCO₃(cr)	AmOHCO₃(cr)	AmOHCO₃(cr)
Dominant species	Am(CO ₃) ₂ ⁻ , AmCO ₃ ⁺	Am(CO ₃) ₂ ⁻ , AmCO ₃ ⁺ , Am(OH) ₂ ⁺	AmCO ₃ ⁺ , Am ³⁺	AmCO ₃ ⁺ , Am ³⁺
Solubility	1.7e-8	2.0e-9	4.9e-8	4.7e-8
Modelling case	Case 1, 2, 4, 5 and 7	Case 6	Case 3	-



Procedure to Select Kd Values for H12 Report

Kd Values for H12 Report

element	Kd Values (m ³ /kg)		Remarks
	min.	max.	
Np	1	50	Diffusion data under reducing conditions exist.
Pu	10	100	Diffusion data under reducing conditions do not exist. Kd is much larger than other actinides.
Am	10	50	Diffusion data exist. Mechanistic modelling is possible.
Cs	0.01	0.05	Mechanistic modelling is possible.

Mechanistic Sorption Model for Am and Cs (1)

- Kd values for Am, Cs were calculated based on ion exchange / surface complexation model for module A and B
- Code and TDB
 - Code : PHREEQC ver. 2.3 (Parkhurst. D.L., 1995)
 - TDB : JNC-TDB (Yui et al., 1999)
- Results
 - Sorption coefficient for Am
 - Module A : 3.4 m³/kg
 - Module B : 5.0 m³/kg
 - Sorption coefficient for Cs
 - Module A : 6.2e-2 m³/kg
 - Module B : 1.5e-1 m³/kg

Mechanistic Sorption Model for Am and Cs (2)

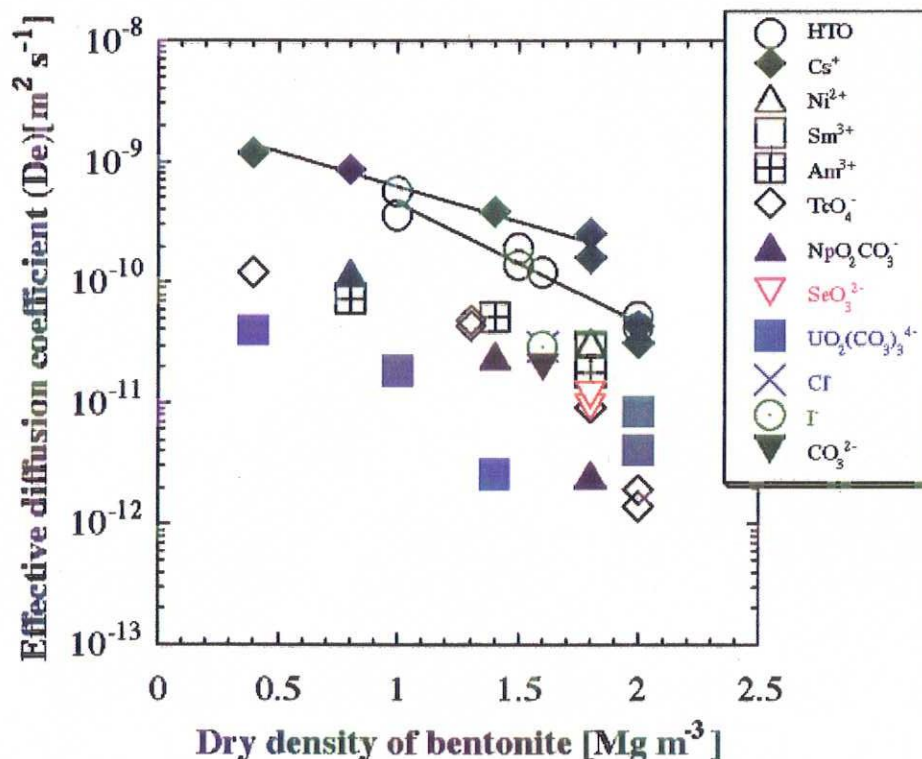
- Constants

■ Ion exchange reactions, K_{GT} : Gaines and Thomas selectivity coefficient

$2\text{ZNa} + \text{Ca}^{2+} = \text{Z}_2\text{Ca} + 2\text{Na}^+$	$\log K_{GT} = 0.69$	JNC(2000)
$\text{ZNa} + \text{K}^+ = \text{ZK} + \text{Na}^+$	$\log K_{GT} = 0.42$	JNC(2000)
$2\text{ZNa} + \text{Mg}^{2+} = \text{Z}_2\text{Mg} + 2\text{Na}^+$	$\log K_{GT} = 0.67$	JNC(2000)
$\text{ZNa} + \text{H}^+ = \text{ZH} + \text{Na}^+$	$\log K_{GT} = 1.88$	JNC(2000)
$2\text{ZNa} + \text{Am}^{3+} = \text{Z}_2\text{AmOH} + 2\text{Na}^+$	$\log K_{GT} = -2.6$	Lothenbach and Ochs (2000)
$3\text{ZNa} + \text{Am}^{3+} = \text{Z}_3\text{Am} + 3\text{Na}^+$	$\log K_{GT} = 2.28$	Lothenbach and Ochs (2000)
$\text{ZNa} + \text{Cs}^+ = \text{ZCs} + \text{Na}^+$	$\log K_{GT} = 1.60$	Lothenbach and Ochs (2000)

■ Surface complexation reactions

$\text{Surf_sOH} + \text{H}^+ = \text{Surf_sOH}_2^+$	$\log K(+) = 5.67$	JNC(2000)
$\text{Surf_sOH} = \text{Surf_sO}^- + \text{H}^+$	$\log K(-) = -7.92$	JNC(2000)
$\text{Surf_sOH} - \text{H}^+ + \text{Am}^{3+} = \text{Surf_sAm}^{2+}$	$\log K = 0.23$	Lothenbach and Ochs (2000)
Site concentration	$6.5\text{e-}5 \text{ mol/g}$	JNC(2000)
Specific surface area	$29 \text{ m}^2/\text{g}$	JNC(2000)



Effective Diffusion Coefficients
as a Function of Bentonite Dry Density under Oxidizing Conditions

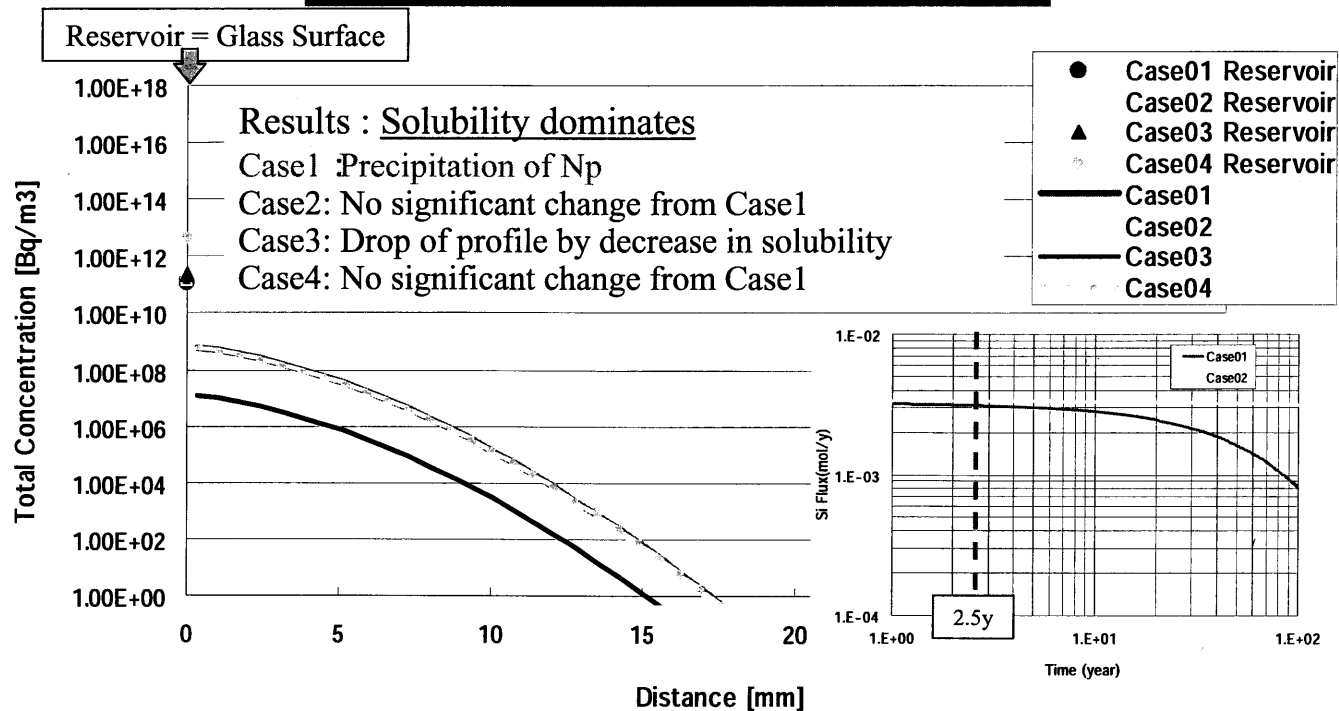
Transport Parameters for Each Case

Item		Case						
		1	2	3	4	5	6	7
Module/Tube No.		A/2		B/2	A/3			
Temp. (°C)		30			90			
Solubilities (mol/l)	Am	1.7E-8		4.9E-8			2.0E-9	
	Pu	9.9E-7		1.2E-7			2.4E-9	
	Pa	1.1E-8		1.1E-8			1.1E-8	
	Np	6.9E-8		1.4E-9			4.2E10	
	Cs	soluble		soluble			Soluble	
Kd (m ³ /kg)	Am	10				50		3.4
	Pu	10				100		
	Pa	1				20		
	Np	1				50		
	Cs	0.01				0.05		
Dp (m ² /s)	Am	2.9E-10						
	Pu	2.9E-10						
	Pa	2.9E-10						
	Np	2.9E-10						
	Cs	6.6E-10						
Ben- tonite	Porosity	0.30						
	Dry Density (kg/m ³)	2890						
Glass k ⁺ (g/m ² /d)		0.017			1.1			
Si	Solubility (mol/l)	3.5E-3						
	Kd (m ³ /kg)	0.01	0.5					
	Dp (m ² /s)	2.9E-10						

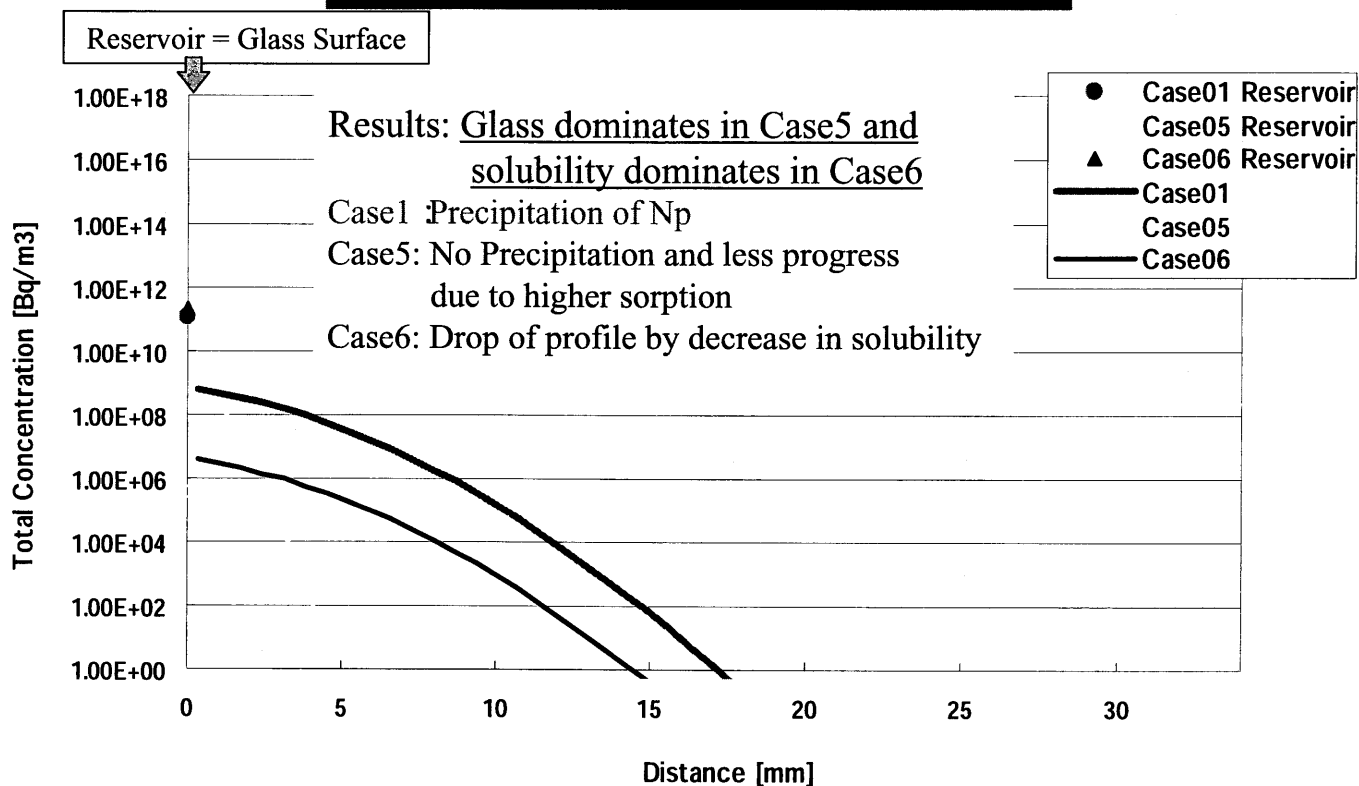
Geometry, Volume, Weight for Each Case

Item	Case							
	1	2	3	4	5	6	7	8
Buffer Geometry (Height/Inner/Outer)	263/ 45/ 79			263/ 72.5/ 125				
Number of cell	50			77				
Mixing cell flow (m ³ /y)	0							
Mixing cell volume (m ³)	1E-3							
Glass surface area (m ²)	0.074			0.12				
Glass volume (m ³)	2.2E-4							
Glass weight (g)	580							
Initial amount of Si (mol)	4.4							
Reservoir volume (m ³)	1E-6							

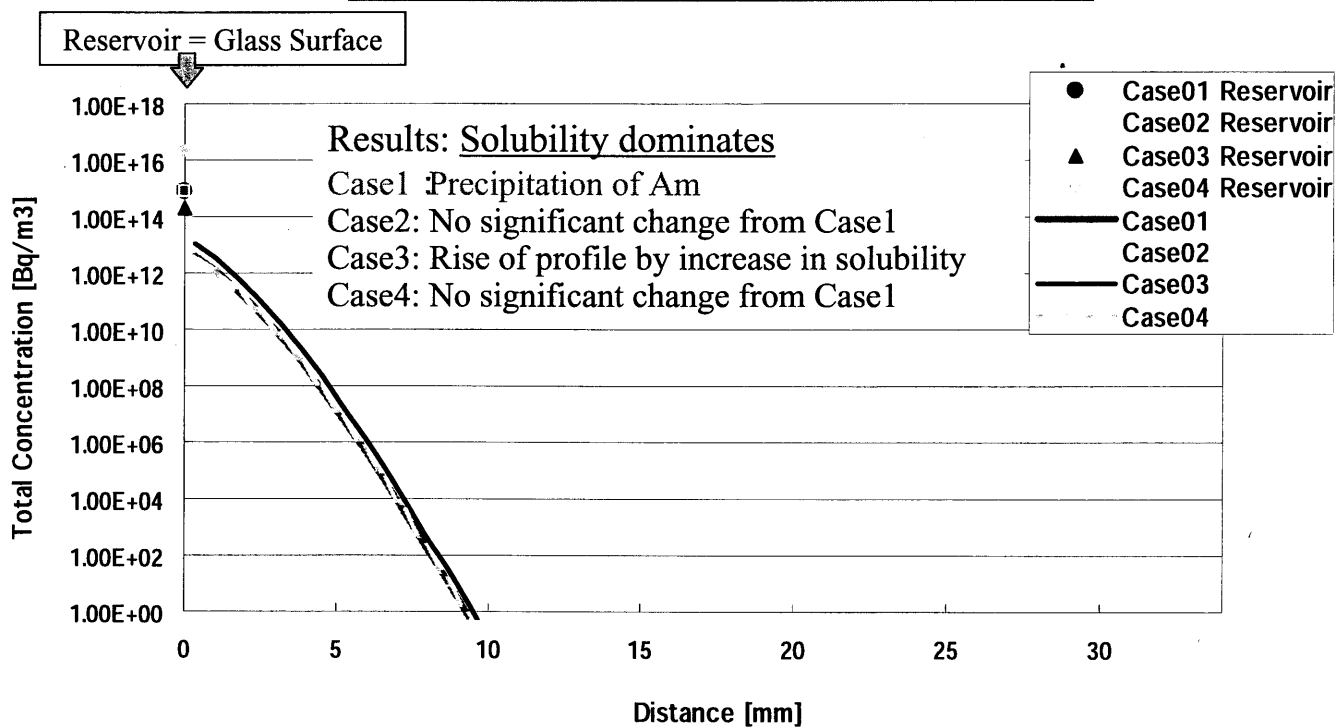
Concentration Profile at 2.5 years <Np Dope Glass : Np237>



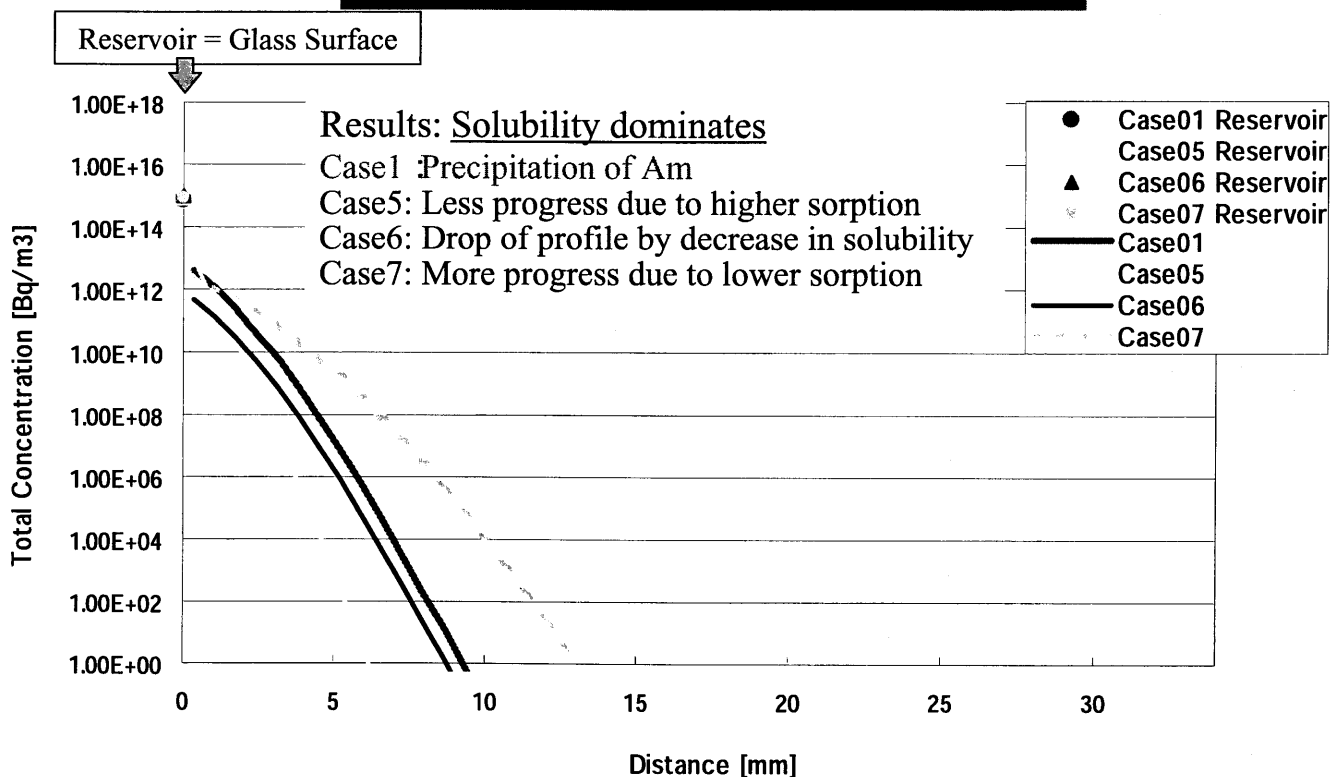
Concentration Profile at 2.5 years <Np Dope Glass : Np237>



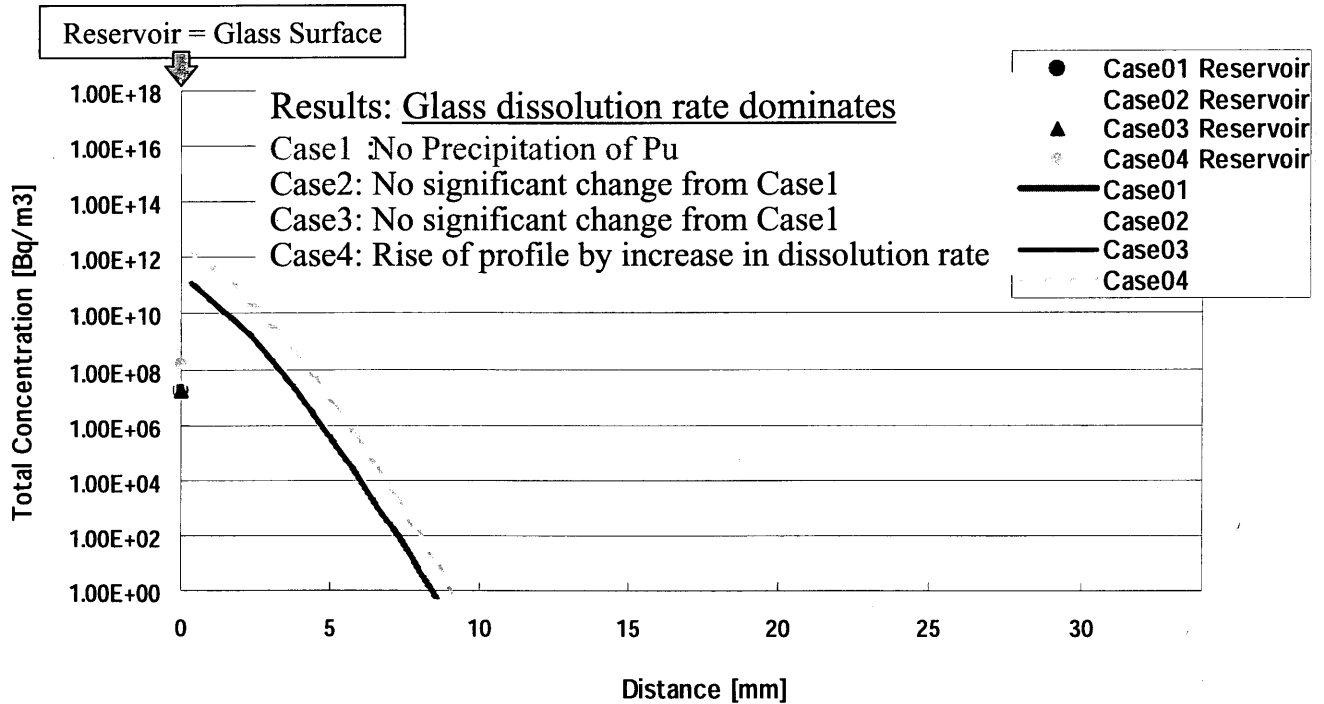
Concentration Profile at 2.5 years <Am Dope Glass : Am241>



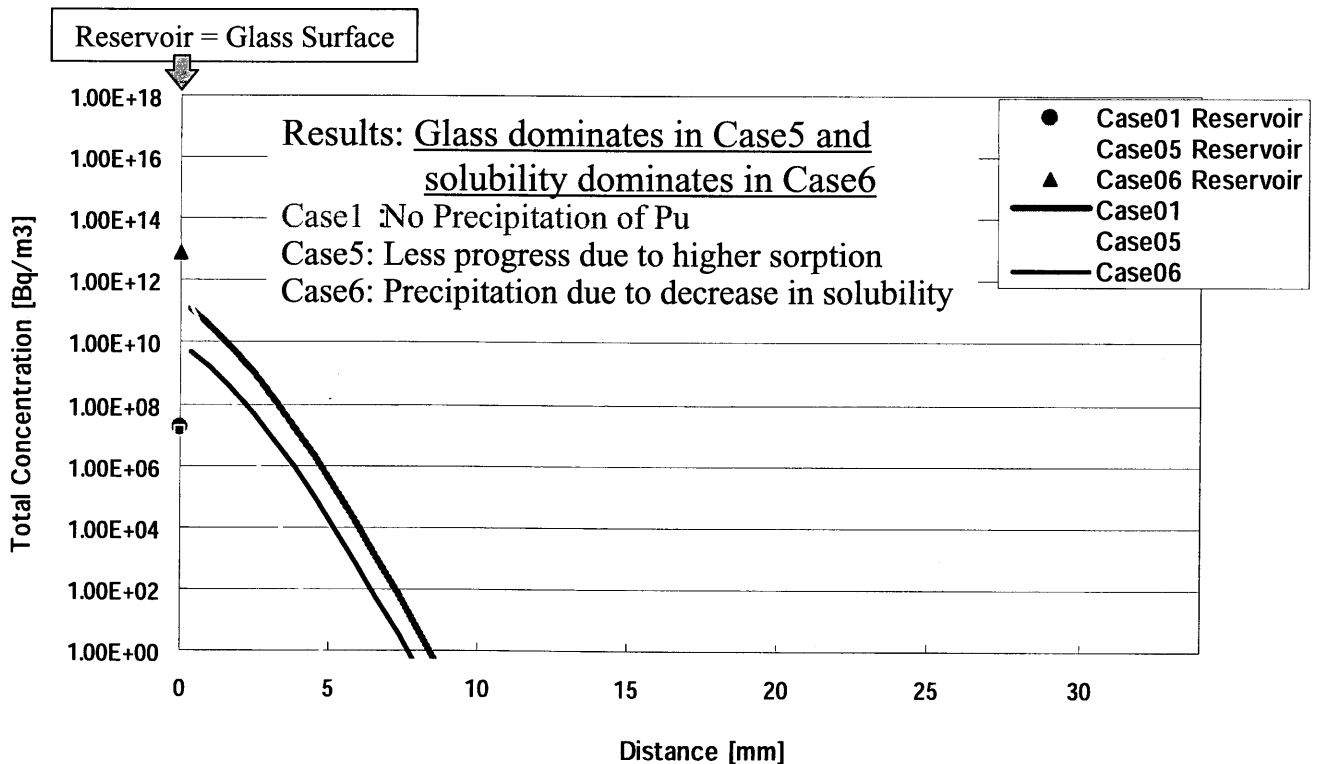
Concentration Profile at 2.5 years <Am Dope Glass : Am241>



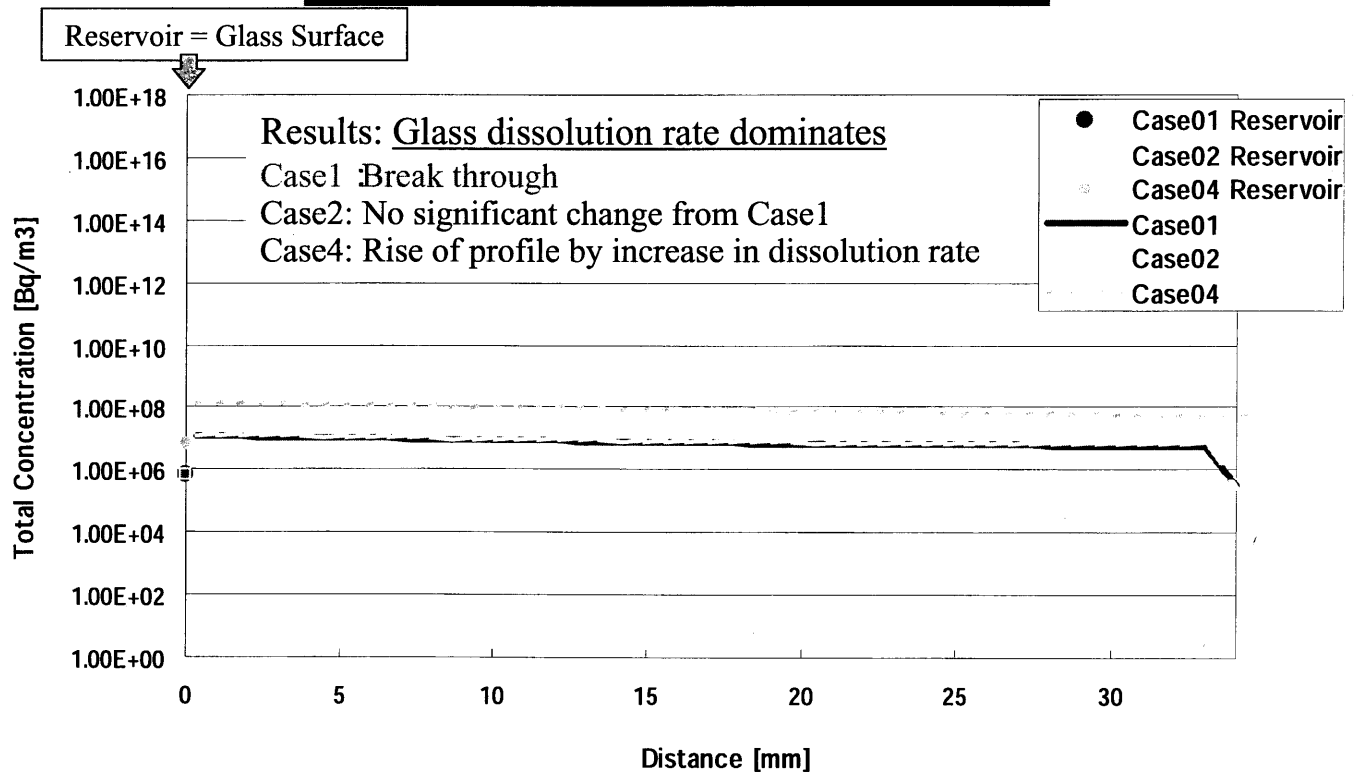
Concentration Profile at 2.5 years <Pu Dope Glass : Pu238>



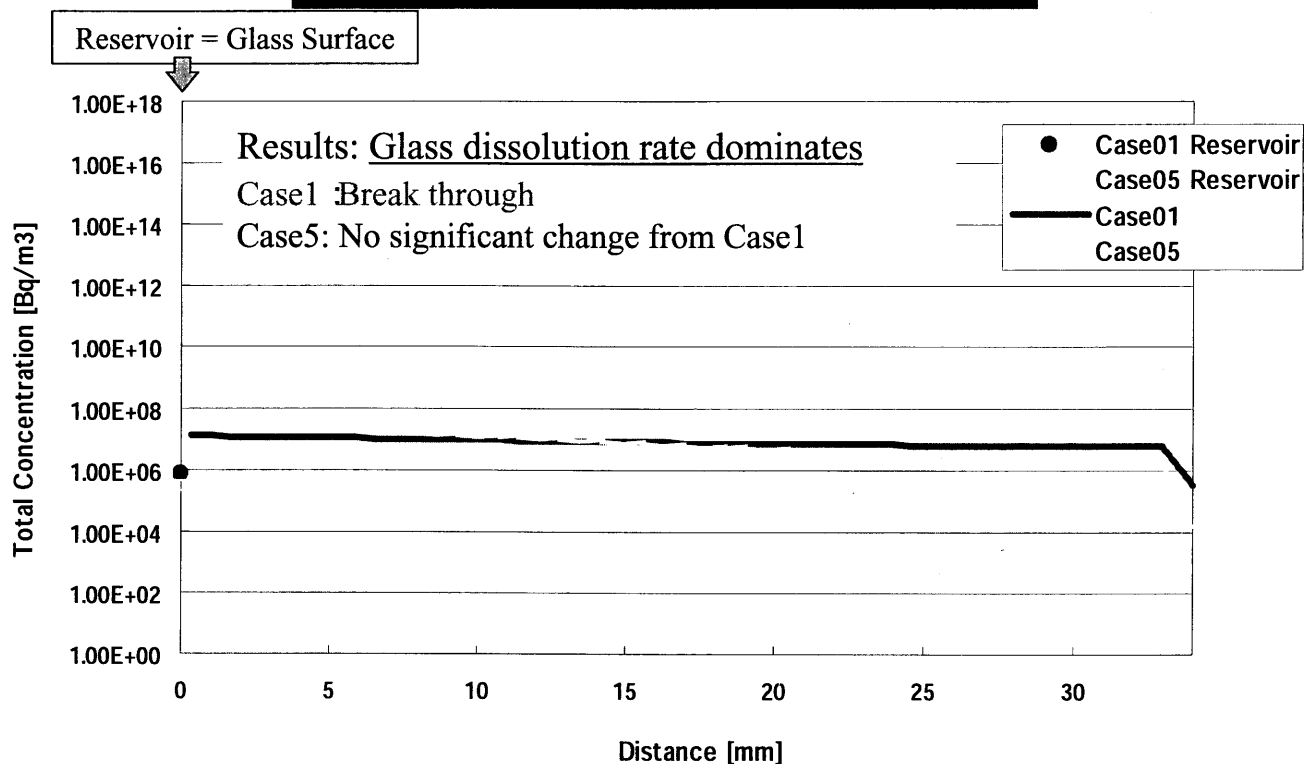
Concentration Profile at 2.5 years <Pu Dope Glass : Pu238>



Concentration Profile at 2.5 years <Am Dope Glass : Cs137>



Concentration Profile at 2.5 years <Am Dope Glass : Cs137>



Discussion

1. Porewater chemistry :

- Surface characteristics of clay minerals in buffer material are needed .
- Analyzing of porewater chemistry outside the system should be corrected based on geochemical modelling.

2. Glass dissolution :

- Alteration diffusion barrier should be included.
- Incongruent dissolution for insoluble element, e.g., actinides has to be discussed.

3. Solubility :

- Real solubilities are needed in highly compacted bentonite by both modelling and diffusion measurement.



Discussion

4. Sorption :

- Relevant diffusion studies should be reviewed to derive real K_d values.
- Mechanistic sorption modeling is not possible for Pu, Np due to a lack of data for actinides (IV). If reducing condition is confirmed, K_d values for Pu are the same as those of Am (III) because Pu redox state is likely III.

5. Diffusion :

- Mechanistic prediction of effective diffusivity for each element is possible if the porewater chemistry is confirmed.

6. Initial / Boundary Condition :

- Experimental geometry is very complex and sampling / analysis is needed not to be affected by another glass samples.



Conclusion

- Blind predictions before dismantling and analyses have been conducted by using H12 models and database, but it's likely sensitivity analysis.
 - Si sorption on bentonite not significant
 - glass dissolution rate not so sensitive even if no precipitation
 - solubility limit for Am, Np, but not for Pu, Cs
 - Cs profile almost broke through
 - actinides migration detected up to 5~10 mm after 2.5 yrs, but strongly dependent on detection limit



CORALUS Meeting
October 30, 2003

JNC Topics Related to CORALUS Project

K. Kawamura and M. Yui
JNC-Tokai



Bentonite – Water Interaction

■ Dominant Reaction

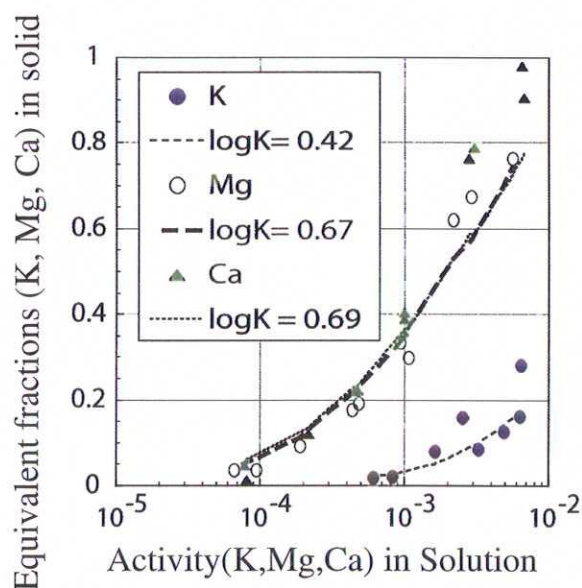
- Mineral equilibrium (e.g. chalcedony, calcite, pyrite)
- Ion exchange of smectite
- Protonation/deprotonation of smectite

■ Difficulties in Experiments

- Application of model derived from batch type experiments to highly compacted bentonite system (microstructure effects on porewater chemistry)



Cation exchange isotherm for purified Na-smectite



- Thermodynamical expression (Gaines & Thomas, 1953) successfully covers the experimental isotherms for exchange reactions of Na-K, Na-Mg and Na-Ca.

- Selectivity coefficients are derived:

$$\log K_{G\&T}(\text{Na-Ca}) = 0.69$$

$$\log K_{G\&T}(\text{Na-Mg}) = 0.67$$

$$\log K_{G\&T}(\text{Na-K}) = 0.42$$

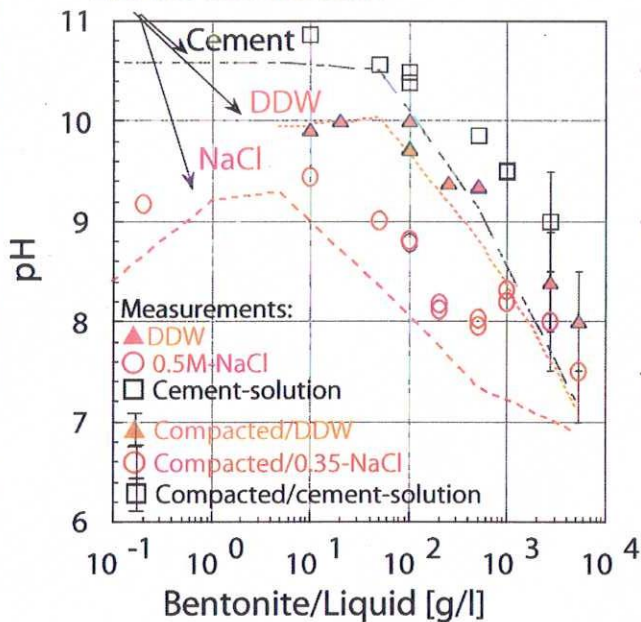
Experimental conditions:

the liquid/smectite ratio 100ml/g, the reaction time 48hrs,
the ionic strength 0.1, at room temperature

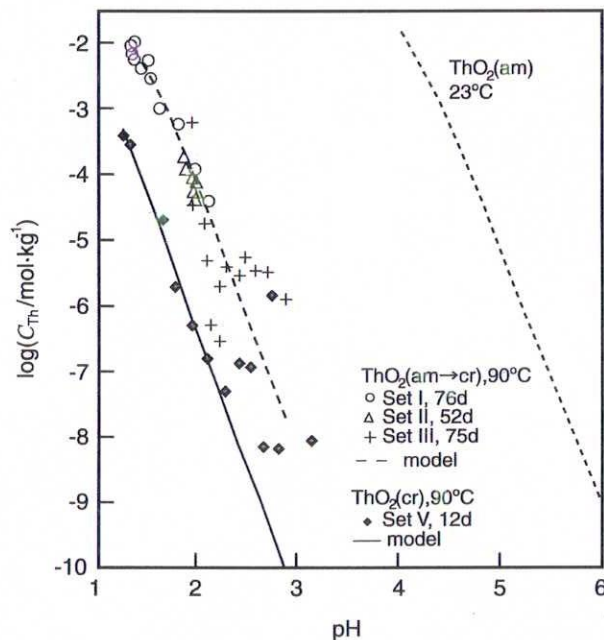


Modeling result - pH

Model calculations

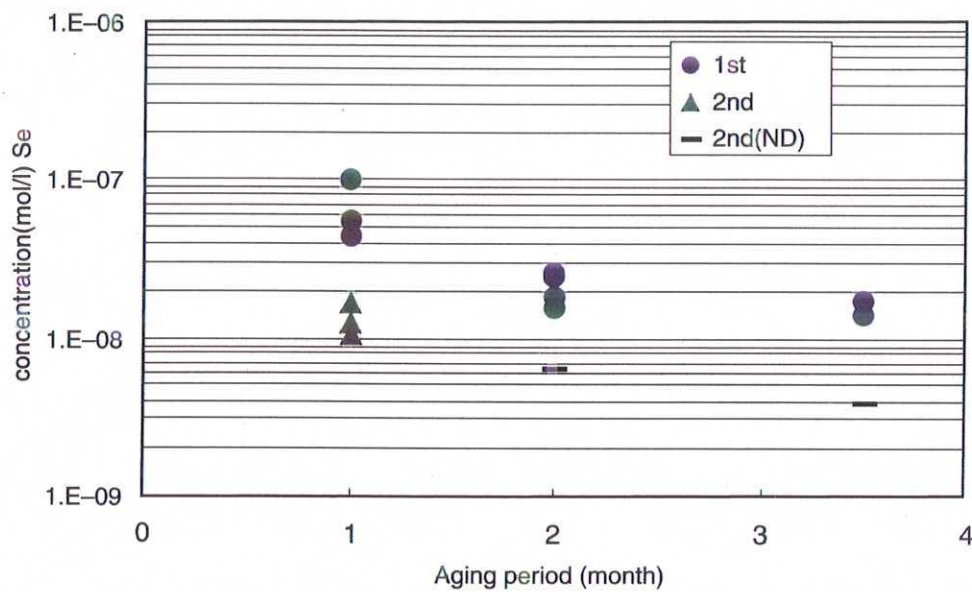


- ▼ The pH trends with B/L can be reproduced qualitatively by the model including the edge sites
- ▼ It is suggested that the surface deprotonation is one of the most dominant reactions at high B/L
- ▼ The model, quantitatively, tends to estimate pH even lower at higher B/L



Experimental ThO₂(am→cr) and ThO₂(cr) solubilities in 0.1M NaCl at 90°C. ThO₂(am→cr) data are for sample Sets I to III that were originally equilibrated at 23°C and then equilibrated at 90°C. The lines represent predicted solubilities of various Th solid phases.

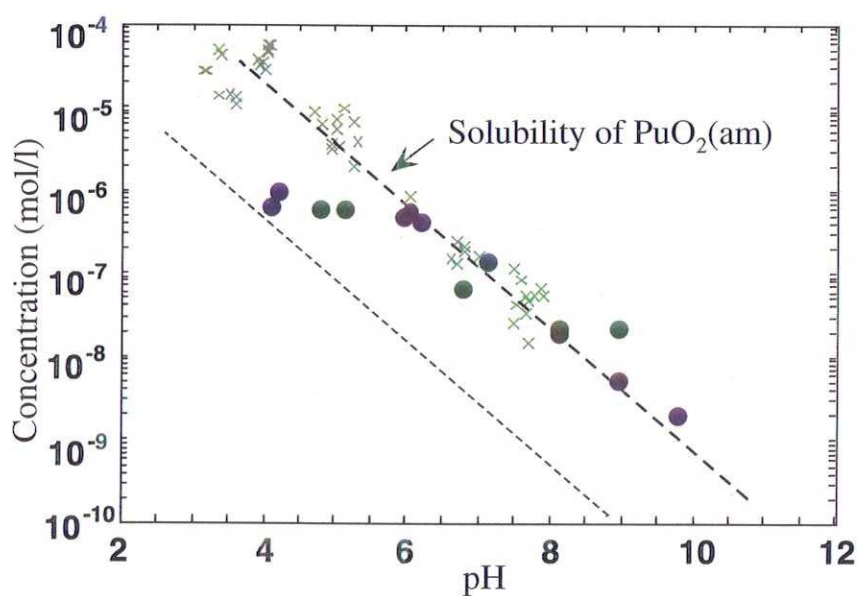




Se concentration as a function of time in two types of experiments
(1st : with bentonite, 2nd : Fe-Se system , ND means detection limit of ICP-MS)



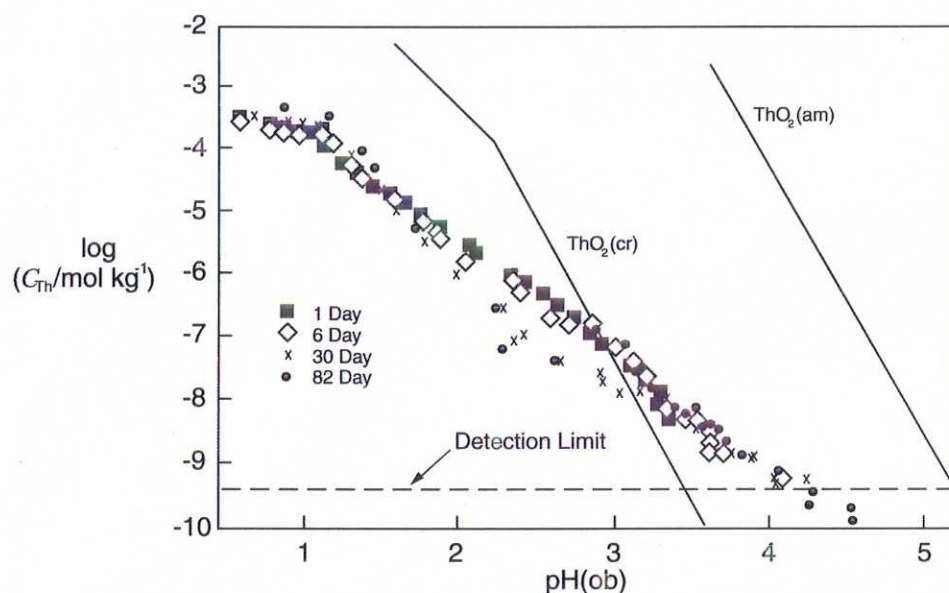
Solubility Measurements by Using Pu-doped Glass



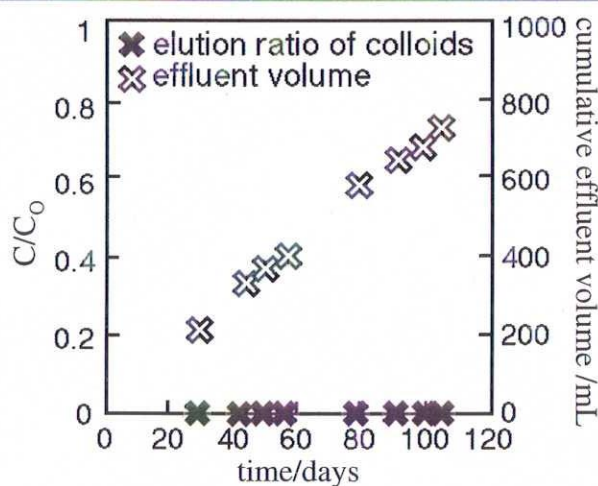
● ; Experimental results of leaching experiment with crushed Pu-doped glass
 × ; Solubility Measurements of $\text{PuO}_2(\text{am})$ (Rai et al. 1980)



Aqueous Th concentration in glass/water suspensions



Colloidal Transport through the Compacted Sand-Bentonite Mixture



C : Eluted colloids concentration
 C_0 : Injected colloids concentration (70ppm)

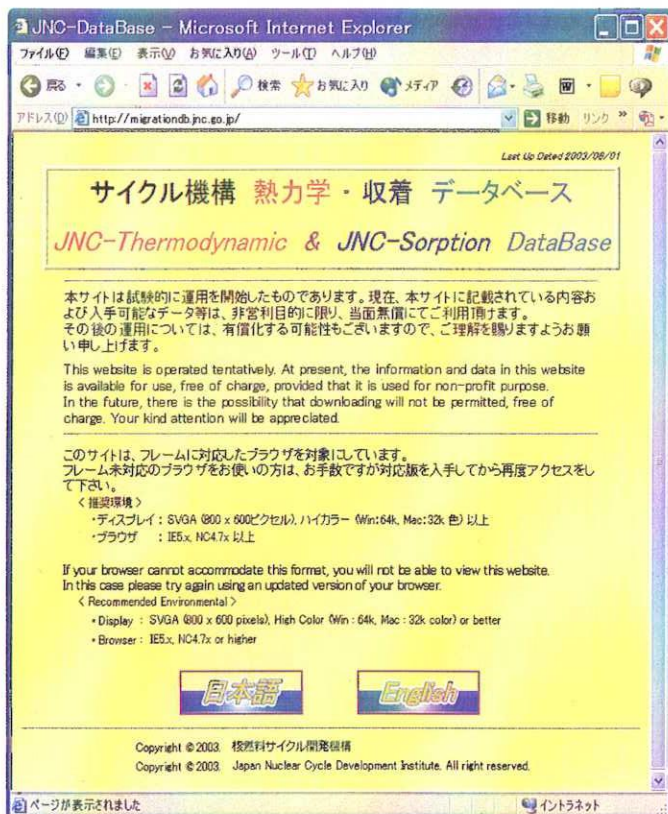
Fig.

Colloid filtration by compacted sand-bentonite mixture containing 50wt.% sand and saturated with 0.5M NaCl solution at dry density 1800kg/m^3 (Kurosawa S., et al., 1996)



5.5 サイクル機構のデータベース紹介

Information of JNC TDB/SDB WEB site



JNC Thermodynamic and Sorption Database (JNC TDB/SDB) website is open to the public (1st of August 2003).

The address of website is
<http://migrationdb.jnc.go.jp/>.

JNC TDBs are available for the Geochemical codes *PHREEQE*, *PHREEQC*, *Geochemists' Work Bench* and *EQ3/6*.

Before downloading any database, you need registration to use the database.

5.6 ガラス溶融炉用耐火物の特性比較

ER 2161

THE MATERIAL

INTRODUCTION

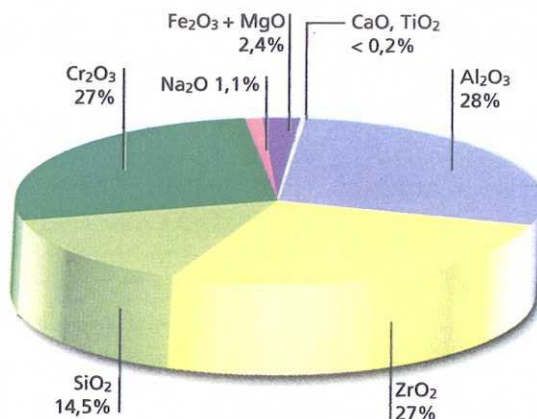


Fused cast material with Alumina-Zirconia-Silica-Chromium Oxide.

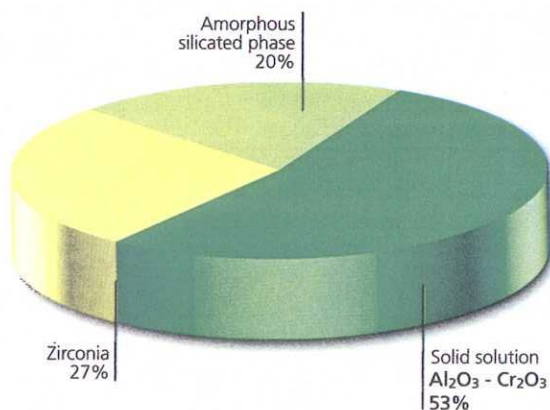
Using the RT casting process, this material makes rectangular shapes or other simple shapes.

ER 2161 can be used with practically all colored, flint or white glass. In the case of special glasses, please contact the SEPR Sales Engineers.

TYPICAL CHEMICAL COMPOSITION



TYPICAL CRYSTALLOGRAPHIC ANALYSIS



PHYSICAL CHARACTERISTICS

TRUE SPECIFIC GRAVITY	4110 kg/m ³
COLD CRUSHING STRENGTH	3.5. 10 ⁶ Pa (3500 kg/cm ²)
REFRACTORINESS UNDER LOAD OF 2. 10 ⁵ Pa	> 1750°C



BEHAVIOR IN USE

CORROSION RESISTANCE RATINGS IN THE PRESENCE
OF VARIOUS GLASS COMPOSITIONS:

	A	B	C	D
ER 1681	100	100	100	100
ER 1685	110	110	110	110
ER 1711	130	130	130	130
ER 2161**	340	380		> 300
ER 1195			500	300

A: SODA-LIME GLASS at 1550°C
 Results obtained from PFT laboratory tests (see p. 8 and 9)
B: INSULATION FIBER GLASS AT 1500°C
 Industrial results
C: HARD BOROSILICATE GLASS AT 1550°C
 Industrial results
D: OPAL-FLUORIDE GLASS AT 1550°C
 Industrial results
 **nb: risk of coloration in extra white glass.

BLISTERING

Blistering rating in soda-lime glass
at 1100°C: 4.

STONING

Stoning rating in soda-lime glass
at 1450°C: 1 to 2.



Monofrax**K-3 & E**

Monofrax K-3 and E offer the best corrosion resistance of any fused cast refractory. Due to the coloring potential of the chrome constituent, these materials are recommended for select applications. Regular cast and void free are available casting techniques for Monofrax K-3, whereas Monofrax E is available in void free castings.



K-3



E

Typical Physical Properties**K-3**

Bulk Density.....258 lb/ft³ (4.13g/cm³)
 Apparent Porosity.....10%

E

Bulk Density.....288 lb/ft³ (4.61g/cm³)
 Apparent Porosity.....<1%

Typical Chemical Composition

	K-3	E
Al ₂ O ₃	58%	8%
Cr ₂ O ₃	28%	76%
SiO ₂	2%	2%
MgO.....	6%	8%
Fe ₂ O ₃	6%	6%
Other Oxides.....	<1%	<1%

Recommended Block Dimensions**K-3 Regular Cast, EPIC-3**

Thickness	Width	Length
3"(75)	10"(250)	15"(380)
4"(100)	12"(300)	18"(450)
5"(125)	13"(325)	24"(600)
6"(150)	14"(350)	28"(700)
7"(175)	15"(380)	32"(800)
8"(200)	16"(400)	36"(900)
9"(225)	16"(400)	40"(1000)
10"(250)	17"(425)	45"(1125)
12"(300)	18"(450)	54"(1375)

Recommended Block Dimensions**E EPIC-3**

Thickness	Width	Length
3"(75)	9"(225)	12"(300)
4"(100)	10"(250)	16"(400)
5"(125)	11"(280)	20"(500)
6"(150)	12"(300)	24"(600)
7"(175)	13"(325)	28"(700)
8"(200)	14"(350)	32"(800)
9"(225)	14"(350)	36"(900)
10"(250)	15"(380)	40"(1000)
12"(300)	16"(400)	48"(1200)

Monofrax Properties

Monofrax refractories are manufactured by fusing oxide minerals in an electric arc furnace and pouring into molds. The resulting properties provide excellent resistance to erosion and corrosion in contact with molten glass and insulation in superstructure applications. Contact Monofrax's experienced applications engineers for specific information about your application.

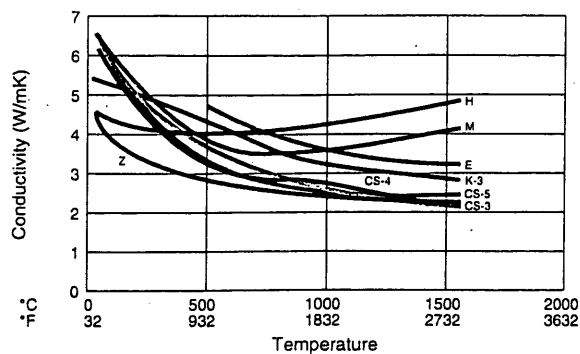
Typical Chemistries (%)

	ZrO ₂	Al ₂ O ₃	SiO ₂	Na ₂ O	Cr ₂ O ₃	MgO	Fe ₂ O ₃	Other
CS-3.....	34.....	49.....	15.....	<2.....	—.....	—.....	—.....	trace
CS-4.....	36.....	48.....	13.....	<2.....	—.....	—.....	—.....	trace
CS-5.....	40.....	46.....	13.....	<1.....	—.....	—.....	—.....	trace
Z.....	93.....	1.....	5.....	trace.....	—.....	—.....	—.....	trace
M.....	—.....	94.....	1.....	4.....	—.....	—.....	—.....	trace
H.....	—.....	93.....	—.....	6.....	—.....	—.....	—.....	trace
K-3.....	—.....	58.....	2.....	trace.....	28.....	6.....	6.....	trace
E.....	—.....	8.....	2.....	trace.....	76.....	8.....	6.....	trace

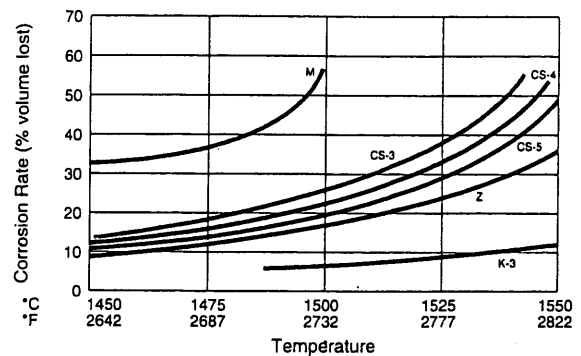
Typical Physical Properties

	Bulk Density lb/ft ³ (g/cm ³)	Apparent Porosity %	Linear Change Under Load % ¹	MOR		Cold Crushing Strength ² kpsi(kg/cm ²)
				Cold ² psi(kg/cm ²)	Hot ³	
CS-3.....	238(3.81).....	<1.....	0.....	9700(680).....	930(65).....	48(3370)
CS-4.....	244(3.91).....	<1.....	0.....	8600(605).....	990(70).....	47(3300)
CS-5.....	248(3.97).....	<1.....	<+1.....	10200(720).....	1120(79).....	49(3450)
Z.....	332(5.32).....	0.....	-2.....	11700(825).....	640(45).....	45(3160)
M.....	219(3.51).....	1.....	0.....	3800(270).....	3270(230).....	33(2320)
H.....	209(3.35).....	2.....	0.....	600(42).....	1130(80).....	9(635)
K-3.....	258(4.13).....	10.....	0.....	6300(445).....	4540(320).....	28(1970)
E.....	288(4.61).....	<1.....	<1.....	4800(340).....	3525(248).....	30(2110)

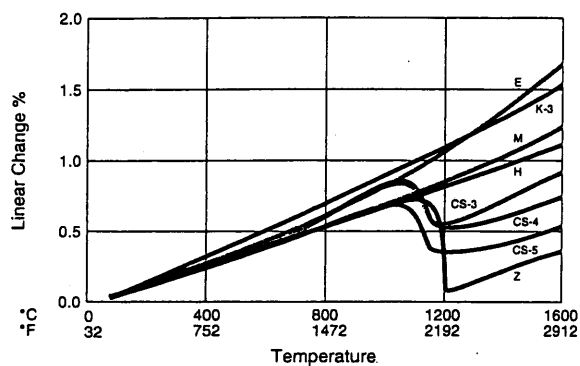
Typical Thermal Conductivity



Corrosion Rate vs. Temperature
(Soda-Lime Glass)



Typical Thermal Expansion⁴
Refractoriness Under Load



- 1 DIN-51053, 29 psi, 100 hours
- 2 ASTM C-133
- 3 ASTM C-583, 2750F, 3 hours
- 4 ASTM C-832, 29 psi

Typical Electrical Resistivity

