



WSRC-RP-2000-00876TL

October 18, 2000

Roger L. Gilchrist
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Dear Roger:

Final Report – Peer Review Committed Assessment of the Proposed Long-Term Performance Strategy for Hanford Immobilized Low Activity Waste (U)

The attached report presents the consensus findings and recommendations from the international experts asked to review the subject report. Dr. George Wicks coordinated the Peer Review Committee (PRC) meetings and reports. The PRC included Prof. Bernd Grambow, Prof. Werner Lutze, and Dr. Etienne Vernaz.

The attached report not only includes the issues raised by the PRC, but their insights on approaches to resolve the noted issues and their detailed assessments. Some of the comments could be addressed in future work on the Hanford Immobilized Low Activity Waste Task and will be coordinated by the Hanford Site customers.

If there are questions related to this report please contact either Dr. George Wicks (803) 725- 3190 or Bill Holtzscheiter (803) 725-2170.

Sincerely,

A handwritten signature in cursive script, appearing to read 'E. William Holtzscheiter'.

E. William Holtzscheiter
SRTC Manager,
Immobilization Technology Section

EWH/kah

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**FINAL REPORT - Peer Review Committee (PRC) Assessment of the
Proposed Long-Term Performance Strategy for Hanford Immobilized
Low Activity Waste (ILAW) (U)**

Bernd Grambow
Werner Lutze
Etienne Vernaz
George Wicks (Chair)

September 2000

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TABLE OF CONTENTS

I. INTRODUCTION

Mission Statement
Peer Review Committee (PRC) Members

II. EXECUTIVE SUMMARY

III. PRC's SEVEN MAJOR POINTS OF CONSENSUS

IV. PRC's FIFTEEN MOST IMPORTANT RECOMMENDATIONS

V. PRC COMMENTS IN DETAIL (summarized and grouped into key topics)

- 1.0 Modeling approach
- 1.1 Importance of secondary phases
- 1.2 Effect of ion exchange
- 1.3 Glass corrosion model
- 2.0 Laboratory testing
- 2.1 Other test methods
- 2.2 Required tests with radioactive glass
- 2.3 Materials interactions tests
- 2.4 Role of natural analogues
- 2.5 Laboratory testing strategy
- 3.0 Field testing
- 4.0 Modeling the disposal system.
- 5.0 Other issues

APPENDIX I: Preliminary reports by B. Grambow, W. Lutze and E. Vernaz

APPENDIX II: Documents

Primary Document
Supporting Documents

I. INTRODUCTION

A peer review process was conducted by a team of national and international experts on a proposed strategy for predicting performance of low-activity waste glass recommended for disposal at the Hanford site. The peer review process consisted of the following 2-part mission:

Mission Statement

1. Assess and critique the draft document entitled "A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford", by B.P. McGrail, W.L. Ebert, D.H. Bacon and D.M. Strachan, PNNL-11834, February 1998, and
2. Provide general and specific comments as well as recommendations on the proposed strategy to assess long-term performance of the low-activity waste glass systems.

Peer Review Committee PRC Members

The peer review committee consisted of Prof. Bernd Grambow, (Ecole des Mines de Nantes, Laboratoire Subatech, BP 20722, 44307 Nantes Cedex 3, France), Prof. Werner Lutze of the University of New Mexico, (Lutze Consulting., Albuquerque, NM, USA), Dr. Etienne Vernaz (Commissariat à l'Energie Atomique, Marcoule [CEA/VALRH0], France) and Dr. George Wicks (Chair), (Westinghouse Savannah River Technology Center, Aiken SC, USA).

Hereafter, the paper reviewed by the PRC "A Strategy to Conduct an Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford", by B.P. McGrail, W.L. Ebert, D.H. Bacon and D.M. Strachan, PNNL-11834, February 1998, is referred to as *the document*.

II. EXECUTIVE SUMMARY

Most of the team's interactions were conducted electronically via e-mail. Several meetings were held in April, 2000 in Bruges, Belgium, piggy-backing on an international workshop on "Glass in its Disposal Environment", which was attended by all PRC members. In Belgium, the PRC team discussed and summarized its findings and formulated recommendations, which were then presented to the customers requesting this review, who were also present at the workshop and PRC side-meetings. Prior to the interactions, preliminary findings of the PRC had been forwarded earlier to customers to meet certain schedules. During the meeting in Bruges, the PRC also learned that changes were being considered in the original strategy. These changes were not submitted to the PRC for review.

The PRC compliments the authors on their work presented in the document. The committee recognizes both the importance of this effort and the difficulties in achieving all objectives.

The final report provides

- points of consensus reached by the team (Section III)
- general recommendations to improve the proposed strategy (Section IV)
- more than 100 specific comments, questions and suggestions in response *to the document* (Section V). There are many questions and concerns the committee believes need to be addressed, to fully meet all goals of this task and to increase confidence in the final results.

In Section V, comments have been taken from the members' interim reports, summarized and catalogued into the sections and topics of the document reviewed. This involves a constructive, systematic summary of key points made by PRC members in each of the areas of interest. Individual PRC reports, provided by each PRC member, are included in Appendix I, along with a listing of the most important support documents used during the evaluation (Appendix II). We recommend that the PRC member reports be studied in detail, to obtain additional and more specific information, in each of the relevant areas.

The overall finding of the PRC is that the proposed strategy to conduct an analysis of the long-term performance of low-activity waste glass in a shallow subsurface disposal system at Hanford is meritorious and should be pursued, but only after serious consideration of all issues described in Sections III and IV of this report.

III. PRC's SEVEN MAJOR POINTS OF CONCENSUS

1. The proposed strategy represents a technically sound, state-of-art approach with the potential of providing important information in support of performance assessment activities for Hanford immobilized low activity waste.
2. PRC questions and concerns should be addressed fully and additional work conducted in order to reach the stated goals of *the document*.
3. The use of statements given in *the document*, such as "well accepted mechanistic model" and "the processes that control glass corrosion are well understood and rate expressions have been developed and tested", may over-interpret the state-of-art of our understanding of this field; the limitations of the mechanistic model must be discussed more fully and defined.
4. It is not clear to the committee how data from the proposed experimental testing program will be used in the strategy detailed in the document, and more importantly, how relevant those data will be to actual disposal conditions and the evaluation of performance of the product in the disposal environment.
5. It has not been shown or discussed in detail that the use of rate accelerating tests will not cause changes in the corrosion mechanism, thus producing data not suitable to support the strategy.
6. The experimental program consists of three main sets of tests; only a few of these have been "qualified", i.e. used and critically evaluated by different laboratories, or standardized. The usefulness, applicability and effectiveness of several of the proposed testing procedures have only been addressed by the authors of *the document* and therefore, are difficult to evaluate by the PRC.
7. There is a temperature dependence of the (pseudo)equilibrium constant K. The test procedure provides no means for measuring the temperature dependence of K. This is considered a serious omission. A seventh parameter (ΔH) needs to be determined.

IV. PRC's FIFTEEN MOST IMPORTANT RECOMMENDATIONS

1. Use the rate law in *the document* as a working hypothesis and determine parameters necessary to see if it applies to the described case. If it does not apply, the reasons need to be studied and explained.
2. If the data for supporting the PA strategy are limited, as appears to be the case, the predictive model should use realistic conservative bounding case assumptions and parameters.

- 3 An effort must be made to provide convincing evidence that the model will apply to the "real system".
- 4 The applicability of the rate law to the present system has been questioned by PRC members; in response, the authors of *the document* should describe more clearly why they believe the model applies and what they think are the limitations.
- 5 Quantify uncertainties and conservatism; perform error propagation analysis, sensitivity studies by varying input parameters and variables of the model.
- 6 Assess initial transient effects of possible bursts of radioactivity that may result from ion-exchange or surface deposition of radionuclides; assess the role of the alteration layer(s) with regard to its retention capacity for critical radionuclides, i.e. buffering of bursts.
- 7 In light of changes made in the strategy while the current review was in progress, the PRC points out that an additional review would be beneficial to support revisions of the strategy and procedures. Peer review of the entire final version of *the document* is important, considering its significance for the disposal of low activity waste glass at Hanford. (It was not the task of the reviewers to take into account changes proposed or made by the authors of the document while the review was in progress.)
- 8 The procedure to be used and assumptions made for the fitting of thermodynamic constants of observed glass alteration phases needs to be explained in more detail.
- 9 The value selected for the reaction order parameter [σ] should be one [$\sigma = 1$]; if it is assumed or shown not to be one, the deviation must be justified. σ must not be used as a fitting parameter (this point was made very clear in the oral discussion with the customer in Belgium).
- 10 The choice of species and the stoichiometry of the affinity term [$1-(Q/K)^\sigma$] need to be justified and should not be used as a fitting parameter.
- 11 The effect of high temperatures (T) and high pH in accelerated and other tests, need to be assessed, including the effects that pH and T may have on the formation of alteration phases. This is especially important, if temperature and pH values deviate significantly from those expected in the disposal environment (near field).
- 12 The strategy of accelerated testing should assure that the data generated are relevant to the chemical conditions in the disposal site; for example, VHT and PCT generate pH values as high as 14, clearly not relevant to burial conditions. Usage of such data must be justified in *the document*.
- 13 The sorption capacity of the Engineered Barrier System (EBS) needs to be evaluated with respect to elements in the affinity term.

- 14 Caution must be exercised when laboratory data, obtained under controlled and idealized conditions, are applied to describe waste form performance in a less well defined repository environment. This point must be addressed more explicitly and the use of the data better justified in *the document*.
- 15 The use of laboratory tests never applied before or by anyone except the customer is problematic; such tests should be subjected to peer review, standardized or at least be evaluated by using a reference material (reference glass such as ARM) whose corrosion performance is known and documented.

V. PRC COMMENTS IN DETAIL (Summarized and grouped into key topics)

Following is a compilation of individual comments provided by members of the PRC, which provided the first important step of the review process. These comments include reviewers' statements, opinions, questions, concerns, and specific recommendations on relevant items. The listing is intended to provide a systematic, collated summary of key points grouped into categories following the organization and presentation of topics given in *the document*. Duplications are intentional because they emphasize that different reviewers made the same point in their individual reports (Appendix I). Not all of the comments made in the individual reports have been ordered and listed in this section. When it was felt that a certain critical point was made clear, additional comments were not added. This is why we recommend that Appendix I be consulted, in addition to the core text of this report.

The listing of over 100 comments given below, together with the attached individual reports, constitutes the basis for the meetings and discussions held in Belgium, which resulted in the PRC's seven main points of consensus (Section III) and its fifteen most important recommendations (Section IV).

The PRC chairman received approval from each PRC member that the content and the wording of Sections III and IV accurately represent the committee's findings. The information provided in this section, Section V, was compiled by the PRC chair with support from other PRC members. Word-by-word approval from committee participants was not deemed necessary for each of the comments below. Words, phrases or parts of phrases in quotation marks have been taken from Appendix I and in some cases, words in quotation marks have been edited for brevity, without changing the essence of the statement. The numbers given in () in the section headings, relate to the respective sections given in *the document*.

1.0 Modeling Approach (3.0)

- Fig. 3.1 should be shown in this introductory section of *the document*. It provides a good graphical representation of the role of modeling in the PA strategy and of what follows in *the document*.

1.1 Importance of Secondary Phases (3.1)

- It is recommended “to describe the relation between glass composition and secondary phase composition in more detail”.
- “.... one needs to speak of the hydrated glass (gel) as a reaction product”.
- With respect to the “metastable phases” that occur, “it does not become clear what to do” with them.
- “.... since the composition of natural glass and waste glasses will be quite different, what do we learn from the analogues?”
- It is recommended “to distinguish two kinds of metastability; that described in the paper, and the inherent metastability of a given phase in the course of a paragenetic sequence of phase transformations”.
- “.... which acceleration procedures are envisioned?”
- “I am not aware of many publications, where.... it was shown that these high temperature phases were of any relevance at low temperature conditions”- how will this important relationship be shown?
- “.... formation of reaction products to achieve steady state can be accelerated by conditions such as higher S/V ratios. However, at a higher S/V, only the initial stages of reaction progress are relevant, long-term reaction products at high S/V may not form at lower S/V, even if one waits millions of years. No discussion was found in the paper, which S/V is considered realistic, in terms of acceleration”.
- The authors “should describe more clearly what is meant by acceleration and metastability.” Otherwise their statement in the text “.... a means must be found for accelerating the transformation process during laboratory testing without altering the fundamental process itself” becomes “misleading or meaningless, and by no means can it guide an experimental testing strategy”.
- The authors correctly state that at low temperatures (15° C), metastable and amorphous phases may persist for long periods of time. If that is indeed the case, “an explanation is needed on why it is necessary to accelerate the transformation process”. Also, “the untransformed phase may have a different equilibrium constant (K) than the transformed phase”- so how is this taken into account?
- “.... transformation may not be avoidable or comes unnoticed at higher temperatures. 15° C is not a test temperature - why not?”
- “I do not see information in *the document* on how you make sure that the fundamental transformation process is not altered”.

- “.... what are the implications for modeling long-term glass corrosion under service conditions, if information on phases at 15°C is ambiguous” (unavailable)?
- “.... the potentially protective role of the surface layers should also be discussed”. The testing strategy should be designed “in a way to show or rule out this potential (protective) effect”.
- Inclusion of a listing of typical secondary phases, such as clays, hydrous oxides, zeolites, etc., would be helpful.
- It must be shown that accelerated tests do not change the corrosion mechanisms and that what happens to the glass under accelerated conditions at short periods of time is what actually happens to it over long periods of time, at the real (lower) storage temperature. If the mechanisms do change, is there any relevance at all to the testing data and how could it possibly be used for long term predictions?
- The potential importance of the secondary phases formed and possible effects on release of species of interest is acknowledged. However, do these same phases form and have similar effects on species of interest in the presence of package components and under the anticipated geologic and hydrologic storage conditions?
- What is the stability of the phases formed over long periods of time and their long-term effects on species released from the glass? This type of information could be important (for glass performance) and should be assessed.

1.2. Effect of Ion Exchange (3.1.2)

- “The implication of ion exchange/water diffusion for long term glass corrosion was already discussed in the literature much earlier than assumed by the authors”.
- To take this effect into account, “.... in a testing strategy, diffusion coefficients and distribution coefficients would have to be determined”.
- “.... we fail to understand the assertions in the report, presented as a recent discovery, by which allowing for ion exchange can affect the long-term rate of radionuclide release by several orders of magnitude”.
- “.... suppression of ion-exchange (as suggested by the authors) by modifying glass composition is certainly worth an investigation”. The question then is how does this affect the test program and to what extent is this attempt limited by waste composition?
- An ion-exchange related increase in pH was shown to increase the rate of radionuclide release by three orders of magnitude.... modifying glass composition is

a worthwhile consideration.... additionally, burial conditions and package components can play an important role, e.g. buffering the leachant and controlling glass dissolution. Since ion-exchange could be affected by these external conditions, its potential significance should be considered in more detail in the proposed strategy.

- “.... the primary long-term objective is not so much to minimize interdiffusion as it is to design glass compositions that are not too basic and contain elements such as boron, if possible, which provides a buffer capacity to ensure a sufficiently low equilibrium pH in the repository”.
- As stated by the authors, ion exchange may have a strong effect on glass corrosion, so it needs to be studied in the proposed program and its contribution must be better defined.
- Ion exchange may indeed follow a linear time dependence in certain cases, but there is no data or analyses given to support this view

1.3 Glass Corrosion Model (3.2)

- The top down approach is logical but there are pitfalls that must be addressed. For example, “.... the overall glass dissolution model is rather complex and observed experimental data may be explained alternatively by two or more submodels”.
- A “main weakness..... is the confidence placed in a complex kinetic law, presented as universal and fully applicable to any type of glass.... recent work (on French nuclear glasses) has demonstrated that this law is inapplicable in a large number of experimental situations. Extreme prudence is necessary with regard to LAW glasses for which no experimental validation of such a law has been reported.....”
- It may take an iterative process of varying test conditions to reduce model uncertainty.
- “.... there is a temperature dependence for the (pseudo)equilibrium constant K. Neither the rate law nor the test procedure provides for measuring the temperature dependency of K. This is considered a serious omission in the approach. This would add a seventh parameter (ΔH) to be determined”.
- “.... it is advisable in measuring K to take only silica into account.... adding other elements to the affinity function does not significantly improve the experimental fit, but does considerably increase the uncertainty and increase difficulty of transposing laboratory measurements to the conditions of an actual repository”.
- “.... special attention has to be given to the determination of the ion-activity product Q.Q is not a glass property but a property of the hydrodynamics of the glass water system. Consequently, Q-values in an experiment may be of no relevance for

the real system. The testing strategy should provide means to determine the stoichiometry of the rate limiting reaction”.

- “.... the report does not specify which elements must be taken into account in calculating the ion activity product Q ”.
- “.... even if the parameters for the affinity term and the initial rates are well determined, and if applicability of the rate law has been proven to be valid by comparison to the experimental data, this validity range applies only to rates 1000 times higher than those predicted”.
- The testing strategy does not provide means to assess very low glass corrosion rates, which would best represent what would be expected in an actual disposal scenario.
- “.... it is recommended to specify the range of rate variations for which the applicability of the rate law is tested experimentally or by observation on naturally weathered glasses. In case the model yields reaction rates lower than ever measured, it is furthermore recommended to use the lowest measured rates rather than the modeled rates for the prediction.” (Similar to using final rates for long term predictions).
- The tests selected to determine σ and K are based on non-standard tests. These tests have not undergone documented round robin testing nor have they been approved by anyone. There is a need to initiate a process that leads to a peer review of the testing procedures and subsequent, higher credibility of the data.
- “.... if the reaction order parameter σ turns out not to be 1, will the authors try to understand what the cause is, and how will they do it?”
- “.... a reaction order of less than 1, cited in some of the authors’ work, appears to be an artifact used to slow down the approach to equilibrium and to better fit the experimental data without taking into account transport phenomena within the alteration films”.
- Assigning K values is a matter of how well the glass alteration products are known. An analysis of existing K data of selected minerals may be useful to evaluate the potential impact of K on long-term glass corrosion rates.
- “.... identification of alteration phases has been qualified in the document as key input information for modeling. This is correct but deserves more attention than expressed in the document.” There should be a section describing the effort made to determine this information which could involve a very costly and time-consuming program.
- Concerning the data shown in Figure 3.2, it is not clear why the line is where it is and what the scattering means.

- “a hypothesis (solubility hypothesis taking main network formers into account) is apparently postulated by the authors, but no dissolution equation is proposed”.
- In glass studies in a saturated leachate, it is noted that there is no thermodynamic equilibrium between the pristine glass and solution. “C*... does not correspond to the intrinsic solubility of the glass, but is merely a dynamic parameter depending on the operating conditions”.
- “.... at no time is the role of the alteration film mentioned in the document with regard to the glass alteration kinetics, nor with regard to its strong retention capacity for certain radionuclides”.
- Under near-saturated conditions, “.... the gel becomes highly protective and is the principal cause of the very significant drop in the alteration rate at high reaction progress”; under these conditions, “.... the rate of glass dissolution is mainly controlled by the properties of the gel layer developed during glass leaching, and not by the chemical affinity of the hydrolysis reaction”.
- “.... it is clear today that the chemical affinity concept and protective gel concept are not opposed, but must be combined to match experimental reality”.
- “.... the notion of a diffusion barrier” is indispensable to account for the fact that alteration virtually ceases under conditions that do not correspond to a thermodynamic equilibrium”.
- With respect to fabrication of the waste forms and ultimate releases during disposal, “.... determining the surface area is one of the major problems that is practically not addressed in the report”.

2.0 Laboratory Testing (4)

Issues in this section relate to the following sub-sections in *the document*:

Single Pass Flow-Through Test (4.1)

Vapor Hydration Test (4.2)

Product Consistency Test (4.3)

- “.... the relationship between service condition tests and accelerated tests remains unclear”. It was stated in the text that service condition tests are conducted to verify that the techniques used in accelerated tests do not change the alteration mechanism, but later it is also stated that service condition tests are conducted at higher temperatures than expected in the repository. “By which procedure is it ensured that an elevated temperature has no effect on the corrosion mechanism?”

- In the test strategy for determining model parameters, it appears that the SPFT test is the only experiment to be used to derive model parameters, while the other tests will be used primarily as characterization or service tests. The strategy for obtaining k , E_a , and η by SPFT is well formulated and it is recommended that these tests be conducted as stated. However, for experiments involving the affinity term, it is not convincing that the approach chosen to determine the parameters for the affinity term will reach that goal. "Additionally, the stoichiometry of the rate controlling reaction is unclear". The SPFT test is suggested based on inherent problems with batch tests but, "the suggested alternative of using the SPFT test is not convincing and may give unreliable results".
- While SPFT can be used to measure initial dissolution rate versus temperature and pH (k , E_a and η) as indicated, "it is applicable only over a very limited range". On the other hand, the use of SPFT "... to measure K is apparently invalidated".
- From Figure 10 in the supporting literature (ref. 1, Appendix II), the uncertainty in the data shows that one cannot distinguish between different models for the stoichiometry of the rate limiting reaction. Also, in the referenced work, it is reported that the results for K and σ differ considerably from those of Bourcier for a similar glass, "... clearly indicating the insensitivity of the test for σ ".
- "... at the lowest flow rate the effect of the affinity term becomes visible but much lower flow rates would have to be used to study the process of radionuclide release under silica saturated conditions". Also, "... it is suggested to include a PCT test at constant pH into the test strategy for obtaining affinity related parameters" (pH can be controlled online by pH-stat titration).
- PCT tests conducted at high S/V can play an important role in model development for long-term glass corrosion under near saturation conditions. "The test (using PCT for simulating relatively high S/V conditions as in disposal scenarios) should allow determination of diffusion / distribution constants for the ion exchange process as well as it might impose limits on precipitation rate constants for secondary phases".
- "... the proposed strategy does not provide a clear concept on how to make use of the test results for long-term predictions".
- "... the top down strategy of the authors is appealing but can only be used if the models are validated in all ranges of application".
- If the batch reactor based SPFT test is not able to simulate the expected low flow regime in the disposal site, it is possible that the PUF test can help. This test provides a promising experimental setup and unique ability to monitor the coupling between secondary phase formation and under-saturated flow hydrodynamics.
- "... for performance assessment it is very important to validate the accelerating nature of the test, before using it for this purpose".

- The term “acceleration” needs to be made clearer and better defined, because it can lead to erroneous conclusions regarding performance assessment. This can be especially confusing with respect to the PUF test.
- Since the testing strategy is very dependent on the water infiltration scenario, it should be described and worked out clearly.
- With very low water infiltration rates, vapor phase hydration may become important so respective tests too, can be helpful, as recommended by the authors. However, the goal of such tests should be made clearer and the use/applicability of the data to glass performance assessment must be explained and evaluated.
- The VHT has been used to replicate weathering on volcanic glasses, but it is not a generally accepted methodology in archeology to use this technique to simulate long-term weathering effects. However, it can be useful to confirm what has been observed with other methods. “If new information is obtained by this test, it is recommended to seek independent confirmation prior to inclusion into a model”.
- “Although the VHT is of interest for increasing the effect of secondary phase precipitation on the alteration kinetics, VHT is little representative of repository conditions because of the high temperature and the probably very high pH in a very thin condensed water layer”.
- Sentence #10 in section 4.2 in *the document* should read: The water (not solution) evaporates from the sample when the test is terminated and a solution is not available for analysis.
- “.... usage of a standard leach test (PCT) is certainly a good idea”.
- “.... there are localities in natural glass systems with very limited flow of water, particularly, if we look deeper into the rock. This would probably match the repository situation best”.
- PCT may be good enough to simulate corrosion conditions; however, “.... depending on the significance of corrosion in fractures, it may just measure one of the water-driven glass corrosion processes because of S/V limitation”.
- There is no test that addresses corrosion in fractures and pores. “I suggest that this issue be discussed and considered or discarded with reason”.
- “.... pH excursion may be a problem at high S/V because of glass composition. That may be a reason to limit S/V in PCTs”.
- “I do not see how the results of the PCT can be used to confirm K and σ values measured by other tests”. “Does this mean that once the values are known, one can

separate the obscuring effects imposed by PCT conditions and get the same K and σ as with the SPFT? How do you know? Or do the authors want to say that the values can be compared and that new insight may be gained from the potential differences?"

- "... the impact both on the initial pH excursion (clearly visible in the PUF tests) and on the initial release of major elements must be assessed; it is advisable to measure the interdiffusion coefficient of LAW glasses".
- The PUF represents a new test for the waste management community so most investigators in this field are not familiar with it. Its potential and limitations, as well as the validity and usefulness of the data, are difficult to assess for someone who has no experience with the test and no possibility to compare results between laboratories. "... taking the extraordinary magnitude of the overall Hanford LAW vitrification and disposal project into account and the enormous costs, it is not too much to ask for inclusion of another organization using the PUF and confirm its effectiveness and the results obtained by the authors. There is just insufficient outside expertise to fully evaluate the PUF".

2.1 Other Test Methods (4.4)

- There are a number of standardized tests in the field that are not part of the strategy proposed in the document. These tests have been quality assured and received extensive peer review, including inter-laboratory round robin testing. "... the value of work completed by the Materials Characterization Center and others and the wide spread application of many of the tests not proposed as experimental tools should not be underestimated" when it comes to defending test procedures and their results.

2.2 Required Tests with Radioactive Glass (4.6)

- A ranking of radionuclides with respect to radiotoxicity as a function of time and with respect to mobile radiotoxicity also as a function of time, should be provided.
- The objectives of radioactive testing and expected results should be made clearer. For example,
 1. radioactive tests are used to demonstrate that no radiotoxic element is dissolving faster than the glass matrix;
 2. radioactive tests will help identify maximum concentrations of radionuclides for service conditions
 3. radioactive tests will identify secondary host phases for radionuclides
 4. radioactive tests can provide the most realistic and useful data possible
- For these tests, it is important to ensure that the glass is produced in a similar way as the real glass product (redox conditions, cooling history, etc.). How will it be done?

- In these tests, the maximum solution concentrations and solubility controlling host phases should be determined for the entire range of variations in the expected disposal conditions (scenario dependent).
- The radiophases are sometimes difficult to characterize due to low concentrations of radionuclides in them, or if the radionuclides form insoluble oxides or hydroxides - is there enough material to identify the phases?
- "Colloid formation constitutes an additional phenomenon difficult to model. How will it be modeled?"
- In PUF, how will radionuclide adsorption be separated from precipitation?

2.3 Materials Interactions Tests (4.7)

- "The description of materials interaction tests is vague, probably due to the absence of a clear design of the disposal facilities". Will this situation improve soon? If not, it must be stated in the document that best estimates were made concerning materials interaction.
- "... a clear statement of the main objectives of the tests should be provided"
- "... as long as a detailed design is not available, it is of no value to use the PUF tests which might simulate certain unrealistic hydrodynamic characteristics of the systems. In contrast to the authors, I believe batch tests like the PCT to be better suited to obtain screening results for materials interactions, without implying a particular design.....also, I disagree with the authors that the effect of cement would be restricted to an interfacial region". Why do the authors believe this is the case?
- Since carbon steel may be used, "... it is suggested to perform some PCT materials interaction tests with carbon steel and with radioactive glass".
- Experiments on laboratory mockups are suggested as a means of relating the results of field tests and laboratory tests; extend the scope of the validation by an experiment "... using a full-size non-radioactive glass block, and validate the environmental coupling phenomena by implementing a reduced-scale integral mockup experiment".

2.4 Role of Natural Analogues (4.8)

- "Lab tests with natural glasses are only meaningful if this testing strategy is combined with an assessment of the behavior of the natural glass under natural conditions.... if such a large project is outside of the funding level of the present project, it is

suggested to delete all tests with natural glasses from the testing strategy". But natural analogues may still be included in the study based on a literature survey.

- "Reading this section gave me the impression that there is no strong commitment to study natural analogues".
- "... use of the PUF is justified, if it can be shown that the test provides results useful to support predicted long-term corrosion behavior of the ILAW." It is stated in this section that a small number of tests should be conducted. What are the conditions? Why have natural glass samples not yet been selected? Which samples will be used and will the authors seek expert advice? And what is the timing of these activities?
- Since a main component of the ILAW repository is concrete, which will, most likely, affect the composition of water (leachant), it may be important to study a natural analogue for concrete. This may not need to be an experimental effort but instead, information could be extracted from the "Maqarin Natural Analogue Study" and analyzed for relevance to Hanford ILAW;
- "... it is not clear to me how long-term testing of natural glasses at ANL will impact the ILAW project and vice versa. How will the results obtained at ANL be incorporated into the ILAW database? What kind of information will be obtained from ANL to support at least potentially the long-term ILAW performance predictions? I have the impression that the two programs are not well coordinated".

2.5 Laboratory Testing Strategy (4.9)

- "... I suggest more studies of radioactive glasses".
- Supporting and confirming experiments to be conducted by other institutions should be added to the matrix.
- See additional and more detailed comments made earlier in the other sections on the many different aspects of the proposed testing program.

3.0 Field Testing (5.0)

- "... lysimeter tests are potentially important in verifying the described models. However, I think it is important to use the same glass as suggested for the experiments in the laboratory" (If the selected glass has a high corrosion rate, its alteration mechanism may be different than that of the real glass); "... also, glass dissolution mechanisms could vary with water flow rate. I think with a high water flow rate, various artifacts are created, which are meaningless for long-term predictions".

- "... the field test is only addressed by saying that some experiments should be run at a steady flow rate and with a glass of low chemical durability. There is no design of an experiment and no link to modeling is shown". Explain why this exercise has been proposed at all?
- "... I recommend that a lysimeter type field test be designed with input from other experts, reviewed, and conducted to expand and support the database generated in the laboratory".
- At the recent Bruges, Belgium workshop on 'Glass in its Disposal Environment', it was general consensus that an important contribution can be made by field tests, especially to support or validate existing or proposed models. It would be useful to examine some of the most successful field testing programs conducted in the international waste management community, to see if this existing forum and international infrastructure of experience and expertise, can be used to obtain data useful to this effort.

4.0 Modeling the Disposal System (6.0)

- "... basically, I agree with the general modeling strategy, provided my comments on the rate law (long term rates, temperature dependency of saturation constant K) are taken into account. However, the validity of any modeling strategy depends on the database used. This database is not provided for this review, not even in the supporting documents. I suggest to provide these data to the review team before the ongoing review process is terminated".
- "... no strategy is provided by the authors on how to treat sorption processes or colloid generation by modeling"- how will this be addressed?
- "... the proposed code STORM would be well suited to treat the problem of water access controlled glass corrosion rates, as it considers overall mass balance of the water. However, the code AREST CT, which does not have this capability, may lead to erroneous predictions.... (I would assume aqueous diffusion as an important release controlling mechanism, while there may not be sufficient water to allow diffusion)".
- "...Figure 6.1 in *the document* is very illustrative and reflects a sound modeling approach, described in the text.... again, I suggest that other institutions with proven modeling capabilities be invited to participate; this project should not be limited to one institution, participation of others will increase confidence in the results within and outside the technical community".
- "The report considers only a single strategy based on a very complex kinetic law, coupled with geochemical codes that are also complex (AREST or STORM), without at any point addressing their underlying hypotheses and uncertainties. It thus

postulates an interesting but very sophisticated overall model of unproven robustness.” Several alternative strategies for assessing alteration kinetics, such as the “ r_0S ” and “ $r(t)$ ” approaches (Appendix I), can be used to assist this effort.”

5.0 Other issues

- A short paragraph should be included addressing bacterial activity.

APPENDIX I

PRC Preliminary Reports

- A. **Prof. Bernd Grambow**, (Ecole des Mines de Nantes, Laboratoire Subatech, BP 20722, 44307 Nantes Cedex 3, FRANCE)
- B. **Prof. Werner Lutze**, Lutze Consulting, Albuquerque, NM 87131, USA)
- C. **Dr. Etienne Vernaz**, (Commissariat a l'Energie Atomique, Marcoule [CEA/VALRHO], FRANCE) [this report includes 3 journal papers to clarify points expressed in the contribution]

B. Grambow,

Review of the document

“A Strategy to conduct an analysis of the long-term performance of low activity waste glass in a shallow subsurface disposal system at Hanford.”

General comments

The paper provides a testing and modeling strategy for low level waste glasses based on thorough understanding of glass corrosion mechanism. In general it is expected that the conduct of this strategy will result in important conclusions on the long-term performance of the tested glasses.

However, in practice significant changes of the strategy will have to be performed in the course to the testing procedure. It is the experience of glass corrosion testing over many years that any strategy for deriving glass performance related parameters must be based on an iterative stepwise approach. First tests results will guide subsequent test plans. In contrast, in the present strategy, a large and very expensive experimental matrix is proposed without any provision for feedback in the layout of test plans. A more realistic general strategy would have to describe a set of preliminary tests, describe expected result classes, break points and criteria for decision making for test selection, test continuation and test parameter adaptation based on preliminary results.

An important drawback of the present study is related to accelerated testing. There is no clear definition given on the meaning of this term and the testing strategy to extrapolate effects of surface area, water infiltration rates etc. remains unclear.

Detailed comments

The detailed comments follow the chapter numbers of the document

1.0 Introduction

It is not clear, to whom the document is addressed. Is it intended to inform private vendors on the testing program or is it to obtain approval by supervising organizations etc.?

2.0 Disposal System Description

The purpose of the description of the disposal system could be clarified: is it intended to direct the testing and modeling strategy to expected scenarios of water intrusion, or is it of mere illustrative purpose? I understand, that any testing (and modeling) strategy shall at least cover the described conditions (undersaturated flow, slow infiltration rates, low temperatures) but shall not be limited to these conditions. It could be important to state this understanding, because various water infiltration scenarios may be developed in the course of the disposal concept. This is particularly true, as it is stated on page 2.2 that a detailed design of the disposal facility is not yet available.

3.0 Modeling approach

Fig. 3.1 should be given in the introduction to this section, because it clearly illustrates the prominent role of modeling in the experimental testing strategy (top down approach).

3.1.1 secondary phases

Concerning to the importance of secondary phases, the potentially protective role of surface layers should also be discussed, and the testing strategy should be designed in a way to show or rule out this potential effect. Under conditions close to silica

saturation, this effect may turn out to be of low significance, but in the literature this effect is discussed extensively, and any defensible glass corrosion model should address this question.

To make the paragraph more descriptive I suggest to add a list of typical classes of secondary phases (clays, hydrous oxides, zeolites...). Also one needs to speak on the hydrated glass (gel) as reaction product. In part it is formed by diffusion of water in the glass, but its properties are different than that of the glass. In particular it provides sites for ion exchange to occur.

Concerning the occurrence of metastable phases, it does not become clear what to do. If no "generally accepted theory exists", one may stick to empirism. However, empirical relations can hardly be extrapolated to long periods of time. One may use natural analogues instead. Natural glasses weathering data show that metastable secondary phases (e.g. palagonites on basalt glasses) persist for millions of years. On the other hand, the chapter states that the nature of the secondary phases depends primary on the composition of the glass. Since the composition of natural glass and of the waste glasses will be quite different, what do we learn from the analogues. To circumvent this argumentation, I propose to describe the relation between glass composition and secondary phase composition a little more detailed. By this it will become obvious that the general classes of secondary phases are similar for various types of glasses, but the exact composition of the phases depends strongly on glass composition. Since most of these solid phases are solid solutions, it will become obvious that smooth transitions in the properties of secondary phases are expected when comparing one glass with another. Consequently, the long-term stability of metastable phases on the surface of natural volcanic glasses, or, for example, on buried medieval church glasses may provide sufficient confidence that the experimentally observed metastable phases may be of high stability in the long-term.

Also I recommend to distinguish two kind of metastability: those described in the paper, addressing the effect of Ostwalds ripening, and the inherent metastability of a given phase in the course of a paragenetic sequence of phase transformations. It is still subject of debate whether the first process is of relevance for long-term glass

corrosion, but it is clear that the second is of utmost importance, particularly, if silica rich secondary phases are formed. In contrast to the authors I believe it may not help too much to accelerate the first transformation process (increase crystallinity, Ostwald ripening), but it is very important to study the second process. This second process will however depend more on the variation in the chemical environment caused by dissolved glass constituents and may not require a special acceleration procedure.

Which acceleration procedures are envisioned? Though this will have to be discussed later in the context of this review, the problem may briefly be addressed here in the context of secondary phase formation. It is possible, to get better crystallinity of secondary alteration products by an increase in temperature. Nevertheless, I am not aware of many publications, where it could be shown that these high temperature phases were of any relevance at low temperature conditions. A comparison to reaction products of low temperature weathered natural or medieval glasses may be more promising.

It is often argued, that phase transformations can be accelerated by tests performed at higher ratios of surface area to solution volume ratios. This is only true for certain cases, mainly valid when comparing the test results at high S/V with those of tests at lower S/V. Directly this acceleration only applies to closed systems (batch tests), only indirect to open natural systems (via the equivalent water residence time). For example for a given water flow rate, there will be a mass transfer balance between the quantity of release of glass constituents to an adjacent solution volume and the quantity of water removed by saturated or unsaturated flow from the system. This balance will result in the establishment of steady state concentrations of dissolved glass constituents, steady state pH etc. with associated stability ranges of secondary phase. These steady states correspond to certain stages of reaction progress in a hypothetically constant solution volume. The reaction progress to achieving steady state can be accelerated by higher S/V ratios, but with such tests performed at a higher S/V, only the initial stages of reaction progress are relevant, long term reaction products at high S/V may never form at lower S/V, even if one waits millions of years. No discussion is found in the paper, which S/V would be realistic, which would be accelerating.

In summary the authors should describe more clearly what is meant by "acceleration" and by "metastability". Otherwise the operative statement (page 3.1) "... a means must be found for accelerating the transformation process during laboratory testing without altering the fundamental process itself" becomes misleading or meaningless, and by no means it can guide and experimental testing program.

3.1.2 The effect of ion exchange

The authors state the very important role of ion exchange, and I agree completely. It is not true that ion exchange has been overlooked in recent years, and it became important only by predictive modeling. Since more than 50 years, ion exchange and matrix dissolution were studied as the two most important processes governing glass corrosion. It is however true that "ion exchange" normally is considered as a short term process, with little importance for long-term nuclear waste glass dissolution. The implication of ion exchange/water diffusion for long term glass corrosion however was already discussed in the literature much earlier than assumed by the authors ¹.

Reading the statements on page 3.2 and 3.6 I got the feeling that the effect of ion exchange on radionuclide release is expected to be mainly an indirect effect, caused by the increase in pH. There is no direct release of radionuclides by ion exchange envisioned. This becomes clear from the Equation 3 (Glass $0.4\text{Na} + 0.4\text{H}^+ = 0.4\text{Na}^+ + \text{Glass } 0.4\text{H}^+$) of the supporting document⁷. However, it has been reported in the literature that at pH 4 even Nd-release follows a square root of time dependency¹ and diffusive surface depletion of Nd similar to that of Na was also reported for these conditions². These findings may be explained as follows. For most glasses and low temperature alteration conditions, ion exchange is directly associated to the hydration of the glass network. For better understanding, we may split this into two processes: (1) water diffusion leading to the formation of a hydrated glass and (2) alkali release to allow achievement of an ion exchange equilibrium between the hydrated glass and the adjacent aqueous medium. Similarly, ion exchange equilibria may be adjusted with other species. For example, it is well known, that trivalent lanthanide and

¹ B. Grambow, W. Lutze, R. Müller, „Empirical rate law for dissolution of R7T7 glass in salt brines“ Mat. Res. Soc. Symp. Proc., Sombret. ed. (1990)

² Scholze, Mat. Res. Soc. Symp. Proc., Lutze ed., (1982)

actinide elements are sorbed on clays by ion exchange processes, at least at pH values lower than 6. The surface layer of glasses and probably also the hydrated glass acts very much like a clay. Alkali release is mainly diffusion controlled, because water penetration is diffusion controlled. It depends on solution pH and other geochemical constraints, whether other elements are released by ion exchange. Consequently, in a testing strategy, diffusion coefficients and distribution coefficients would have to be determined.

3.2 Glass corrosion model

I agree to the top down approach, i.e. starting from a model, and then derive the parameters. However there are a lot of pitfalls in this strategy and a careful discussion must be provided by the authors to circumvent these potential problem areas. In particular, the overall glass dissolution model is rather complex and observed experimental data may be explained alternatively by two or more submodels.

- (1) For example, incongruent leaching of glass constituents can result from the selective alkali release or from secondary phase formation. Which element is to be used as an indicator for the dissolution of the glass matrix? If B is used, it must be sure that B is not incorporated into secondary phases. If alkali elements are used, it must be sure that their release is not governed by ion exchange. Consequently, matrix dissolution rates derived from the choice of either alkali or B release may become erroneous if the wrong choice is made.
- (2) Another example: If temporal decrease in reaction rates is observed, it may result from a decreasing rate of ion exchange/water diffusion controlled release with increasing diffusion length in growing surface layers, it may result from saturation effects, or it may result from the effect of surface layers as protective barriers (important at high flow rates)

These two examples show, that there is no direct way from the model to the determination of parameters, in turn it is an iterative process of varying test conditions to reduce model uncertainty.

3.2.1 Rate law:

page 3.4 : In the rate law, provision is taken by assigning an activation energy for the temperature dependency of the initial rate. However, there is also a temperature dependency for the (pseudo)equilibrium constant K. Neither the rate law nor the testing procedure provides means for measuring the temperature dependency of K. This is considered a serious omission in the approach. This would add a seventh parameter (ΔH) to be determined.

Special attention has to be given to the determination of the ion-activity product Q. First its determination depends on the stoichiometry of the rate limiting reaction described by the equilibrium constant K. Second, Q it is not a glass property but a property of the hydrodynamics of the glass water system. Consequently, Q-values in an experiment may be of no relevance for the real system. The testing strategy should provide means to determine the stoichiometry of the rate limiting reaction.

The rate law implies that reaction rates become zero, once Q equals K, i.e. once saturation is reached. This is in particular a very important question, if water infiltration rates are as low as expected in the ILAW concept at Hanford, because in this concept glass corrosion would become close to proportionality to the product of water infiltration rates and the K value. We are back at an old discussion of not using or using of final long-term rates. The consequences are dramatic and may be illustrated in the following numerical example: The proposed rate law has been used for example in the paper⁷. Glass corrosion rates lower than 10^{-17} m/s ($< 10^{-6}$ g/(m²d)) were predicted in the absence of ion exchange (Fig.8 of paper⁷). This is much lower than anything ever measured in any laboratory. The testing strategy does not provide any means to prove or disprove such low rates. Lowest reported rates with LD6-5412 glass are at least a factor of 1000 higher. It is a simple assumption of the rate law, that such low rates are achievable, without any justification or understanding. Even if the parameters for the affinity term and the initial rates are well determined and if applicability of the rate law has been proven to be valid by comparison to the experimental data, this validity range applies only to rates 1000 times higher than those predicted. There is sufficient experimental evidence in the literature showing,

that glass corrosion continues after saturation. This is admitted by the authors of the paper, but the proposed rate law does not allow describe these processes,

It is recommended to specify the range of rate variations for which the applicability of the rate law is tested experimentally or by observation on naturally weathered glasses. In case the model yield reaction rates lower than ever measured, it is furthermore recommended to use the lowest measured rates rather than the modeled rates for the prediction.

This recommendation is similar of using a final rate for long-term predictions, as I have suggested years ago. This suggestion has been criticized as an ad hoc assumption without clear physical basis or understanding. I admit, this is true. However, there is not only no clear understanding of this final rate, there is no physical understanding of the long-term process as such. The final rate was just introduced to prevent overoptimistic predictions in a situation of a lack of general understanding. I proposed certain hypotheses (e.g. ¹) to explain the slow reaction rates close to saturation. The first is secondary phase formation of silica rich entities driving the long-term glass corrosion, the second is resumption of water diffusion/ion exchange, once saturation is achieved. Provisions for both processes are included in the modeling strategy described in the paper. However, one would have to know precipitation (growth, ripening) rate constants to quantify the first process, and these are unknown for the time being, and for the second process, ion exchange, only premature models and approaches are provided in the paper. In particular it is assumed for the ion exchange process, that it does not involve radionuclide release, but only alkali release. Thus, radionuclide release would only be enhanced indirectly by changes in pH. If the pH is buffered in the natural system, ion exchange would thus not contribute to increasing radionuclide release, thus this approach would be unable to explain the observed continuing long-term corrosion after silica saturation.

3.2.2 Rate law for ion exchange

As stated by the authors, ion exchange may have a strong effect on glass corrosion. Consequently, it needs to be studied in the present approach. There is sufficient knowledge in the literature to study ion exchange, to determine the pertinent rate constants and distribution coefficients. A preliminary testing strategy shall be included in the strategy. In particular ion-exchange processes shall be studied at a fixed pH, to test whether or not ion-exchange involves only alkali elements (as suggested by the authors) or also other elements.

Concerning the time dependency of the ion exchange reaction, two different views are given in the paper to review and in the supporting documentation: In the reviewed paper, correctly the square root rate law is used, while in the document⁷ a constant rate $0.174 \cdot 10^{-11} \text{ mol/m}^2\text{s}$ is used. Ion exchange may indeed follow a linear time dependency in certain cases (e.g. once water diffusion through a reaction layer of constant thickness becomes rate determining), but I did not find any analyses of this process to support this view.

4.0 Laboratory testing

Three type of tests are suggested: First there are characterization tests to determine model parameters. A prominent role in the testing strategy have "accelerated" tests, to evaluate in laboratory time the corrosion behavior that will be important over the regulated service life of a disposal system. The question of the meaning of "acceleration" is already described above and will be described further below, using the PUF test as an example. Finally there are tests for service conditions. The relation between service condition tests and accelerated tests remains unclear. It is stated (page 4.1) that "Service condition tests are conducted to verify that the techniques used in accelerated tests do not change the alteration mechanism." However, later on it is stated that "service condition tests " are conducted at higher temperatures than expected. By which procedure it is ensured that an elevated temperature has no effect on the corrosion mechanism?

Test strategy for determination of model parameter

Following the various statements throughout in the paper it appears that only the SPFT test is used for deriving model parameters, the other tests will thus be characterization tests or service tests.

The strategy for obtaining the parameters \bar{k} , E_a , η by a SPFT test in a batch reactor is well formulated (page 4.3-4.4). It is expected that the tests will succeed. If the parameter η is independent on temperature, as implied in the proposed model, it would be sufficient to determine this value at a unique temperature and to determine the other parameters at a constant pH. Nevertheless, since we do not know whether these assumptions are correct, it is recommended to conduct the strategy without modification.

Experiments for the affinity term

Basically I am not convinced from the approach chosen to determine the parameters for the affinity term. Three parameters K , Q , and σ are suggested to be determined simultaneously only from the SPFT test. Additionally the stoichiometry of the rate controlling reaction is unclear. The SPFT test is suggested based on the problems of batch tests with varying solution concentrations (a moving target). However, batch tests can be performed under pH-stat conditions at high S/V (pH-controlled PCT-type test). From the pH dependency of the saturation concentrations of Si, Al... the stoichiometry of the rate limiting reaction can be inferred. The suggested alternative of using the SPFT test is not convincing and may give unreliable results.

The suggestion is based on a recently published paper of McGrail et al. ³, included in the supporting documentation for the present evaluation. Fig. 10 of this publications shows, that the uncertainty in the data do not allow to distinguish between different models for the stoichiometry of the rate limiting reaction. Also it is reported in this reference that the results for K , and σ differ considerably from those of Bourcier for a similar glass (In the reference a value for $\sigma=1$ was used, Bourcier found $\sigma=0.1$), clearly indicating the insensitiveness of the test to σ . The curves and experimental

³ McGrail, Ebert, Baker, Peeler, (1997) „Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate glass for Low-Activity Waste“, J. Nuc. Mat. 249: 175-189

data for Si and Al release from the glass in Fig. 10 and 11 as a function of water flow rate cannot unambiguously be interpreted as referring to the rate limiting reaction. The concentrations of these elements may as well be controlled by secondary phases without any influence on the overall rate of glass corrosion. The data in Fig. 4 may indicate that overall glass corrosion slows down once reaching saturation, but the publication does make no effort to show whether or not Si- and Al-saturation have any influence on the rate of B, Na etc. release. At lowest flow rates the effect of the affinity term becomes visible but much lower flow rates would have to be used to study the process of radionuclide release under silica saturated conditions. It is suggested to include PCT test at constant pH into the test strategy for obtaining affinity related parameters. The pH can be controlled online by pH-stat titration.

PCT-tests at high S/V will also have a more important role in model development for long-term glass corrosion under near saturation conditions. In this way I extend the arguments of the authors to include the PCT in the test strategy, (page 4.5), for simulating quasi-high S/V conditions of the disposal conditions. The test should allow determination of diffusion / distribution constants for the ion exchange process as well as it might impose limits on precipitation rate constants for secondary phases.

How to go from laboratory data and laboratory based models to long term predictions in the disposal site?

The proposed strategy does not provide a clear concept on how to make use of the test results for long-term predictions. A very important point in extrapolation is the relation between expected and simulated flow regimes (water infiltration rates), temperatures and specific glass surface areas. Expected water flow rates are very low and difficult to simulate in the laboratory. Temperatures and specific surface areas are low and will only lead to small reaction progress in the lab. The top down strategy of the authors is appealing but it can only be used if the models are validated in all ranges of application. The tests results and a comparison with a model predictions allows to demonstrate understanding of the test but does not necessarily allow to demonstrate understanding of the real system.

To illustrate the problem of extrapolation, I may use some numerical examples: With a hypothetical water infiltration rate of 0.05 cm/a the water residence time in a 10 m column of glass canisters is 20000 a clearly indicating static conditions when compared to laboratory testing. Maybe, unsaturated static tests would be more realistic than flow tests. With a hypothetical specific surface area of $0.2 \text{ cm}^2/\text{g}$ for the real glass product of density 2.5 g/cm^3 and an open porosity in the glass canisters of 10 vol\% and 20 vol\% water saturation of the void spaces, the S/V would be 0.25 m^{-1} . 20000 years at 0.25 m^{-1} could be simulated in the laboratory in a PCT test by 1 year testing at 5000 m^{-1} , provided the reaction progress increases linearly with the product $S/V \times \text{time}$. Such behavior is observed in some but not all experiments at high S/V . Often a linear relation is found between the reaction progress and the product of surface area and the square root of time. Consequently, the relation between S/V , time and reaction progress needs to be resolved before doing any such extrapolation. Such strategy is not discussed in the paper.

Alternatively we may use not a static PCT but a dynamic test like the suggested SPFT test. Typical water flow rates per surface area (Parameter q/s) in this test were between 0.03 m/a and 1000 m/a^4 . These data q/s values may be converted to equivalent flow rates for a 10 m column of glass using for example arbitrarily a reference cross section for this column of 1 cm^3 and an open porosity of 10% . With a specific surface area of $0.2 \text{ cm}^2/\text{g}$ and a specific weight of 2.5 g/cm^3 , a total glass surface area of 0.05 m^2 is calculated. Multiplying this value with the lowest q/s value of 0.03 m/a , a volumetric flow rate of 1.5 l/a is obtained. From the open porosity void volume (10%) of the glass column of 100 cm^3 a pore water velocity (or water infiltration rate) of 150 m/a is obtained, i.e. the experimental flow rates are about a factor of 100000 and more higher than those expected in the Hanford ILAW-disposal facility. It does not become clear, how the data obtained at such high flow rates are applicable to the much lower flow rates expected. One may increase the specific surface area of the glass in SPFT by a factor of 100000 to reach similar solution concentrations as expected at lower real flow rates, but I do not know whether this is realistic with that test. Moreover, this is not an acceleration of the real process (similar solution concentration are expected in SPFT test and in the real situation in

⁴ McGrail et al. J. Nucl. Mat. 249,175-189

the same time), it is simply an extrapolation method to be able to use data from high flow rate tests.

If the batch reactor based SPFT test is not able to simulate the expected low flow regime in the disposal site, may be the PUF test can help. The PUF-test is assigned a key role in the testing program. Therefore, a careful examination is required. Test description starts on page 4.6. The test provides a promising experimental setup, useful for testing glass corrosion properties under conditions with undersaturated or saturated pore water volumes, with flow rates between 0.05 and 100 mL/h. In particular the test provides a unique ability to monitor the coupling between secondary phase formation and undersaturated flow hydrodynamics. The first test results⁵ indicate that with respect to glass corrosion, fundamentally different physical and chemical environments are established in undersaturated flow through conditions, when compared to water saturated testing using batch techniques.

The lowest volumetric flow rate in the PUF test of 0.05 ml/h may also be converted to a pore water velocity if porosity and column dimensions are known. Assuming a column volume of 20 cm³, a column diameter of 2 cm² and 40% porosity of the glass powder, a pore water velocity of 5 m/a is calculated, i.e. more than 1000 times higher than expected. One could probably argue that tests with a 1000-10000 fold increase in the glass surface area would simulate well the real situation. It seems to be realistic to achieve this goal.

It is stated, that the PUF test has an acceleration factor of 10-20, when compared to the PCT-test at an S/V of 20000 m⁻¹.

For performance assessment it is very important to validate the accelerating nature of the test, before using it for this purpose. The term "acceleration" is used in a general way without specification. For the context it appears of being referred to the time at which the reaction rate of the glass accelerates. This acceleration of glass dissolution rates with time occurs only for some glasses under certain experimental or environmental conditions, but many glass compositions are known which do not show this behavior. It is known that accelerated glass corrosion is associated to an

increasing pH with reaction progress and/or to the formation of secondary phases (e.g. Zeolites) during the reaction path. Consequently, probably in the sense of the authors, we may interpret the term "acceleration" in an extended way as denoting a faster approach of certain stages of reaction progress, i.e. the reaction proceeds faster with time.

This extended definition does not make the interpretation of "acceleration" much easier, because "reaction progress" can have different connotations. Reaction progress in closed systems and open systems have different meaning. From the point of view of performance assessment, "acceleration" implies that certain stages of the reaction are simulated in laboratory time scale, which are expected under real disposal conditions after very long time. In the extended definition above, it is referred to the closed systems definition, where the continuing accumulation of dissolved glass is possible in the contacting solution volumes or solution surface films.

Associated to this is a paragenetic sequence of solid reaction products. This means that the quality, not the quantity of secondary solid phases is a measure of reaction progress. Alternatively, reaction progress can also be measured by the total flux of dissolved glass constituents from the glass surface into an open aqueous system. Associated to this alternative definition is a measure of reaction progress by the quantity of secondary phases formed.

In application to performance assessment, this unclear definition of "acceleration" may result in erroneous conclusions: Assuming, one has to study the behavior of a glass, where corrosion rates accelerate, once the pH becomes 12. In a PCT-test or PUF-test, this stage can be reached fast. However, this may not mean "acceleration" in the sense of performance assessment of glass performance in a real open system. If the water flux is sufficient fast, or if the natural rock/water system provides a buffer capacity for pH (e.g. CO₂), a high pH may never be reached. pH 12 data would than simply be irrelevant. Alternatively, if the natural water infiltration conditions are well simulated in the PUF test (higher pore water velocities balanced by higher surface area) , the secondary phases are expected to occur in similar time both in the laboratory as in the real system. Further increase in specific surface area or decrease in pore water velocity will than lead to volumetric reaction progress values which are

⁵ McGrail, Martin, Linenmeier, „Accelerated Testing of waste forms using a novel pressurized undersaturated

irrelevant for the real case. Based on this discussion it is recommended to delete any reference to an accelerating effect of the PUF test.

The testing strategy is very dependent on the water infiltration scenario. This should be clearly worked out. For example, for extrapolation and test selection, also the water balance needs to be checked. With an annual water infiltration of 0.05 cm into a layer of glass of 10 m thickness $5 \cdot 10^{-5} \text{ cm}^3$ of water are provided per year for every cm^3 of void space. With a specific surface area of $0.2 \text{ cm}^2/\text{g}$ for the real glass product of a density 2.5 g/cm^3 and an open porosity in the glass canisters of 10 vol% a mass of 10^{-1} g of water is provided for each m^2 of glass surface per year. Since at least about $\frac{1}{2} \text{ g}$ of water are necessary to alter one g of glass (much more to dissolve it) the corresponding water balance controlled glass alteration rate would be smaller than $0.001 \text{ g}/(\text{m}^2\text{d})$. In the laboratory an access of water is always available. Most laboratory measured glass alteration rates are much higher than this rate, indicating that the test results may be irrelevant for this scenario of glass corrosion being controlled by the availability of water, i.e. by the water infiltration rate. If glass dissolution rates obtained in the laboratory are higher than this value of $0.001 \text{ g}/(\text{m}^2\text{d})$, glass dissolution testing would not allow to derive meaningful data for long-term performance assessment. Glass dissolution properties would be almost independent on glass composition (take the cheapest glass), surface area and temperature and would be directly proportional to water infiltration rates.

With very low water infiltration rates, vapor phase hydration may become significant. It has been stated above that a water infiltration rate of 0.05 cm/a would mean that $5 \cdot 10^{-5} \text{ cm}^3$ of water are provided per year for every cm^3 of void space. If the relative humidity is 100%, $2 \cdot 10^{-5} \text{ cm}^3$ of water mass are present anyhow in the vapor phase. Convection of humid air in the pore volumes may thus provide much more water for glass alteration than $5 \cdot 10^{-5} \text{ cm}^3$ of water per year. Consequently this review follows the recommendation (page 4.5) by the authors to include vapor phase hydration tests (VHT at 100%RH) in the test strategy. The objectives of this test shall be clarified. Since no model or rate law is provided to describe vapor phase hydration, the goal of the VHT test shall be, to justify this ignorance by showing that low temperature

hydration rates are much smaller than glass dissolution rates in liquid water at very low water infiltration rates.

4.5 Other test methods:

agree on evaluation by the authors, including on what is stated on the drip test

4.6 Tests with radioactive glass

A ranking of radionuclides with respect to radiotoxicity as a function of time and with respect to mobile radiotoxicity also as a function of time shall be provided.

The test plan is not convincing and test selection (VHT, PCT, PUF) appears arbitrarily. The objectives of radioactive testing and expected results shall be made more clear: e.g.

- (1) radioactive tests are used to demonstrated that no radiotoxic element is dissolved faster than the glass matrix (i.e. there is no selective leaching, no dissolution of seggregated Tc... phases).
- (2) radioactive tests shall identify maximum concentrations of dose relevant radionuclides for service conditions
- (3) radioactive tests shall identify potential secondary host phases for radionuclides.

It is very important to ensure

- a) that the glass is produced in a similar way as the technical product (redox conditions, cooling history...)
- b) that maximum solution concentrations and solubility controlling host phases are determined for the whole range of variations in the expected disposal conditions (scenario dependent)

4.7 Materials interaction tests

The description of materials interaction tests rests vague, probably due to the absence of a clear design of the disposal facilities. In consequence, I think, materials interaction tests shall be restricted to a minimum. A clear definition of the main objectives shall be provided. As long as a detailed design is not available, it is useless to use the PUF tests which might simulate certain hydrodynamic characteristics of the system. In contrast to the authors, I believe batch test like the PCT to be better suited to obtain screening results for materials interaction, without implying a particular design. Also I disagree with the authors, that the effect of cement would be restricted to an interfacial region. This is based on three arguments:

1. There are expected about similar masses of cement and glass
2. Cement reacts faster with water than the glass
3. Even with glass only, the pH plume may extend by more than 20 m (see prediction in the supporting document⁷), and in consequence also the cement alkaline plume will extend by more than 20 m.

A consequence of these three arguments is that batch tests are better than the PUF for simulating such a generic interaction. PUF tests may be used, once the detailed design of the disposal facility becomes available.

The authors expect also that carbon steel might be used. This is very important for the mobility of redox sensitive radionuclides. Consequently, it is suggested to perform some PCT materials interaction tests with carbon steel and with radioactive glass. Tc is expected to become very immobile.

4.8 Role of natural analogues

“Analogy” is no method (page 4.13) but an observation.

I disagree with the approach of the authors: the testing of natural glass in the experimental tests has no implication on the performance of either natural or man made glasses under natural conditions. It only confirms, whether or not the same mechanism are valid in the laboratory tests. In the same way as the suggested laboratory glass one could have also suggested to study an ordinary window glass. Laboratory tests with natural glasses are only meaningful if these testing strategy is combined with an assessment of the behavior of the natural glass under natural

alteration conditions. This would be a full sized natural analogue project, covering analyses of ground water compositions, assessment of hydrodynamics, dating of alteration histories, determination of alteration products and surface layer thickness as a function of age etc.. This should be done with a glass of rather similar composition than the waste glass (similar alkali content) and should be studied in geological areas with similar low water infiltration rates. I am not in the position to judge the suggestion of using obsidians from Oregon, because the glass composition (alkali content) is not given by the authors.

If such a large project is outside of the funding level of the present project, it is suggested to delete all tests with natural glasses from the testing strategy.

Natural analogues may still be included in the study based on a literature study.

5.0 Field tests

Lysimeter tests are potentially important in verifying the described models. However, I think it is important to use the same glass as suggested. If the glass has a high corrosion rate, its alteration mechanism may also be different than that of the real glass. Consequently, the outcome of the test would be meaningless. Also, glass dissolution mechanism would vary with water flow rate. I think, with a high water flow rate, various artifacts are created, which are meaningless for long-term predictions.

6 Modeling approach

Basically I agree with the general modeling strategy, provided, my comments on the rate law (Long term rates, temperature dependency of saturation constant K...) are taken into account. However the validity of any modeling strategy depends on the database used. This database is not provided for the present review, not even in the supporting documents. It is suggested to provide these data to the review team until the ongoing review process is terminated.

The only data presented are those on page 4 of the document⁷. There are no data on Tc, Am and only a single one (Pu(OH)₅⁻) on Pu. This Pu-specie is probalby

irrelevant, due to carbonate complexation. There are no thermodynamic data on cement or iron alteration products. There are no solid phases containing U(IV), but there are aqueous species. Also there are no sorption constants for radionuclides. No strategy is provided by the authors how to treat sorption processes or colloid generation by modeling.

In particular, the proposed code STORM would be well suited to treat the problem of water access controlled glass corrosion rates, as it considers overall mass balance of water⁶, however, the code AREST CT which does not have this capability may lead to erroneous predictions. Particularly it would assume aqueous diffusion as an important release controlling mechanism (see ⁷), while there may not be sufficient water to allow diffusion.

⁶ McGrail and Bacon, PNNL 10830 (1998)

⁷ Chen, McGrail, Engel, „Source term Analyses for Hanford low activity tank waste using the reaction/transport code AREST-CT.

Peer review of document PNNL-11834, February 1998

by

Dr. Werner Lutze
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“A strategy to conduct an analysis of the long-term performance of low-activity waste glass in a shallow subsurface disposal system at Hanford”

Authors: B. P. McGrail et al.

General comment

The guideline for this review is the stated purpose of the testing program: *demonstrate a scientific understanding of the processes controlling long-term glass corrosion so that the models describing these processes can be used with confidence in extrapolating to the expected service conditions (p. 4.1).*

Comments by sections

Sections 1 through 3.0: no comment.

Section 3.1 states correctly that glass dissolution rates are known to decrease with time and that the rate cannot become zero because glasses are thermodynamically unstable in water.

Section 3.1.1 emphasizes the significance of secondary phases. I fully agree. Here is a concern: The authors state correctly that at low temperature (15°C) metastable and amorphous phases may persist for long periods of time. I need an explanation why it is necessary to find a way for accelerating the transformation process? The untransformed phase may have a different K (equilibrium constant) than the transformed phase.

Transformation may not be avoidable or comes unnoticed at higher temperatures. 15°C is not a test temperature. Why? 20°C is not so different from 15°. I do not see information in the document on how you make sure that the fundamental transformation process is not altered.

What are the implications for modeling long-term glass corrosion under service conditions, if information on phases at 15°C is ambiguous?

Section 3.1.2 emphasizes the significance of ion-exchange. The ion-exchange related increase in pH in solution was shown to increase the rate of radionuclide release by three orders of magnitude, as the authors say. Suppression of ion-exchange by modifying glass composition is certainly worth an investigation. It would be useful to get some ideas as to how the test program could be affected by the outcome of ongoing research. Also, to what extent is this research limited by the waste composition? Na has to go into the glass and the waste volume should not increase.

To my knowledge, the auto-catalytic effect can be started also by the solution. If the aqueous phase has the ‘right’ composition when it contacts the corroded glass, then the glass may keep dissolving at the forward rate or at the rate water is delivered. This

process may be significant only in localized regions and may not contribute much to the overall release of radionuclides from the waste form.

Section 3.2.1 gives the rate law in eq. (1) and its simplification for glass dissolution in eq. (2). Eq. (2) appears to reflect state of art experimental evidence.

However, ion-exchange and matrix dissolution are parallel processes. Ion-exchange is a solid state diffusion process (mostly M^+/H^+) and is at least in the beginning faster than matrix dissolution. Using the SPFT test at constant pH and temperature, J_{Na} should be time-dependent and J_{Si} not. So, J_i is not the flux of any ion, at least not in the beginning (e. g., Gong et al., J. Nucl. Mater. 265, pp. 12-21, 1999).

Section 3.2.1.1: no comment.

In section 3.2.1.2, the parameters σ and K are discussed. I agree that the experimental techniques proposed in section 4.1 are in principle best suited to obtain a value for σ . Using more than one experimental procedure is meritorious. However, it is unfortunate that the tests selected are just those that have not yet become standard tests, have not participated in round robin experiments, and have not been approved in any other way such as, e. g., some of the MCC tests. This comment applies also to the VHT (section 4.2) and PUF (section 4.4). Hence, there is a need to initiate a process that leads a peer review of these test procedures. The ILAW project is the first and probably the last of its kind and so enormous that every effort should be made to avoid unnecessary critique.

If the reaction order parameter σ turns out not to be 1, will the authors try to understand what is the cause, and how will they do it?

Assigning K values is a matter of how well the glass alteration products are known. Pure phases for which K values may be known, are less frequently encountered than solid solutions as glass alteration products. As the reaction progresses and solution composition changes, the composition of solid solutions changes. Hence, there may be a need for solid solution models linking composition to K . If this task is too ambitious, an analysis of existing K data of selected minerals may be useful to evaluate the potential impact of K on long-term glass corrosion rate. There is, e. g., a solid solution model for clays, developed by B. Fritz, Strassbourg (I will get the reference). The potential mismatch between the calculated and the real long-term rate of 3 to 4 orders of magnitude is large enough to question the value of the whole study. This point deserves at least as much attention as the selection of experimental procedures.

Identification of alteration phases has been qualified as key input information for modeling. This is correct but deserves more attention than expressed in the document. There should be a section describing the effort made to yield this key information. As the authors know, this involves a costly and time consuming phase analysis and identification program.

Section 3.2.2 deals with ion-exchange and diffusion-controlled processes. Obviously, the authors prefer to leave the discussion on how ion-exchange should be included into the mathematical treatment of glass corrosion for when more results of their current studies are available. Nevertheless, my comment above is still valid.

Looking at the experimental data in figure 3.2, it is not clear why the line is where it is and what the scattering means. Without discussion it may be speculated that the amount of excess Na and the slope depend on S/V.

Sections 4 to 4.1.3: no comment.

In section 4.1.4 the selection of SPFTs is made and a testing strategy is developed.

Figure 4.3 shows that the selected test procedures provide numerical values for k , E_a and η with reasonable precision. This is very encouraging. The selected pH range seems to be sufficient to cover service conditions.

Section 4.2: The vapor hydration test has in fact been used to replicate weathering phenomena on volcanic glasses. To my knowledge, the test is not a generally accepted method in archeology to simulate long-term weathering effects. Not that this was claimed by the authors, but the implication is that its usage to accelerate corrosion of waste glasses cannot be supported by usage of this test in another discipline. Nevertheless, VHT can be used as a complementary test and it helps, if it confirms what was found by the other methods. If unconfirmed information is obtained by this test, it is recommended to seek independent confirmation prior to inclusion into a model. An extremely high concentration in 'solution' (in the water film present at 100% RH) is reached almost instantaneously. This situation supports supersaturation and enhances precipitation and nucleation. The speed at which Ostwald's principle is observed may be different and the phases may not be the same as under service conditions. The pH at which alteration phases form, may be very high for the entire duration of the test. If the pH is high, dissociation of silicic acid may be high and Al species may be soluble. Under these conditions, the glass may corrode with the forward rate of reaction ($Q/K \ll 1$). The authors point out that the rate measured is not the glass dissolution rate but the rate at which alteration phases form. pH excursion is less a concern with obsidians and tektites because of their comparatively low content of alkali. Similar comments were made by the authors in section 4.3 when discussing high S/V ratios. They apply to VHT for the same reason.

Sentence #10 in section 4.2 should read: The water (not solution) evaporates from the sample when the test is terminated and a solution is not available for analysis.

Section 4.3 deals with PCT tests. Obviously, the more flexible method B has been selected and it is argued that experimental corrosion conditions covered by this test resemble service conditions. If this is so, usage of a standard leach test is certainly a good idea.

A comment on S/V, flow, and other parameters: As stated by the authors, the PCT is a static test only approximating the slow flow conditions of the 'open' repository system.

It may not be unreasonable to approximate the large volume of waste glass by a volcanic rock formation with a lot of glass phase in it. The natural system is heavily fractured and open. So is the waste glass system.

There are localities in natural glass systems with very limited flow of water, particularly, if we look deeper into the rock. This would probably match the repository situation best. Looking at volcanic glass alteration phenomena shows that a lot of

alteration takes place at high S/V ratios. In the natural system, corrosion progresses along cracks or pores and spreads from there into the bulk glass. Water penetrating the cracks and pores is likely to be consumed by the chemical reactions with the glass. Hence, there may be very little, if any material (radionuclide) transport in a fluid phase. In other words the glass acts as a desiccant. This mechanism may contribute significantly to the overall corrosion process in the repository and may constitute a significant fraction of the total amount of glass corroded at any time. If this is so, the proposed limit of $S/V \cdot 20,000 \text{ m}^{-1}$ may be looked at twice. Crack widths of $50 \mu\text{m}$ to $1 \mu\text{m}$ would yield a range of S/V between 10^6 m^{-1} to $2 \times 10^4 \text{ m}^{-1}$. In places where substantial transport of leachate is possible, corrosion would probably take place at $S/V < 20,000 \text{ m}^{-1}$. The reaction rate may not be much higher than within the fractures because of silica saturation in solution.

PCT may be a good enough simulation or approximation of the actual corrosion conditions. I support application of this test. However, depending on the significance of corrosion in fractures, it may just measure one of the water-driven glass corrosion processes because of S/V limitation.

Actually, there is no test that addresses corrosion in fractures and pores. If an S/V increase by a factor of 20 occurred upon cooling of the ILAW (COGEMA gives a factor of 10 for their commercial HLW glass) a substantial fraction of water could penetrate and 'disappear' in fracture surfaces. This would be a beneficial effect in terms of radionuclide release. I suggest that his issues be discussed and considered or discarded with reason.

I wonder whether consumption of carbonate is an issue with the PCT test. CO_2 may be consumed rather early in water penetrating the interior of the (highly fractured!) waste glass body.

pH excursion may be a problem at high S/V because of glass composition. That may be a reason to limit S/V in PCTs.

I do not see how the results of the PCT can be used to confirm K and σ values measured by other tests. Does this mean that once the values are known one can separate the obscuring effects imposed by PCT conditions and get the same K and σ as with the SPFT? How do you know? Or do the authors want to say that the values can be compared and that new insight may be gained from potential differences?

Section 4.4: The claims made in this section regarding the information to be obtained from PUF tests seem reasonable. To critically evaluate the PUF, I should have had some exposure to this fairly complicated procedure as I did with many other tests. It appears that the PUF has been used only by its inventors.

Taking the extraordinary magnitude of the overall Hanford LAW vitrification and disposal project into account and the enormous costs, it is not too much to ask for inclusion of another organization using the PUF and confirm its effectiveness and the results obtained by PNNL. Enough materials combinations and variables have been suggested in the document to split work between two (or more) organizations and to provide for sufficient overlap to compare results. I consider time and budget constraints as insufficient reasons to sacrifice the extra credibility gained by including other organizations. I maintain that the peer review of the document can not provide this credibility. There is insufficient outside expertise to fully evaluate the PUF.

Section 4.5: I wonder why so much effort was put into all these tests. E.g., I am not sure that Dr. Barkatt would agree with the comments made by the authors. It may be true that the proposed tests cover what can be expected from these other test methods and

lend themselves in a better way to modeling with standard computational methods and tools. And yet the value of work completed by the Materials Characterization Center and others and the wide spread application of many of the tests not proposed as experimental tools in the document should not be underestimated. It could be recognized by inviting outside institutions to apply these tests to ILAW samples provided by PNNL or others and to compare the results with the ones from work proposed in this document.

Section 4.6: Finally, all success of modeling exercises is measured by how well the long-term release of radionuclides can be predicted. Therefore, experiments with radioactive glasses are very important. Experiments with elements such as Tc, Se, and I are scarce. Solubility-limiting phases, if any, have not been characterized sufficiently. We know that TcO_2 is insoluble and there are some stable I- and Se-minerals. Colloid formation constitutes an additional phenomenon difficult to model. How will it be modeled? There are many cases, particularly for Pu, where modeling did not provide much more than a trend (e.g., work by Grambow et al.). The radiophases are sometimes difficult to characterize because of the low concentration of the radionuclides in them, or if the radionuclides form insoluble oxides or hydroxides, there is just not enough material to identify the phases.

Hence, experiments with radioactive glasses should begin soon and given high priority and modeling should focus on these elements. Spectroscopic methods may be useful to characterize species in solution.

The authors indicate that the funding level of the LAW program may limit experiments with radioactive glass. None of the radionuclides and their concentration levels in the glass, even when enhanced, require sophisticated radiation shielding. Experiments can be conducted in glove boxes and modification of the experimental devices for remote handling is not necessary. Here, the PUF may be particularly valuable as it offers the possibility to 'condition' (equilibrate) the water contacting the glass and to pass the leachate through various materials that may change the speciation of dissolved radionuclides. The positioning of the various materials in the column is an important issue, as pointed out. How will radionuclide adsorption be separated from precipitation?

Section 4.8: Reading of this chapter gave me the impression that there is no strong commitment to study natural analogues. This may be justified but not by the content of this chapter. The PUF should not be applied to study natural glasses simply because no natural glass has yet been subjected to this test. Use of the PUF is justified, if it can be shown that the test provides results useful to support predicted long-term corrosion behavior of the ILAW. It is stated in this chapter that a small number of tests should be conducted. What are the conditions? Why have natural glass samples not yet been selected? Why, e.g., has Dr. Ewing, owner of one of the most complete natural glass collections, not been contacted for advice? For testing, the authors prefer natural glass samples with an alkali content much higher than basaltic glasses. The suggested potential site for such a glass is a suite of obsidian flows at Newberry Crater, Oregon. Obsidians are glasses with alkali contents lower than that of basaltic glasses.

The main component of the repository, besides ILAW, is concrete. Its alteration may affect the composition of the water (leachant) over long periods of time. It may be interesting and important to study a natural analogue for concrete. This need not be an experimental program. Instead, information could be extracted from the "Maqarin Natural Analogue Study" and analyzed in terms of its relevance for the Hanford ILAW

repository situation. The Maqarin site in northern Jordan is considered to be a natural analogue for waste with low to intermediate level radioactive waste. The site has been studied by NAGRA (Switzerland), NIREX (UK), Ontario Hydro (Canada) and SKB (Sweden). Studies have established its general applicability as an analogue to cementitious repositories. Reports are available from NAGRA and SKB.

It is not clear to me how long-term testing of natural glasses at ANL impacts the ILAW project and vice versa. How will the result obtained at ANL be incorporated into the ILAW database? What kind of information is expected to be obtained from ANL at least to potentially support long-term ILAW performance predictions? I have the impression that the two programs are not well coordinated.

Section 4.9: The test matrix looks fine, except I suggest more studies of radioactive glasses (add one temperature to PCT and PUF). Suggested experiments to be conducted by other institutions would have to be added to the matrix.

Section 5: Though the chapter deals with field tests, it is not clear whether the authors strongly support such an activity or whether the chapter was written for the sake of completeness. Whereas tests in the laboratory are described in sufficient detail and a description of the apparatus is given, the field test is only addressed by saying that some experiments should be run at a steady flow rate and with a glass of low chemical durability. There is no design of an experiment and no link to modeling is shown.

I recommend that a lysimeter-type field test be designed with input from others, reviewed, and conducted to expand and support the database generated in the laboratory. Field tests conducted in the past brought people together with different experience and background and provided a forum to discuss results nationally and internationally. Radioactive waste disposal is a problem worldwide. Given the skeptical to negative resonance to everything nuclear in several countries, opportunities to work together and to generate increased confidence should not be missed. A field test at Hanford may be such an opportunity.

Section 6: Obviously, extensive modeling capabilities and expertise have been established at PNNL to conduct an ILAW repository performance assessment. This makes it possible to immediately digest the database generated on site and to provide quick feed back between modelers and experimenters. Fig. 6.1 is very illustrative and reflects a sound modeling approach as described in the text.

Again, I suggest that other institutions with proven modeling capabilities be invited and financially supported to contribute to this effort. The project should not be limited to one institution. Participation of others will increase confidence in the results within and outside the technical community.

Finally: A short paragraph should be written dealing with bacterial activity. Construction of the repository introduces new or redistributes indigenous bacteria. In the presence of enough organic matter (roots wood etc.) redox reactions may be mediated by microbes. Usually, this results in a change of the redox potential of the water by consumption of dissolved oxygen. After that, other elements may be reduced. I do not see any deleterious effect that this may cause. Bioactivity may be very limited because there is not sufficient organic matter.

Review of PNNL-11834 Report

*A Strategy to Conduct an Analysis of the Long-Term Performance
of Low-Activity Waste Glass
in a Shallow Subsurface Disposal System at Hanford*

by

Dr. Étienne Y. Vernaz

CEA Senior Expert (France)

1. INTRODUCTION

The report is generally clearly written, and the proposed strategy (determine environmental factors and materials, determine important alteration process, develop models, etc.) is based on a rigorous methodology. Particular care was given to describing the "disposal system", as is essential for assessing the pertinence and magnitude of each mechanism. The proposed tests are generally interesting.

The main weakness from our standpoint is the total confidence placed in a complex kinetic law, presented as universal and fully applicable to any type of glass. The most recent work involving French nuclear glasses and various simplified glass compositions has demonstrated that this law is inapplicable in a large number of experimental situations. Extreme prudence is necessary with regard to LAW glasses for which no experimental validation of such a law has been reported to the best of our knowledge.

The following discussion reviews the kinetic law, as well as various strategies for dealing with the uncertainties related to it. The role of interdiffusion, the pertinence of the proposed tests, environmental coupling and geochemical modeling will also be considered.

2. RATE LAW FOR HYDROLYSIS AND DISSOLUTION

The report refers to a "well accepted mechanistic model", stating that "This model requires that six parameters be determined...", and adding that "the processes that control glass corrosion are well understood and rate expressions have been developed and tested".

It is our view that these positions must be largely qualified.

The rate law used in this report, initially proposed by Aagaard and Helgeson:

$$J_i^a = v_i k e^{-Ea/RT} \left[1 - \left(\frac{Q}{K} \right)^\sigma \right] \prod_j a_j^{-n_j} \quad (1)$$

has been adopted by many authors (including ourselves) and widely used in an attempt to describe the alteration of nuclear glass. Indeed, this rate law has been so widely cited and referenced (for lack of a better one) that it may seem to be applicable to complex glasses and to benefit from an international consensus. Its apparent completeness suggests that each element i in the glass and j in solution is correctly taken into account on the basis of solid theoretical underpinnings.

In fact, this is not at all the case, and recent work in France [Jégou, 1998; Gin, 1998; Gin, 1999; Vernaz, 2000] has highlighted many significant experimental and theoretical limitations in the application of this law to nuclear glass.

Consider, for example, the $\prod_j a_j^{-n_j}$ term that is fundamental to Eqn (1). It assumes that most of the glass hydrolysis products j affect the initial rate (i.e. when the $(1 - Q/K)$ term is near 1) of glass dissolution. However, as the catalytic effect of these species on the initial rate r_0 has been found by experience to be negligible, the $\prod_j a_j^{-n_j}$ terms are arbitrarily disregarded—except for H^+ , as the pH-dependence of r_0 has been well established.

The n_j coefficient applied to the H^+ ion (typically 0.39 for a nuclear glass at 50°C) is based on an experimental fit, but cannot be associated with a stoichiometry—contrary to its own definition ("stoichiometric coefficient for the j th reactant species").

Similarly, the affinity function $(1 - Q/K)$ suggests that a thermodynamic equilibrium exists between the glass and solution when $Q = K$ (or a quasi-equilibrium with a "residual" final rate: $r_f \cong 10^{-4} r_0$ would assume that $Q = 0.9999K$).

2.1 Overall Solubility Hypothesis

If all the glass elements are taken into account to calculate the free hydration energy of the glass [Paul; Jantzen & Plodinec; Advocat; ...] the measured activities in solution will never be such that $Q \neq K$, and no significant drop in the alteration rate should be observed during most experiments. This, of course, is not the case, as illustrated by Figure 1 for the French R7T7 glass.

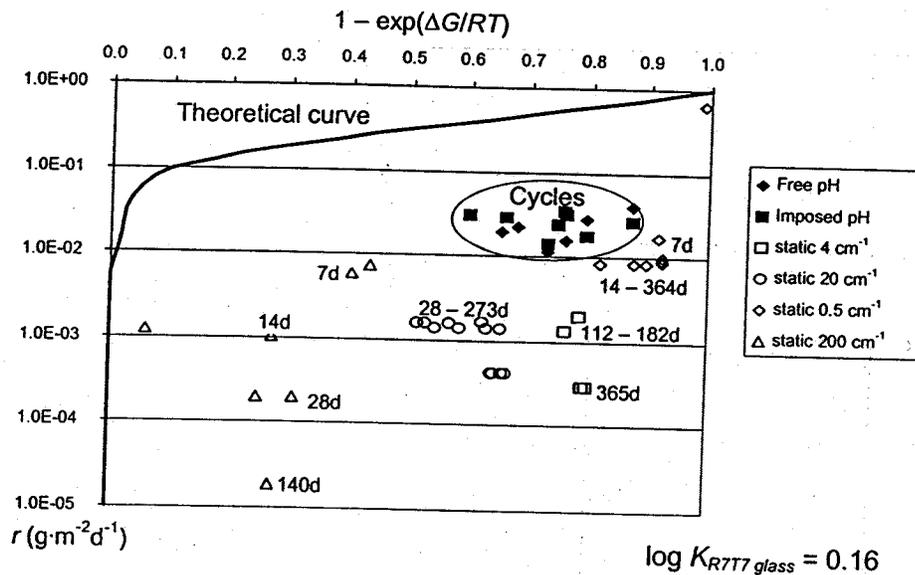


Figure 1.

Although this point is acknowledged by the authors ("assigning K to a hypothetical phase including all the glass elements has not proven successful in modeling...") *the report does not specify which elements must be taken into account in calculating the ion activity product Q .*

2.2 Solubility of a Residual Hydrated Glass

The hydrolysis reaction does indeed occur in a glass dealcalinized by interdiffusion, from which most of the mobile elements (Na, Cs, Mo and even B) have been leached. A semi-global solubility hypothesis taking the main network formers (SiO_2 , Al_2O_3 , Fe_2O_3 , etc.) into account was therefore proposed [Bourcier ...]. *A similar hypothesis is apparently postulated by the authors of the report, but no dissolution equation is proposed. The choice of species and stoichiometric coefficients taken into account is decisive, however, for calculating the affinity term. The values of these coefficients and the reactor order σ used by the authors in the referenced publication [J. Nucl. Materials 249 (1997) 175-189] resemble parameters used to obtain a close fit much more than they appear to be substantiated by a validated dissolution equation.*

A reaction order of less than 1, cited in some of the authors' work, appears to be an artifice used to slow the approach to equilibrium and better fit the experimental data points without taking into account the transport phenomena within the alteration films.

The experimental investigations carried out in France have demonstrated the weaknesses of a semi-global solubility hypothesis based only on Si and Al. In many cases where Al is controlled

in solution by secondary precipitation, this type of model predicts an alteration rate near r_0 ($Q = 0$), whereas in fact alteration occurs at a very low rate.

2.3 Solubility Based on Silica Alone

Assuming the hydrolysis of silica is the kinetically limiting reaction, Grambow proposed to describe the glass hydrolysis reaction by considering only silica hydrolysis (Eqn (2)) and by limiting Q to the activity of H_4SiO_4 in solution.



Strictly speaking, this is not an elementary step, as four bonds must be broken in turn for a silica tetrahedron to enter solution. Nevertheless, as it is very difficult to determine the activity of the hydroxide surface groups, the rupture of the final bond is assumed to be critically limiting—an assumption that we consider highly unlikely.

In any event, both of these theories have been disproved today by an experiment (Figure 2) showing that a pristine glass specimen, immersed in a leachate previously saturated with a specimen of the same glass, is altered at virtually the initial dissolution rate r_0 .

Pristine glass behavior in a saturated leachate

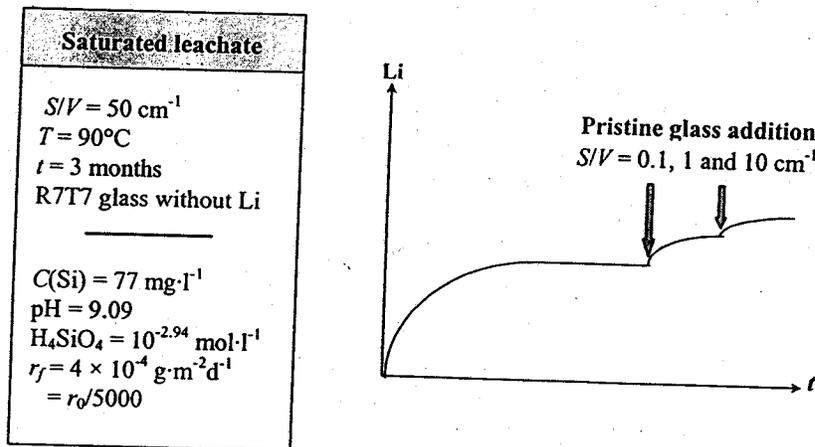


Figure 2.

There is thus no thermodynamic equilibrium between the pristine glass and solution. This is corroborated by the fact that introducing a pristine glass coupon causes the silica concentration at saturation C^* to reach a new equilibrium C_2^* (or even C_3^* if the experiment is repeated). C^* therefore does not correspond to the intrinsic solubility of the glass, but is merely a dynamic parameter depending on the operating conditions.

2.4 Role of the Alteration Film

At no time is the role of the alteration film mentioned in the report with regard to the glass alteration kinetics, nor with regard to its strong retention capacity for certain radionuclides.

The gel that forms at high flow rates on the French nuclear glass has been shown to be nonprotective, and even capable of accelerating subsequent alteration because of its high silicon sorption capacity. Under near-saturation conditions, however, the gel becomes highly protective and is the principal cause of the very significant drop in the alteration rate at high reaction

progress; the affinity function under these conditions is responsible for reducing the rate by less than an order of magnitude.

For this glass, our conclusions were as follows:

- From a scientific standpoint:
 - The rate of glass dissolution is mainly controlled not by the chemical affinity of the hydrolysis reaction, but by the properties of the gel layer, which evolve considerably during glass leaching.
 - The apparent steady-state silica concentration corresponds neither to a glass solubility limit, nor to an intrinsic solubility of the gel. It is an empirical parameter reflecting the dynamic (and not thermodynamic) equilibrium between the quantity of silica hydrolyzed from the glass and gel, and the silica condensed in the gel.

- From an “operational” standpoint:

It is clear today that the chemical affinity concept and protective gel concept are not to be opposed, but must be combined to account for experimental reality:

- Even if the glass alteration kinetics are not controlled by “chemical affinity”, this concept remains the only one we have that can account for the “apparent saturation conditions” under which protective gels develop.
- The notion of a “diffusion barrier” is indispensable to account for the fact that alteration virtually ceases under conditions that do not correspond to any thermodynamic equilibrium between the glass and solution.

2.5 Conclusions Regarding the Kinetic Law

It is not our intention here to generalize as applicable to the Hanford glasses (which are still poorly known by our team and cover a wide composition range) the conclusions drawn for the R7T7 glass (with a narrowly specified composition) on the basis of over 15 years of research. Nor is it to reopen the debates among experts concerning the origin of the low rates observed under saturation conditions.

It is appropriate, however, to acknowledge the conclusions that can be drawn from many studies of high-activity nuclear glasses.

The kinetic laws of alteration applicable to current glasses should be considered as phenomenological laws containing a healthy dose of empiricism, and not as universal laws arising from well established thermodynamic concepts.

Such laws can be used with a suitable confidence level over a limited range of compositions and environments within which the variability of all the parameters has been established. On the other hand, extreme prudence is required when using them with new glass compositions and environments for which their validity has not been demonstrated.

3. STRATEGY FOR MANAGING UNCERTAINTY AND RANKING PARAMETERS

The report considers only a single strategy based on a very complex kinetic law, coupled with geochemical codes that are also complex (AREST or STORM), without at any point addressing their underlying hypotheses and uncertainties. It thus postulates an interesting but very sophisticated overall model of unproven robustness.

Several alternate strategies can be considered for assessing the alteration kinetics of a glass and the "glass source term".

3.1 The " r_0S " Strategy

The first—and probably the simplest and most robust, but also the most penalizing—of the many possible scenarios is the " r_0S " strategy. The glass alteration rate is assumed constant over time and equal to its hydrolysis rate in pure water: r_0 . The quantity of glass altered per unit time is thus assumed constant at a value equal to the product of r_0 by the glass surface area S . All the elements in the altered glass are assumed to be released (source term), and none is retained in secondary alteration products.

Except for a relatively brief initial period during which some radionuclides may be released by interdiffusion at a rate exceeding that of glass hydrolysis (see below), the initial rate r_0 can be considered as the maximum alteration rate. This rate can generally be assumed to depend only on the glass composition, the temperature and the pH. Some catalytic effects have been reported, notably in the presence of humic acids [Gin, 1997], but they can generally be disregarded in realistic environmental scenarios (their effect does not exceed a factor of 2).

If the temperature and pH are maintained sufficiently constant by the environment, estimating the alteration kinetics is limited to measuring r_0 (for example at 15°C and pH 9 or 10) and determining the glass surface area S accessible to water.

If the temperature and pH are likely to vary, the dependence of r_0 on these two parameters can be determined relatively precisely, as shown in Figure 4-3 of the report, based on simple and generally accepted equations (even if the pH dependence law is purely empirical).

We therefore propose to establish a hierarchy among the parameters. In the case of low-activity glasses, which will therefore be leached at low temperatures, the initial dissolution rate should be assigned the greatest importance, whether measured directly at the disposal equilibrium pH and temperature or calculated from its measured evolution versus the temperature (Ea) and pH (n).

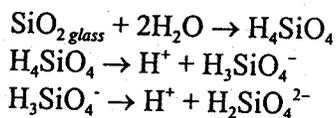
Finally, in the case of industrial glass blocks fractured during cooling, *determining the surface area S remains one of the major problems that is practically not addressed in the report.*

Note: This simple approach has been successfully used in France to assess the release rates for heavy metals from vitrified non-nuclear wastefoms (domestic waste incineration ashes, clinker, asbestos, etc.) in surface disposal. Considering the low temperatures of the utilization scenarios and the pH buffered by atmospheric CO₂, this simplified approach is sufficient to demonstrate that the heavy metal concentrations in the leachate near the vitrified wastefoms remain below the permissible limit for drinking water. It is not impossible that a similar strategy could be applicable here, considering the low specific activity of the glass and the low temperatures (15°C).

3.2 The " $r(t)$ " Strategy

A strategy based on the evolution of the alteration rate over time is certainly more realistic (less penalizing), and has been largely developed in France for the R7T7 high-level waste glass. *For this glass*, the resulting alteration rate is 100 to 1000 times lower (depending on the temperature) than for the r_0S strategy, subject to the reserves noted above. The kinetic law used in this case may take into account a chemical affinity function, the recondensation of an increasing silicon fraction in the alteration gel, the diffusion of species within the gel, or a combination of all these phenomena.

- If an affinity function is used, it is important not to lose sight of the fact that the solubility product K is only an apparent solubility that does not correspond to an intrinsic thermodynamic solubility of the glass. It is an empirical parameter used to account for "the apparent saturation conditions observed in solution". It must therefore be measured under conditions (S/V , flow rate, temperature, pH, etc.) as close as possible to the actual environmental conditions and its variation range must be determined.
- It is advisable in measuring K to take only silica into account ($K = C_{Si}^*$). Adding other elements (Al, Fe, etc.) to the affinity function does not significantly improve the experimental fit, but does considerably increase the uncertainty on this parameter (an infinite number of Al_aSi_b products can result in the same value for K !) and increases the difficulty of transposing the laboratory measurement to the conditions of an actual repository.
- The evolution of the apparent total silicon solubility C_{Si}^* versus the pH must be measured and not simply calculated from silicic acid dissociation equations. For many glasses—and for the French R7T7 glass in particular—the actual C_{Si}^* versus pH variation does not correspond to the evolution predicted from the classic equations:



It would be a serious error, for example, to assign a value to C^* at pH 10 based on measurement data obtained at pH 7 or pH 13 (notably for the PCT test).

- Finally, if allowance is not made for transport phenomena in the alteration film, but only for an affinity function, the weight of the function in the diminishing alteration rate must be limited to the extent demonstrated in the laboratory by immersing a pristine glass coupon in a saturated leachate; the result typically does not exceed a factor of 10. The $(1 - Q/K)$ term should therefore be limited to a value of 1/10, and must not be allowed to approach zero as proposed in this report.

4. EFFECT OF ION EXCHANGE

We fail to understand the assertions in the report, presented as a recent discovery, by which allowing for ion exchange can affect the long-term rate of radionuclide release by several orders of magnitude. Interdiffusion, as with any diffusion phenomenon, diminishes with the square root of time (as shown in Figure 3.2), and is thus a predominantly short-term phenomenon. If the glass compositions developed for low-activity waste have high interdiffusion coefficients, this will represent a short- or medium-term problem, but not a long-term concern. We understand even less the referenced article (Y. Chen, B.P. McGrail and D.W. Engel, 1997) in which interdiffusion is modeled by a "measured rate constant" of $1.74 \times 10^{-11} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$! If interdiffusion is indeed involved here, the rate is never constant: it is infinite at the first instant, and tends toward zero after an infinite time.

Competition exists between the interdiffusion phenomenon, which removes the alkali metals from the glass, and the surface reaction that transforms the glass into a gel by hydrolysis and condensation. If hydrolysis is assumed to occur at a constant rate r^* , the problem (competition between a linear phenomenon and an inverse square phenomenon) can be solved analytically (Boksay, 1968): after a time, a dealkalinized glass region of constant thickness advances into the pristine glass at the rate r^* ; sooner or later (provided the hydrolysis rate does not drop completely to zero) hydrolysis prevails over interdiffusion.

- The thickness of the dealkalinized region is then constant at: $\lambda = D/r^*$.

- The time constant before reaching steady-state conditions is: $\tau = D/r^{*2}$.

4.1 Initial Transient Effect and Possible Bursts of Radioactivity

Interdiffusion may indeed lead to an initial release of alkali metals or alkaline earth metals in appreciable amounts, *and the impact both on the initial pH excursion (clearly visible in the PUF test) and on the initial release of major elements (e.g. Cs and Sr) must be assessed; it is therefore advisable to measure the interdiffusion coefficient of LAW glasses.*

If, for example, the estimated interdiffusion coefficient D at pH 9 is $10^{-20} \text{ m}^2\cdot\text{s}^{-1}$ and the residual alteration rate r^* at 20°C is $10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, then $\lambda = 3 \text{ }\mu\text{m}$ and $\tau = 32 \text{ years}$.

In this hypothesis, the impact of the formation of a 3-micron dealkalinized zone in a few decades must be evaluated. Given the glass surface area accessible to water, it is a simple matter to establish the inventory of Na, Cs, Sr, etc. present in this zone and capable of being mobilized by interdiffusion.

Only if this impact is considered too penalizing by the safety analysis would it be necessary to develop a research program to minimize "alkali ion exchange".

Note: Minimizing the rapid release of alkali metals and alkaline earth metals by interdiffusion has been investigated by glassmakers to avoid polluting the contents of glass bottles. Adding 1 to 2% MgO to the glass composition drastically reduces this release.

4.2 Negligible Role of Long-Term Interdiffusion

The pH under static conditions (or with very low renewal of the medium) results from the competition between ion exchange and glass dissolution. In static laboratory tests at high S/V ratios, ion exchange is clearly the predominant factor determining the pH. Conversely, in a repository environment the pH will arise from the convolution of the species arising from ion exchange, from glass dissolution (which increases with the pH), and the species added and removed by the medium.

Let us disregard for a moment the impact of the environment on the pH and consider the evolution imposed by the glass in the presence of water flowing at a low rate. As we have already seen, a dealkalinized zone will eventually form with a constant thickness λ , after which the alkali metals will be released at the same rate as the other elements at a rate determined by the hydrolysis reaction. The excess alkali will gradually be eluted by the flowing water. Ultimately, therefore, the pH will be determined by dissolution and not by interdiffusion.

In fact, the environment cannot be completely disregarded. Both calculated and experimental findings show that the catastrophic scenario of a divergent series (increasing pH \rightarrow increasing glass dissolution \rightarrow increasing pH \rightarrow increasing glass dissolution ...) rarely occurs when the repository environment includes a buffering medium (atmospheric CO_2 , bicarbonates, clay, etc.). However, an equilibrium pH above 10 or 11 has a major effect on the glass source term.

The primary long-term objective is therefore not so much to minimize interdiffusion as it is to design glass compositions that are not too basic, and if possible that contain elements such as boron, which provide a buffer capacity with sodium to ensure a sufficiently low equilibrium pH in the repository.

5. PERTINENCE AND REPRESENTATIVENESS OF THE PROPOSED TESTS

The existing tests are generally well described and pertinently analyzed.

5.1 Characterization Tests

The SPFT is proposed as a universal test for determining all the parameters of the kinetic law.

While this test can indeed be used to measure the initial dissolution rate versus the temperature and pH (k , Ea and n parameters) as indicated in Figure 4.3, it is applicable only over a very limited range as discussed in the referenced report [McGrail, 1997]. If the flow rate/glass surface area (Q/S) ratio is too high the results are not significant, and if it is too low the results are no longer independent of the flow rate. In Figure 4 of the referenced document, only a narrow range around $Q/S = 10^{-7} \text{ m}\cdot\text{s}^{-1}$ is applicable. This operating point must further be adapted according to the temperature and pH.

On the other hand, the use of this test to measure K and σ is apparently invalidated even by one of the authors in the referenced document [McGrail *et al.*, *J. Nucl. Materials* 249 (1997) 175-189]. With a solubility based simply on silica, the resulting C^* value is 1.5 times lower than for quartz! With a solubility based on the product of $C_{\text{Si}}^{\alpha} \cdot C_{\text{Al}}^{\beta}$ the author concludes that "the simple flow rate variations do not provide the necessary or sufficient data to distinguish between the forms of a mixed Si-Al rate law".

We therefore recommend using a PCT at an imposed pH to measure the apparent glass solubility. The measurement should be repeated at several pH and temperature values bracketing the assumed repository conditions to determine the sensitivity of this parameter to the temperature and pH.

5.2 Accelerated Tests

Although the VHT is of interest for increasing the effect of secondary phase precipitation on the alteration kinetics, it is poorly representative of repository conditions because of the high temperature and the probably very high pH in the very thin condensed water layer.

The pH in this layer should be calculated in order to estimate the initial dissolution rate at the test temperature and pH. The important parameter is the ratio between the rate measured by the VHT and the forward rate.

- If this ratio is equal to 1, the impact of the newly formed phases prevents saturation conditions with respect to the glass from persisting at high temperatures and high pH values. It is impossible to know whether this phenomenon will occur over the long term at low temperature and lower pH, as both the nature of the phases and their precipitation kinetics will be different.
- If, however, this ratio remains much lower than 1, i.e. if the glass remains stable with respect to the secondary alteration products despite the high temperature and pH, then the apparent saturation conditions with respect to the glass can be expected to continue over the long term at low temperature.

The test is thus highly penalizing, but conservative. We fail to see the advantage of repeating it at 4 temperatures.

We can say the same for the PCT, which—when applied to LAW glasses—results in very high pH values and could lead to the exclusion of glasses on the basis of phenomena that will never occur. A prolonged PCT at a pH imposed by a pH-stat to avoid any organic buffering effect

would be much more realistic in our opinion. A short-term PCT-A without any imposed pH should nevertheless be maintained to eliminate glass compositions that cause the pH to exceed a specified limit (liable to occur in the innermost regions of closed cracks). We agree that the S/V ratio for the PCT should be limited to $20\,000\text{ m}^{-1}$ to avoid artifacts.

Finally, the PUF may also be useful for simulating the initial release of alkali metals by interdiffusion and the pH excursion mentioned above (§ 4.1).

5.3 Material Interaction Tests

This point is not developed in detail, probably as the disposal concept has not yet been fully defined. Nevertheless, it must be emphasized that the choice of environmental materials can have a major impact on the long-term behavior of the glass, mainly in the following respects:

- by modifying the flow rate and pH of the leaching solution in contact with the glass;
- by adding a dissolved silica sorption capacity that must be evaluated (mainly in clays and metal canister corrosion products);
- by modifying the nature of the secondary phases compared with those observed in the VHT or PCT.

Tests must be implemented to assess these three aspects. Moreover, integral experiments on laboratory mockups are suggested as a means of relating the results of field tests and laboratory tests.

6. CONCLUSION

The authors have done an excellent job with a very thorough analysis of a very difficult task. This has sometimes led to excessive confidence in complex laws coupled with complex models.

We therefore suggest the following changes:

- Simplify to the maximum the laws used.
- Provide more explicit information concerning the hypotheses implicit in the calculation codes (notably for the geochemical models).
- Analyze the uncertainties on the model hypotheses and parameters, but also perform a sensitivity study for each parameter and hypothesis.
- Extend the scope of the validation by an experiment using a full-size nonradioactive industrial glass block, and by implementing a reduced-scale integral mockup experiment to validate the environmental coupling phenomena. (The third validation required in France for very high-level glass does not appear to be applicable here, considering the low activity level).

Note: The authors appear logically to have based much of their approach on prior work in the USA on high-level glass disposal at Yucca Mountain. As a result, many of the proposed tests are conducted in pure water, at high temperatures and in the absence of environmental materials. The conditions described for these low-activity wasteforms are closer to those envisaged in France for HLW glass than for Yucca Mountain: lower temperature, steady low flow rate, backfilling around the glass, etc.

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Attachments
(Dr. E. Vernaz Review)

APPARENT SOLUBILITY LIMIT OF NUCLEAR GLASS

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ABSTRACT

Most nuclear glass alteration models are based on a first-order kinetic law of the general type $r = r_0(1 - C_{si}/C^*)$ or $r = r_0(1 - Q/K)$. It is generally assumed that the establishment of quasi steady-state concentrations in solution corresponds to an intrinsic glass solubility limit that may be expressed either in terms of the dissolved silicon concentration C^* or as an ion activity product at saturation K . Experimental research over the last five years in France has shown that the quasi steady-state concentrations observed in solution do *not* correspond to a thermodynamic solubility limit with respect to the glass. This assertion is supported by a large body of experimental evidence that is discussed in this paper. The signification of the C^* parameter is therefore reconsidered, and its implications on long-term behavior modeling are discussed.

EVOLUTION OF THE APPARENT SOLUBILITY C^* OVER TIME

In most static experiments with borosilicate nuclear containment glass samples, the silicon concentration in solution is observed to rise to a quasi steady-state value that is reached after a time that depends on the S/V ratio and is generally considered to be the glass solubility limit. The glass alteration rate as measured by a tracer element such as boron (which is not retained in the gel layer) is then observed to drop considerably.

This major drop in the alteration rate was long associated with the onset of a thermodynamic solubility limit and modeled by a first-order law^[1]. During experiments at moderate S/V ratios (typically not exceeding 2000 m^{-1}), the final evolution of the boron concentrations over time became nearly unmeasurable. Under these conditions, the evolution of the dissolved silicon concentration—much slower than that of boron because of silicon retention in the gel as saturation conditions were reached—was no longer detectable, suggesting that a solubility limit had been reached.

During an 800-day experiment with SON68 (R7T7-type) glass at 90°C at a very high S/V ratio ($200\,000 \text{ m}^{-1}$), the Si and B concentrations in solution were observed (Figure 1) to increase in a virtually linear manner between 28 and 800 days, resulting in constant alteration rates under "saturation" conditions of $2.0 \times 10^{-4} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for boron and $4.3 \times 10^{-6} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for silicon. The difference in the Si and B release rates corresponds to a silicon retention factor of some 98% in the gel, a value consistent with high silicon concentrations in solution^[2]. The silicon concentration in solution

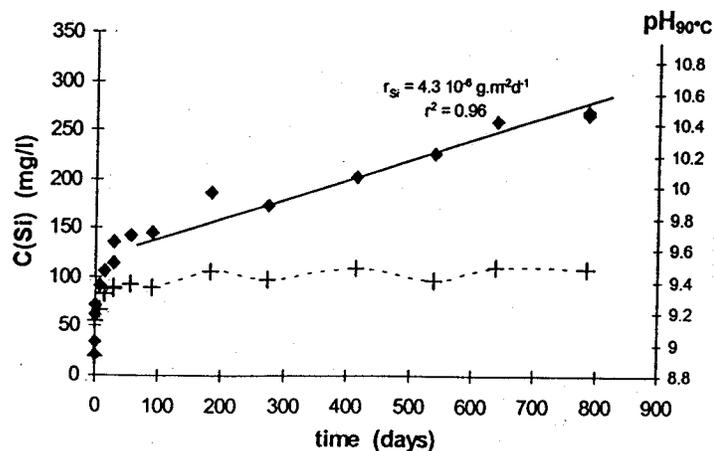


Figure 1. Static leaching of SON68 glass in pure water at 90°C at $S/V = 200\,000 \text{ m}^{-1}$: dissolved silicon concentration (\blacklozenge) and pH ($+$) versus time

rose from 136 ppm after 28 days to 268 ppm after 800 days. Identical results were measured in solution before and after ultrafiltration, confirming that this was indeed dissolved silicon and not colloidal forms. No significant pH variation was observed: the pH remained constant at 9.44 ± 0.05 between 28 and 800 days.

We can therefore conclude that the “steady-state” dissolved silicon concentrations observed at lower S/V ratios are thus only apparent. In fact, C^* is not constant: during extended alteration experiments at high S/V ratios, the concentrations continue to rise slowly, and this increase cannot be attributed to a pH variation or to the formation of colloids.

MODIFICATION OF STEADY-STATE CONDITIONS BY GLASS RENEWAL

Two experiments were conducted by C. Jégou^[3] and S. Gin^[4] with SON68 glass powder at 90°C. During an initial “static” experiment, the glass was simply leached under static conditions and solution samples were analyzed at regular intervals: during the second “cyclic” experiment, the altered glass powder was replaced by pristine glass powder every 7 days. The static experiment was conducted at an S/V ratio of 1500 m^{-1} ; the steady-state pH was 9.0, and the silicon concentration in solution tended toward a quasi steady-state value C^* on the order of 50 ppm. The S/V ratio for the cyclic experiment was 1000 m^{-1} , and the pH was maintained constant at 8.5 by a pH-stat.

If the glass alteration kinetics were independent of the altered surface area, but depended only on the dissolved species concentration in solution (chemical affinity law), the alteration kinetics should be identical in both cases, with only a slightly lower steady-state concentration (~40 ppm) for the cyclic experiment because of the lower pH and S/V ratio. The actual behavior was quite the contrary:

- 1) The steady-state dissolved silicon concentration C^* increased each time the altered glass was replaced by pristine glass, tending toward a new quasi steady-state concentration C^* higher than C^* . This behavior could be repeated indefinitely (Figure 2), although the amplitude of each increase diminished at the highest dissolved silica concentrations.
- 2) The glass was altered at its initial rate until a protective gel layer formed.

We interpret this experiment by considering that C^* is not an intrinsic glass solubility limit, but simply shows that glass alteration virtually ceases due to the formation of a gel layer that becomes highly protective under certain “saturation conditions”. Each time fresh glass was added, it dissolved

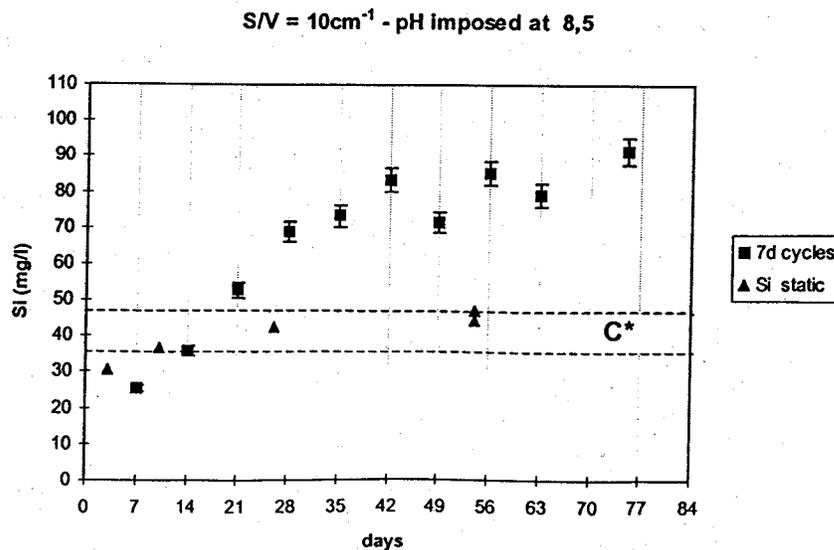


Figure 2. Static leaching behavior of SON68 glass at 90°C with and without glass powder renewal.

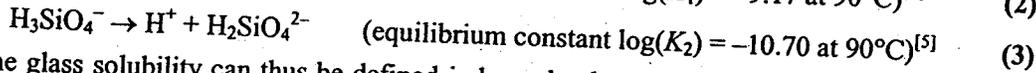
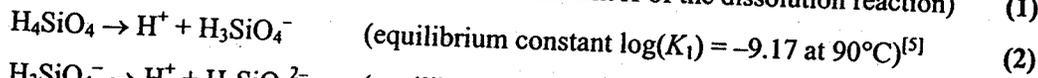
virtually at its initial rate, regardless of the concentration in solution, until a protective gel formed. The gel formed at a faster rate when the solution was highly concentrated with silicon. The new quasi steady-state silicon concentration was thus only the result of the quantity of glass that had to be dissolved to form a new protective gel, less the silicon fraction retained in the gel. As the latter increased significantly with the silicon concentration in solution,

it is logical that the increase in C^* was smaller with each new cycle.

The much slower alteration kinetics observed during the static experiment are therefore not related to a major drop in the chemical affinity of the glass dissolution reaction. C^* is not an intrinsic glass solubility limit related to the glass composition; it is instead a quasi-equilibrium arising when the alteration virtually ceases as the "saturation conditions" lead to the formation of a protective gel. The higher the leachate concentrations (Si, Al, etc.), the faster "saturation conditions" are obtained.

INFLUENCE OF pH ON THE APPARENT SOLUBILITY OF SON68 GLASS

It is well known that the apparent solubility C^* of borosilicate glass is pH-dependent. It is generally acknowledged that this dependence is similar to that of any purely siliceous polymorph, i.e. related exclusively to the dissociation of silicic acid, and can be described by the following equation system:



The glass solubility can thus be defined independently of the pH, as the concentration (or, more rigorously, as the activity) of H_4SiO_4 at saturation, i.e. the equilibrium constant of Eqn (1). Although in the case of SiO_2 , this solubility is highly dependent on its crystallographic and chemical properties (quartz, chalcedony, amorphous silica, etc.), the pH-dependence always has the same form (within the uncertainty limits on the K_1 and K_2 constants).

The pH-dependence of the apparent solubility of SON68 glass was measured by static tests lasting 594 days with the 63–100 μm glass powder size fraction at $S/V = 5000 \text{ m}^{-1}$ at a pH regulated by a pH-stat. The steady-state dissolved silicon concentrations in the ultrafiltered solution are plotted versus the pH in Figure 3. The C^* curve for SON68 glass versus the pH is clearly different from that of silica: the evolution is minimal between pH 6 and 10, and appreciably slower than for silica at higher pH values.

C^* therefore does not correspond to the solubility of a siliceous polymorph, but rather to a concentration range in which the condensation reactions of hydrolyzed species are very rapid, and result in the formation of a protective gel. The contribution of other elements that are sparingly soluble between pH 7 and 10 (e.g. Al, Ca, Zr, Fe, etc.) probably accounts for the much lower pH-dependence of the apparent solubility of nuclear glass than of silica within this range. One consequence of this result is that the C^* variation with the pH cannot be calculated from Eqn (1–3), as in all geochemical codes, but must instead be measured experimentally for each glass.

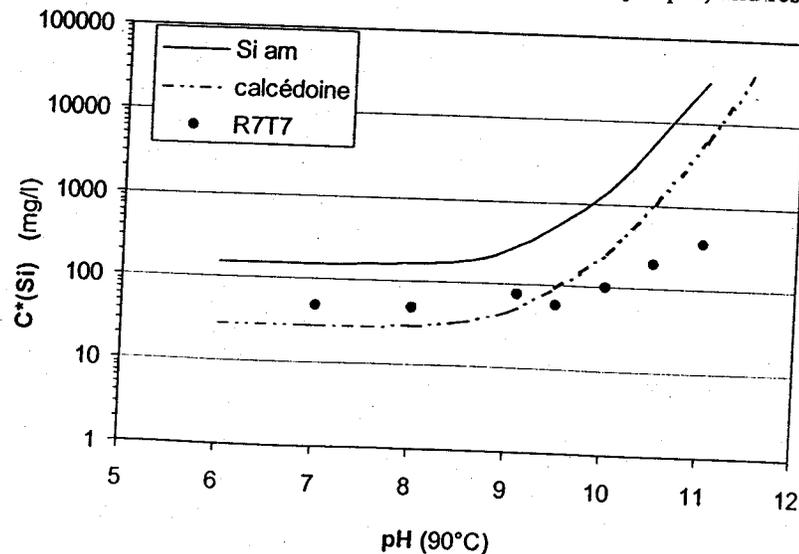


Figure 3. Apparent solubility of SON68 glass at $S/V = 5000 \text{ m}^{-1}$ and imposed pH; comparison with silica and chalcedony.

INFLUENCE OF THE S/V RATIO ON THE APPARENT SOLUBILITY C^*

Experiments were conducted with SON68 glass at 90°C at various S/V ratios ranging from 50 m^{-1} to 200 000 m^{-1} . As shown in Figure 4, the value of C^* is highly dependent on the S/V ratio; typically, for the French SON68 nuclear glass, C^* varies from 35 to 200 ppm according to the S/V ratio. This variation has long been attributed to the pH variation, as the equilibrium pH is well known to increase with the S/V ratio due to the increasing role of interdiffusion. The pH did indeed vary from 8.6 to 9.5 in these experiments. However, the preceding experiments showed that this pH variation accounted for an increase of only 10 $mg \cdot l^{-1}$. Moreover, even if the previous results are disregarded and the pH-dependency is calculated based on the dissociation of silicic acid, a pH variation from 8.6 to 9.5

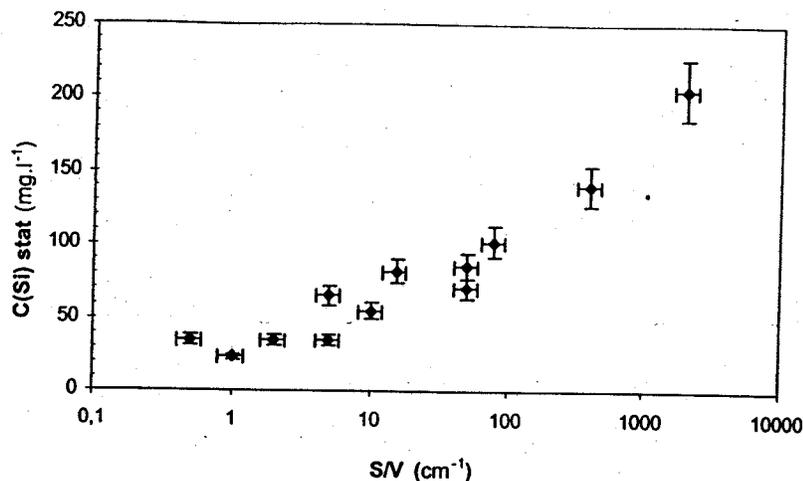


Figure 4. Apparent solubility C^* of R7T7-type nuclear glass versus S/V ratio in static alteration experiments: C^* corresponds to a quasi steady-state dissolved Si concentration after 1 year of alteration.

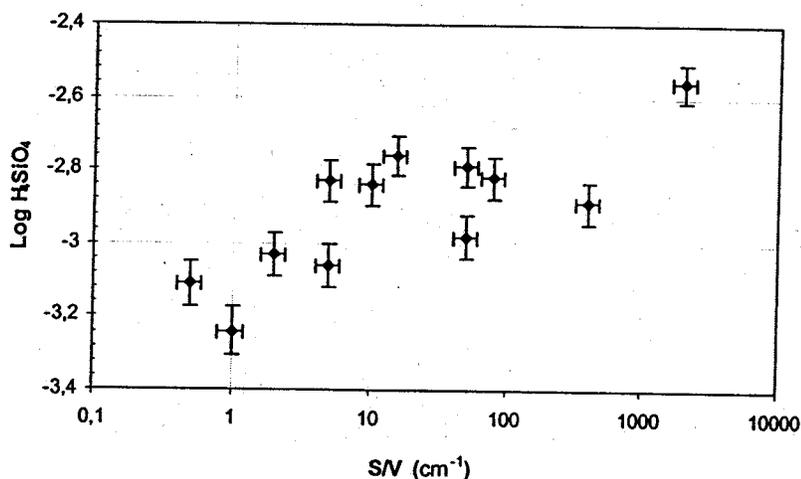


Figure 5. Apparent solubility C^* expressed as $H_4SiO_4^*$ versus S/V ratio, calculated from silicic acid dissociation

could only account for an increase in C^* from 40 to 95 ppm (or even 130 $mg \cdot l^{-1}$ using a different value for K_1). Regardless of the K_1 value, this pH variation is clearly insufficient to explain the dissolved silicon concentrations of 200 $mg \cdot l^{-1}$ in the ultrafiltered solution at the highest S/V ratio.

Figure 5 shows that the solubility can be calculated in terms of " H_4SiO_4 at saturation", even if we no longer consider this calculation to be correct. Even in this form, C^* varies from $10^{-3.2}$ at $S/V = 50 m^{-1}$ to $10^{-2.6}$ at $S/V = 200 000 m^{-1}$. The primary reason for the evolution of C^* is thus not the pH but the S/V ratio: C^* increases with S/V .

MODIFICATION OF STEADY-STATE CONDITIONS ACCORDING TO THE SPECIMEN LEACHING HISTORY

As previously noted, when a static leaching experiment is disturbed after reaching apparent saturation with a quasi steady-state dissolved silicon concentration C^* , new steady-state conditions $C^{*'}$

are established after the disturbance (which may involve solution renewal, immersing a pristine glass coupon in the saturated leachate, removal of the altered glass, etc.)^[4]. In addition, however, this value also depends on the way steady-state conditions were obtained, i.e. on the specimen leaching history.

Two SON68 glass coupons were altered for 86 days under static leaching conditions at 90°C with an S/V ratio of 500 m^{-1} (Figure 6). The specimens were identical, except that one was a pristine glass coupon and the second had previously been altered for 7 days at 90°C under flowing conditions with a high flow rate so that it developed a nonprotective alteration film $1.2 \text{ }\mu\text{m}$ thick. The pH was about 8.9 in both cases.

As expected for this pH and S/V ratio, the apparent solubility of the pristine glass was about 35 ppm of Si—only half that of the previously altered specimen (68 ppm). This difference has been shown^[6] to arise from the fact that a greater amount of glass had to be dissolved from the previously altered specimen to obtain a protective gel than from the pristine glass. The nonprotective gel formed during the preliminary alteration phase constituted a “silica pump” until it reached saturation, and thus delayed the onset of “saturation conditions” under which the alteration rate drops considerably. Once again, C^* was not the direct cause of the end of alteration, but only reflected the inhibition of alteration when the conditions necessary for the formation of a protective gel were ensured.

APPARENT SATURATION: NECESSARY BUT NOT SUFFICIENT TO IMPEDE ALTERATION

The final leaching experiment we will discuss here was conducted not with SON68 glass but with a simple ternary (SiO_2 , B_2O_3 , Na_2O) glass having the same proportions of the constituent elements as SON glass^[7]. The normalized mass losses for each of the three constituent oxides are shown in Figure 7 for a static leaching experiment at 90°C at $S/V = 400 \text{ m}^{-1}$.

The glass dissolved at a relatively high rate, and the silicon concentration in solution reached a steady-state concentration corresponding to the solubility of

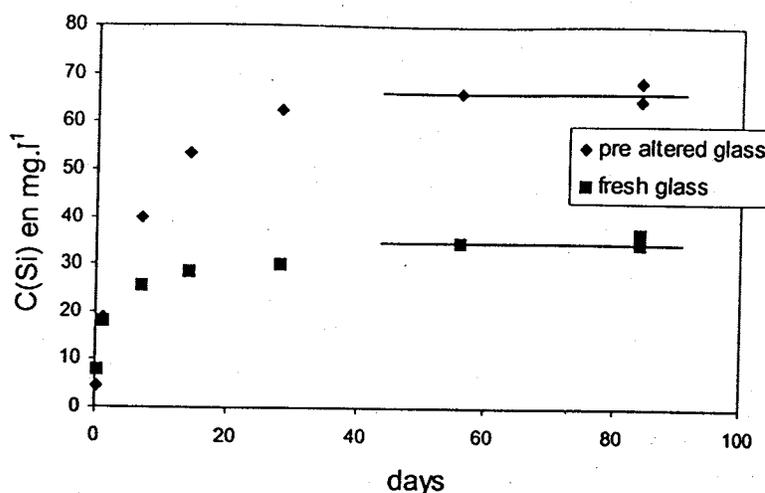


Figure 6. Dissolved silicon concentration versus time during static leaching of pristine and previously altered SON68 glass specimens at 90°C at $S/V = 500 \text{ m}^{-1}$

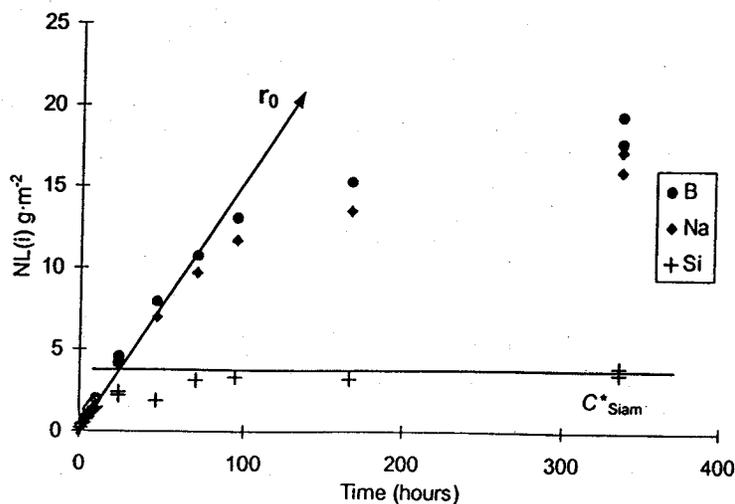


Figure 7. Static leaching of a ternary (SiO_2 , B_2O_3 , Na_2O) glass at 90°C at $S/V = 400 \text{ m}^{-1}$

amorphous silica after less than 100 hours. Despite reaching this very high steady-state concentration, the glass continued to dissolve at a rate near its initial rate r_0 . The alteration rate gradually diminished as the thickness of the silica gel deposit increased, but the drop in the rate was much slower than for a nuclear glass.

Reaching "saturation conditions" in solution is thus a prerequisite, but is not sufficient for the glass alteration kinetics to diminish by several orders of magnitude. The presence of glass constituent elements in the gel (Al, Ca, Zr, Fe, REE) is a decisive factor—in addition to saturation conditions—in the formation of protective gels.

GLASS THERMOCHEMISTRY

Calorimetric techniques have recently been used by Y. Linard^[8] to measure heat capacities and formation enthalpies of various borosilicate glasses, including simplified SON68. The entropy of formation was also measured: using the entropy theory of relaxation processes proposed by Adams and Gibbs^[9], the configurational entropy contribution was measured from viscosity measurements. This set of data allowed the author to calculate the Gibbs free energies of dissolution in pure water for the test glasses. By comparison with leaching experiments, Linard showed that the ion activity product in every "saturated" leachate was far (by several orders of magnitude) lower than the glass solubility.

This work strongly supports the conclusions of all these experiments, which indicate that the decrease in the dissolution rate at high reaction progress cannot be associated with approaching an equilibrium between the pristine glass and solution.

DISCUSSION AND CONCLUSION

Historical Background

A long-running debate opposed the proponents of the chemical affinity hypothesis and those of the protective gel hypothesis in accounting for the major slowdown of glass alteration in media with low renewal rates. In the mid-1980s the chemical affinity side appeared to have the most solid backing; this was due to the fact that glass alteration was investigated mainly in media with high renewal rates, far from saturation conditions, in which gel layers that formed were thick^[10] because of the high alteration rates: $r \approx r_0$. Indeed, far from saturation conditions the gel layer is very porous and nonprotective: with little silica in solution, little recondensation occurs in the gel. In recent years, however, considerable experimental evidence has shown that with high S/V ratios and low solution renewal rates the gel layers are thin (because of the slow alteration: $r \ll r_0$) but very compact and highly protective: extensive recondensation in the gel occurs from the highly siliceous solution^[4].

Physicochemical Signification of the Apparent Solubility C^*

The apparent solubility C^* derived from the dissolved silicon concentration at equilibrium simply expresses a quasi-equilibrium between the quantity of silica hydrolyzed from the glass and gel and the quantity condensed in the gel. It is thus a *dynamic and not a thermodynamic equilibrium*.

Nor does the apparent solubility correspond to the thermodynamic solubility of the gel, which is a changing material that does indeed adapt to the solution, but whose composition, structure and texture depend on the conditions under which the equilibrium is reached (S/V ratio, kinetics of elimination of the hydrolyzed species) and not only on the concentrations in solution. As such, it is dependent on the gel formation conditions, and notably on the capacity of the environment to remove the hydrolyzed silica from the gel before it can recondense.

Implications for Long-Term Behavior Modeling

This rapid survey has shown that the silicon concentration at saturation C^* introduced in Grambow's law $r = r_0(1 - C/C^*)$, and still a formal term in the current models combining the chemical affinity and protective gel effects, is thus under no circumstances an intrinsic solubility of the glass—or even of the gel.

Would it not then be more correct to describe the glass alteration kinetics by means of diffusion equations, rather than a first-order law originally based on the concept of chemical affinity? In fact, it is impossible to ignore the solution, which to a large extent—but not exclusively—determines the “saturation conditions” under which the gel becomes highly protective. A first-order law coupled with allowance for silicon retention and diffusion in the gel provides the best description of glass alteration available today. However, considered as a phenomenological law and not representative of a chemical affinity concept, it can account for the observed variability of C^* even for a single glass composition. The predictive capacity of the model is thus directly related to its capacity for predicting the evolution of the C^* parameter according to the environmental conditions (temperature, pH, S/V , silicon diffusion/sorption flow, etc.).

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**PROTECTIVE EFFECT OF THE ALTERATION GEL:
A KEY MECHANISM IN THE LONG-TERM BEHAVIOR OF NUCLEAR WASTE GLASS**

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ABSTRACT

Experimental alteration results are presented in which a French SON 68 (R7T7-type) nuclear containment glass specimen was first altered under static conditions for 600 days at an S/V ratio of 5000 m⁻¹ before transferring it to pure water. The experiment was designed to assess the diffusion barrier properties of the gel formed during the preliminary alteration phase. Contrary to predictions by kinetic models based only on chemical affinity, the renewed alteration of the specimen in pure water was very limited. Measurements at close intervals showed that the maximum alteration rate under these conditions was 7×10^{-3} g·m⁻²·d⁻¹, or about $r_0/300$, whereas a pristine glass coupon in contact with pure water is altered at r_0 .

The renewed alteration behavior is attributed to partial (5–10%) dissolution of the existing gel, resulting in a slight degradation of its protective properties. Saturation conditions, at a different level than in the preliminary phase, were reached within a few days. The saturation of the solution with respect to silicon, generally interpreted as a glass/solution (Grambow's model) or gel/solution (Bourcier's model) equilibrium, is shown to depend not only on the alteration conditions, but also on the specimen leaching history, and is thus not an inherent glass property.

This experiment confirms the idea that the gel formed under saturation conditions controls the kinetics of SON 68 glass alteration by means of a diffusion barrier effect. It also raises a number of issues concerning the concept of a "residual rate" and the possible relations between the quasi steady-state Si concentrations observed in solution and the protective properties of the gel.

INTRODUCTION

It has been established for nearly two decades that, in a medium with little or no solution renewal, the dissolution rate of a nuclear glass diminishes by several orders of magnitude from the initial rate r_0 [1]. Similar behavior has also been reported for basaltic glass, which is considered to be a suitable natural analog of nuclear glass [2,3]. The drop in the alteration rate is generally attributed to the effect of chemical affinity, i.e. the diminishing difference between the chemical potential of the solution (which increases as the solution becomes saturated) and the constant chemical potential of the glass [4,5]. The models describing these kinetics were developed from Grambow's work in the mid-1980s [4] based on considerations arising from transition state theory [6]. On the basis of a single type of experiment, Chick *et al.* [7] also reached the general conclusion that the alteration films did not constitute effective diffusion barriers. Chemical affinity models have encountered not only theoretical but also experimental obstacles, however [8]. The discrepancies between a pure affinity model and experimental results arise from the fact the gel, which constitutes the amorphous portion of the alteration film and is formed by recondensation of silicate species, can under some conditions exhibit highly protective properties and control the glass dissolution kinetics.

This paper describes an experiment similar in principle to the one proposed by Chick *et al.* [7], showing that the conditions under which the gel is formed—and notably silica removal by the dissolution medium—determines the degree of its protective properties.

MATERIAL AND METHODS

The study was performed with nonradioactive SON 68 (R7T7-type) glass [9] with the following weight percentage composition: 45.5% SiO₂, 14% B₂O₃, 4.9% Al₂O₃, 13.3% alkali metals (Na₂O, Li₂O, Cs₂O), 4.0% CaO, 2.9% Fe₂O₃, 2.7% Zr, 2.5% Zn, 3.9% rare earth oxides (Nd₂O₃, La₂O₃, Pr₂O₃, Ce₂O₃), and 6.3% other elements. The experimental procedure involved two steps:

- 1) A SON 68 glass powder specimen with a glass-surface-area-to-solution-volume (S/V) ratio of 5000 m⁻¹ was first altered in static mode for 600 days at 90°C in a PTFE reactor. A magnetic stirring bar was used to homogenize the solution without placing the powder in suspension. Solution samples were taken at regular intervals, ultrafiltered to 10 000 Dalton, then acidified for ICP-AES analysis of the major glass cations. After correcting the concentration values for the effect of acid dilution, the normalized mass losses were calculated from the following relation:

$$NL_i = 10^{-2} \frac{C_i}{X_i \cdot \frac{S}{V}} \quad (1)$$

where C_i is the concentration (mg·l⁻¹) of element i in solution, S/V is the glass-surface-area-to-solution-volume ratio (cm⁻¹) and X_i is the mass fraction of element i in the glass. NL_i (expressed in g·m⁻²) is used to estimate the altered glass quantity when calculated for the mobile elements (B, Na), as well as to assess the retention of less mobile elements (notably Si) in the alteration products. The altered glass thickness is determined by dividing the normalized mass loss calculated for boron by the glass density (2.75 g·cm⁻³ for SON 68 glass). The glass dissolution rate (g·m⁻²·d⁻¹) is defined as follows:

$$r = \frac{dNL_B}{dt} \quad (2)$$

- 2) After the initial leaching period, a perturbation was applied to the system. The saturated leachate was removed from the reactor and replaced by a pure water solution with KOH added to adjust the pH to 9.1 (corresponding to the equilibrium pH measured after 600 days of static leaching). In order to avoid any chemical or structural modifications of the gel, the test specimen was neither cooled nor allowed to dry while the solution was replaced. The powder was rinsed four times in the pH 9.1 solution to dilute the residual leachate. Makeup water was then added to maintain the S/V ratio at 5000 m⁻¹. All these operations were performed within about 5 minutes. Solution samples measuring 1.2 ml each were taken at various intervals up to 60 days after replacing the solution; the samples were filtered to 0.45 μm, then acidified. Two additional samples ultrafiltered to 10 000 Dalton revealed no colloid fraction: the dissolution mechanisms of the alteration tracer elements (B, Na, Li) and the major gel constituents (Si, Al, Ca) could therefore be investigated.

RESULTS

Glass Alteration for 600 Days under Static Conditions

After the initial 600 days of static mode alteration, the gel thickness was estimated at 150 nm based on the boron release, and the alteration rate was 3×10^{-4} g·m⁻²·d⁻¹ (about 5000 times lower than the initial glass dissolution rate at the same temperature and pH [10]). This rate was reached in the 91-day sample, and remained constant thereafter: it could thus be considered as a "final rate". Several phenomena could account for this final rate, including interdiffusion or the precipitation of a

secondary phase, but will not be discussed in this study. The pH reached a steady-state value of 9.1 (measured at 90°C) after 56 days. The Si concentration appeared to reach a quasi steady-state value of about 75–80 mg·l⁻¹ slightly before the pH stabilized, but in fact the Si concentration continued to rise, reaching 120 mg·l⁻¹ after 600 days. Nevertheless, the Si dissolution rate was at least an order of magnitude lower than the matrix alteration rate. This phenomenon had not been previously reported.

Effect of Solution Renewal

Figure 1 shows the evolution of the normalized glass mass losses for boron and silicon when the specimen was submitted to renewed leaching in pure water. This experiment highlights the following points:

- Glass alteration resumed when the specimen was placed in pure water, but at a rate much lower than the dissolution rate of a pristine glass specimen in pure water: the measured rate in this case did not exceed $7 \times 10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, or about $r_0/300$.
- This rate was maintained for about ten hours before it began to diminish.
- Twenty days after the resumption of leaching, the glass alteration rate was identical with the rate measured after 600 days during the first phase of the experiment, i.e. $r_0/500$.
- A quasi steady-state Si concentration was established at about 35 mg·l⁻¹, compared with 75 mg·l⁻¹ during pristine glass alteration in pure water.
- The pH diminished slightly during the test, and stabilized at 9.0.

If the glass dissolution kinetics are assumed to be controlled by solution saturation, the normalized boron mass losses should follow the same evolution as observed for alteration of pristine glass, and the same quasi steady-state Si concentration should be reached after the same time. As the experiment did not lead to these results, we conclude that the glass alteration kinetics are not controlled by solution saturation under these experimental conditions, but rather by the protective properties of the alteration film. In order to specify the mechanisms involved, we must examine the glass behavior during the first few hours after the perturbation.

Figure 2 shows the normalized mass losses calculated for boron and silicon during the first nine

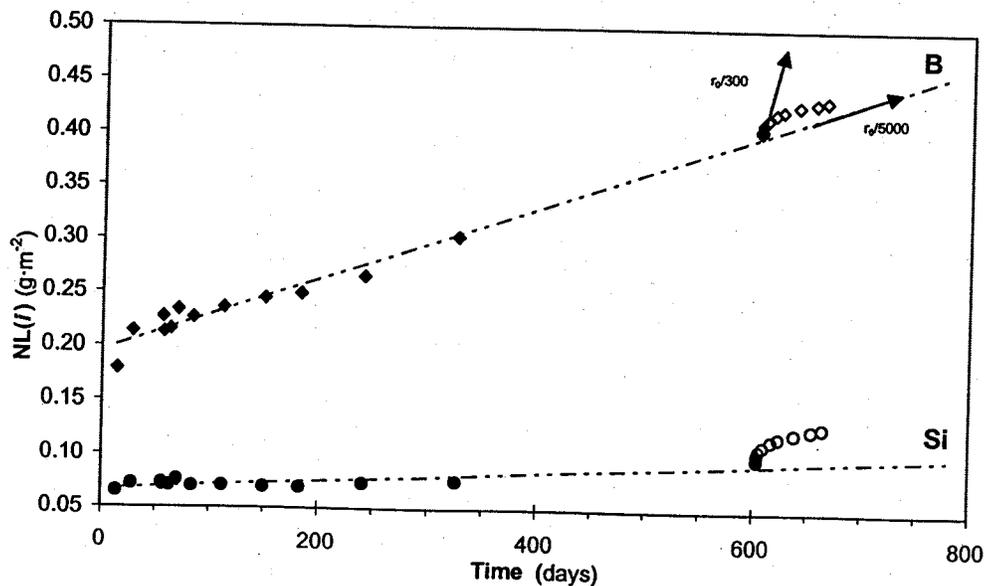


Figure 1. Normalized glass mass losses calculated from the B and Si concentrations in the 600-day static experiment (solid symbols) and after continued leaching in pure water (open symbols).

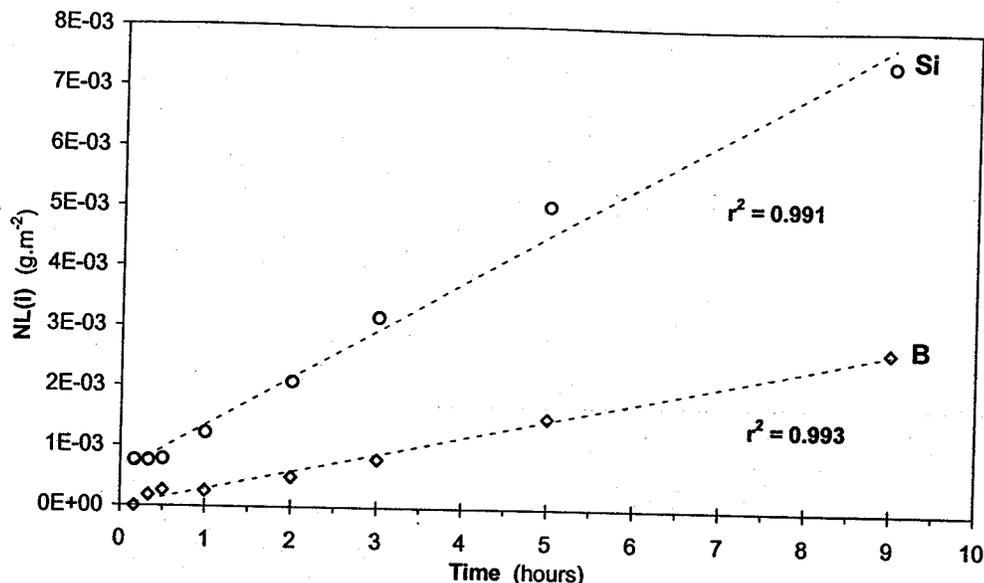


Figure 2. Normalized glass mass losses calculated from the B and Si concentrations in the hours following renewed leaching in pure water. This figure highlights the significant incongruence between boron (alteration tracer) and silicon.

hours after the change in the alteration conditions. The boron and silicon flows were constant during this period. Although this behavior is generally observed under “initial rate” conditions, there were two major differences in this case compared with the initial rate conditions:

- The glass dissolution rate determined from the boron release was 300 times lower than the initial glass dissolution rate at the same temperature and pH.
- The silicon dissolution rate was 2.7 times higher than the boron release rate. Insofar as boron is a glass alteration tracer [11] and silicon is the primary former among the glass alteration products (gel + phyllosilicates), this phenomenon can be explained only if preferential dissolution of the glass alteration products occurred over this time interval.

Assuming the silicon flow arises from dissolution of the gel (dissolution of the phyllosilicates was considered negligible because the solution very rapidly reached saturation with respect to these phases), a material balance shows that the quasi steady-state concentration of $35 \text{ mg}\cdot\text{l}^{-1}$ in solution measured a few weeks after the perturbation was reached by dissolution of between 5 and 10% of the gel present before solution renewal. This quantity corresponds to a dissolved gel thickness of between 7 and 15 nm.

We also observed that within about 20 days after the resumption of alteration in pure water, the glass alteration rate dropped to the same value as the final rate measured at the end of the first 600-day period. The quantity of glass altered during this period was $2.0 \times 10^{-2} \text{ g}\cdot\text{m}^{-2}$, corresponding to a thickness of 7.5 nm. The quantity of gel dissolved and the quantity of glass altered during this period were thus equivalent, suggesting that the glass dissolution in this experiment compensated for the dissolution of the gel, which was destabilized by the solution renewal.

DISCUSSION

This work has shown that the gel formed during static leaching for 600 days at a high S/V ratio is strongly protective: following solution renewal, not only did glass alteration resume at a rate not exceeding $r_0/300$, but also the quantity of glass dissolved to reach Si saturation in solution was ten

times lower in the case of an existing gel film than for a pristine glass specimen. The term "protective gel" implies that it constitutes a diffusion barrier with respect to the reactive species involved in glass alteration [8]. Our conclusion is in apparent contradiction with the results reported by Chick [7], but in fact is not inconsistent: the gel studied by Chick was formed under static conditions in a highly dilute solution (i.e. at a low S/V ratio), and did not constitute a barrier dense enough to limit the glass alteration kinetics. The protective properties of the gel cannot be dissociated from the conditions under which it is formed.

In the experiment discussed here, the gel constitutes a barrier in which the apparent diffusion coefficient for nonreactive chemical species (e.g. B or Li) is 300 times lower than the diffusion coefficient for these species in water: i.e. about $3 \times 10^{-12} \text{ m}^2\text{-s}^{-1}$, assuming a diffusion coefficient of $10^{-9} \text{ m}^2\text{-s}^{-1}$ in water. It is extremely difficult to determine the properties of this gel in greater detail, considering its very limited thickness and high reactivity. Recent examinations suggest that the Si distribution in protective gels that have formed on SON 68 glass is relatively homogeneous throughout the gel thickness. It also appears that a critical density must be reached—notably for silicon—before the alteration rate is significantly affected [12]. Based on the results presented here, the gel should be considered as a dynamic barrier rather than a passivating layer. The exchange dynamics between the glass, the gel and solution are very rapid, as the system stabilized within only a few days after the perturbation. The stabilization was probably only apparent, and the silicon concentration could be expected to evolve slowly as observed during the first phase of the experiment.

Although we have not emphasized the fact that the quasi steady-state silicon concentrations before and after the perturbation were not the same, this is an important result: it shows that the apparent solution saturation with respect to Si, which is generally interpreted in terms of an equilibrium between the glass and solution (Grambow's model [4]) or between the gel and solution (Bourcier's model [13]), depends not only on the alteration conditions but also on the specimen history (see Vernaz and Gin in these proceedings [14]). It must therefore not be considered as an intrinsic glass property. What then is the signification of a steady-state Si concentration? This study shows that Si dissolution does not diminish to zero even after relatively long alteration periods, and thus calls into question of Si saturation itself. Even if we choose to consider these as "steady-state" concentrations, this does not imply that the system has reached thermodynamic equilibrium. A steady-state concentration may result from the equivalence of flows between hydrolysis of the glass and gel, sorption and condensation within the gel, and precipitation of crystallized phases. The concept of solubility in a kinetic law fails to account for the conditions in which the glass dissolves more slowly than in pure water [8]. This notion was investigated by considering an overall glass solubility—or by considering only the glass and gel forming elements, or silicon alone—and generally yields unsatisfactory results. From this standpoint, these observations tend to corroborate the recent results of a thermodynamic approach in which the glass equilibrium constant was determined by taking into account both entropy and enthalpy, and which show that the apparently saturated solution in which glass alteration practically ceases remains largely undersaturated with respect to the glass [15].

There is no obvious relation between "saturation" conditions and the protective properties of the gel, and the large number of relevant parameters makes such a relation difficult to model. This experiment has shown that the gel prior to the perturbation and the gel a few weeks after the perturbation are equivalent, not only with regard to their chemical composition but also in terms of their diffusion barrier effect, despite the very different steady-state Si concentrations. Moreover, recent work suggests that the steady-state conditions observed at advanced stages of reaction progress should be interpreted as the consequence of a given quantity of altered glass, rather than as the cause of the diminishing glass alteration rate [12,16, and unpublished data]. This hypothesis

could explain the inability of chemical affinity laws to describe the alteration kinetics of nuclear glasses correctly (i.e. for a wide range of alteration conditions) [8]. The development of kinetic laws will require a better description of the mechanisms by which the protective gel is formed.

CONCLUDING REMARKS

The impact of a perturbation induced in a glass specimen having reached saturation conditions for several hundred days by placing it in pure water resulted in renewed glass alteration following partial dissolution of the gel. The renewed alteration was limited however, as the alteration of only a few nanometers of glass was sufficient to restore the residual alteration rate and achieve saturation conditions again.

This experiment supports the idea that the gel formed under saturation conditions controls the kinetics of SON 68 glass alteration through a diffusion barrier effect [12,17,18]. It also raises numerous questions concerning the notion of a residual rate, as well as on possible relations between the quasi steady-state conditions observed in solution and the protective nature of the gel. These questions arise mainly from insufficient knowledge of the dynamics of material exchanges between the glass, the gel and solution, and represent a major issue in predicting the long-term behavior of this type of nuclear glass.

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Role and Properties of the Gel Formed during Nuclear Glass Alteration: Importance of Gel Formation Conditions

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ABSTRACT

A French SON 68 nuclear glass sample was experimentally altered to assess the mechanisms limiting the glass alteration kinetics, especially during the transition phase between the initial rate r_0 and the final rate under silicon saturation conditions. A glass specimen was altered at the initial rate for one week to form a silicon-depleted nonprotective gel; the specimen was then leached under static conditions at a glass-surface-to-solution-volume (S/V) ratio of 500 m^{-1} and the alteration kinetics were compared with those of a pristine glass specimen altered under the same conditions. Unexpectedly, after static leaching the previously leached glass was 2.7 times as altered as the pristine specimen, and the steady-state silicon concentration was twice as high for the previously leached specimen. STEM characterization of the alteration films showed that the initial nonprotective gel constituted a silicon pump with respect to the glass, and that the glass alteration kinetics were limited only when a fraction of the gel became saturated with silicon, and exhibited protective properties. This work also shows that silicon recondensation was uniform at micrometer scale: the silicon hydrolyzed at the reaction interface then diffused before recondensing over a length comparable to the gel thickness. In addition to these findings, this investigation suggests a reinterpretation of the effect of the S/V ratio on the glass alteration kinetics and on the steady-state dissolved silicon concentration.

1. INTRODUCTION

The methodology for assessing the long-term behavior of a nuclear glass is based on modeling its alteration kinetics in the projected environment (European Standard ENV 12920), i.e. taking into account the major factors affecting its behavior: temperature, ability of the environment to supply or remove kinetically limiting elements (e.g. silicon), flow rate, pH, solution composition, radioactivity, etc.

The alteration kinetics of borosilicate nuclear glasses are controlled by numerous concurrent mechanisms, including ion exchange between alkali metals (network modifiers) and protons in solution, hydrolysis of covalent bonds in the matrix, condensation of aqueous species at the reaction interface, and precipitation of secondary phases (Vernaz *et al.*, 1992a). The importance of these mechanisms in the overall alteration process depends on the degree of reaction progress and on the alteration conditions. Initially, interdiffusion results in depletion of the alkali cations from the glass, causing the solution pH to rise (Noguès *et al.*, 1985). When the thickness of the interdiffusion zone becomes constant, the glass alteration kinetics are controlled by surface reactions (Boksay *et al.*, 1968). As long as the solution concentration remains relatively low, glass dissolution is congruent and the glass dissolves at its initial rate r_0 , which depends only on the temperature and pH. As the reaction progresses and the solution becomes increasingly concentrated, the glass alteration kinetics diminish—generally by several orders of magnitude below r_0 (Vernaz *et al.*, 1992a).

The leaching behavior of French SON 68 (R7T7-type) nuclear glass has been widely studied since the early 1980s. The principal cause for the diminishing alteration rate of this glass has been attributed to the gel that develops at the interface between the pristine glass and solution (Jégou, 1998; Jégou *et al.*, 1999; Gin *et al.*, 1999; Gin *et al.*, 2000a; Gin *et al.*, 2000b; Jégou *et al.*, 2000). Using different approaches, these authors have shown that solution saturation alone—notably with respect to silicon—is not sufficient to obtain low alteration rates. The gel arises from hydrolysis and condensation of silica species

from the glass (Vernaz *et al.*, 1992a; Jollivet, 1994). The development of a protective gel layer at the glass/solution interface forms a diffusion barrier that limits exchange phenomena. It has also been established that the presence in the gel of elements with high coordination numbers (e.g. zirconium or the rare earth elements) enhances the protective properties of the gel by favoring cross-linking (Ricol, 1995). The characteristic pore dimension in a protective gel is on the order of a nanometer (Deruelle *et al.*, 1999). The gel also tends to retain the actinide elements by sorption and coprecipitation, and thus appreciably enhances the glass containment properties with regard to long-lived radionuclides (Vernaz *et al.*, 1992b; Ménard *et al.*, 1998). Allowance for the gel properties has become a major issue in assessing nuclear glass performance in France.

The degree to which the transport properties in the gel are affected by the pH, the temperature, or the silicon removal capacity of the environment remains unclear. In the mid-1980s, Chick and Pederson (1984) concluded on the basis of a single experiment that the gels formed by nuclear glass alteration were nonprotective. In reality the situation is more complex, and this conclusion cannot be generalized.

In order to understand the mechanisms responsible for the diffusion-limiting properties of a protective gel, we conducted an experiment in which a glass specimen was first altered at its initial rate for one week under flowing conditions, then placed in static conditions to study its alteration kinetics. The open-system alteration conditions resulted in the development of a thick nonprotective gel layer. The alteration kinetics of this previously altered specimen were compared with those of a pristine glass specimen altered under the same static conditions. The alteration films formed during these tests were examined by transmission electron microscopy to determine the mechanisms involved. The alteration kinetics could be expected to be identical for both specimens, as the gel formed under initial rate conditions is nonprotective.

2. MATERIALS AND METHODS

2.1 Glass Fabrication and Specimen Preparation

Nonradioactive SON 68 glass (Pacaud *et al.*, 1990), an R7T7-type nuclear glass with the composition detailed in Table I, was tested here as a powder, using the 160–250 μm size fraction with a specific surface area of $264 \pm 15 \text{ cm}^2\cdot\text{g}^{-1}$ as determined by the BET (Kr adsorption) method. The powder was prepared by grinding and sieving monolithic glass blocks, then cleaned ultrasonically in acetone followed by alcohol and finally deionized water. The powder was dried and stored in a desiccator. Monolithic test coupons measuring $25 \times 25 \times 2.5 \text{ mm}^3$ were also cut from a larger glass bar, polished to 4000 grade with SiC paper, and cleaned in the same way as the powder specimens.

2.2 Experimental Procedure

The experiment was performed in two steps. A glass powder specimen (160–250 μm) was altered in pure water for 7 days under flowing conditions. The glass-surface-area-to-solution-volume (S/V) ratio was maintained at 50 m^{-1} and the flow rate at $1.3 \text{ ml}\cdot\text{min}^{-1}$, corresponding to a solution renewal rate of 1.87 d^{-1} . The test reactor was a 1-liter Savillex PTFE container provided with a magnetic stirrer to agitate the solution without placing the powder in suspension. Two $25 \times 25 \times 2.5 \text{ mm}^3$ glass monoliths wrapped in Teflon gauze (70 μm mesh) were also suspended from a PTFE strip at mid-height in the reactor. The reactor was placed in a temperature-controlled chamber regulated at $90^\circ\text{C} \pm 1^\circ\text{C}$. Solution samples were taken at the reactor outlet at regular intervals during the 7-day test; each sample was filtered to $0.45 \mu\text{m}$ at the test temperature, then acidified by an equivalent volume of 1N nitric acid. The pH was measured at the test temperature at each sampling interval. After 7 days of leaching under these conditions, one monolith was removed from the reactor, rinsed in deionized water, dried for one day at 50°C then weighed to estimate its mass loss and stored in a desiccator.

The altered glass powder and the second monolith were placed in a 120 ml PTFE reactor with 100 ml of water preheated to 90°C ; the S/V ratio was 500 m^{-1} . In order to prevent any chemical or structural changes in the gel, the altered powder was neither dried nor cooled during the transfer. The reactor and its stirring system were placed in a temperature-controlled chamber regulated at $90^\circ\text{C} \pm 1^\circ\text{C}$. One-

milliliter solution samples were taken with a syringe at the following intervals: 1, 7, 14, 28, 56 and 84 days. Each sample was filtered to 0.45 μm at the test temperature, then acidified by an equivalent volume of 1N nitric acid. The 84-day sample was taken in duplicate to detect the presence of any colloidal particles; the second sample was ultrafiltered to 10000 Dalton by centrifuging at 4500 rpm, then acidified by an equivalent volume of 1N nitric acid. The pH was measured at the test temperature at each sampling interval. On completion of the static test, the monolithic coupon was removed from the reactor, rinsed in deionized water, dried for one day at 50°C, then weighed to estimate its mass loss and stored in a desiccator.

In parallel with this static test on a previously altered glass specimen, an identical test was conducted with a pristine glass specimen. It also included a monolithic test coupon reserved for electron microscopic observation of the alteration products. The static test on previously altered glass is designated ST1, and the test with a pristine glass specimen ST2.

2.3 Solution Analysis

The solution was analyzed by ICP-AES for Si, B, Na, Li, Al and Ca (with approximately 3% uncertainty).

2.4 Interpretation of Results

The following parameters were calculated from the solution analysis results:

- **Normalized glass mass loss**

After correcting the concentrations for acid dilution, the normalized mass losses were calculated from the following relation:

$$NL_i = \frac{C_i}{X_i \cdot \frac{S}{V}} \quad (1)$$

where C_i is the concentration ($\text{mg}\cdot\text{l}^{-1}$) of element i in solution, S/V is the glass-surface-area-to-solution-volume ratio (m^{-1}) and X_i the mass fraction of element i in the glass; the result is expressed in $\text{g}\cdot\text{m}^{-2}$. The normalized mass loss is used to assess the quantity of altered glass when calculated for the mobile elements (B, Na), as well as the retention capacity for less mobile elements (notably Si) in the alteration products.

- **Retention factor of element i in the alteration film**

The retention factor f_i of element i in the glass alteration products is defined using boron as a glass corrosion tracer (Scheetz *et al.*, 1985) according to the following relation:

$$f_i = \frac{NL_i}{NL_B} \quad (2)$$

- **Initial glass dissolution rate**

The glass dissolution rate ($\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) is defined by the following expression:

$$r_{(i)} = \frac{dNL_i}{dt} \quad (3)$$

2.5 STEM Characterization of Alteration Products

Ultramicrotome cross sections of the three altered glass monoliths prepared according to the technique described by Ehret *et al.* (1986) were observed using a Scanning Transmission Electron Microscope (Philips CM 120) equipped with a semi-quantitative EDS X-ray analysis system (EDAX). Chemical determination of Si, O, Al, Fe, Zr, Na, Nd, Ni, Zn, Ca, P and Mo was performed with a 15 nm electron

beam and an acceleration voltage of 100 kV, with the semi-quantitative results presented as element ratios. Only the changes in the Si/O ratio are discussed here, although the same results are obtained for the Si/Fe, Si/Zr and Si/Ce ratios.

3. RESULTS

3.1 Preliminary Open-System Glass Alteration

The solution analysis data are shown in **Table II**. Under the test conditions, glass dissolution was practically congruent. Steady-state concentrations were reached for the analyzed elements after about one day; the solution pH remained stable at about 8.2. The mean glass dissolution rate was $0.52 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, a value very near the initial rate at the test temperature and pH. Advocat *et al.* (1991) reported an initial rate of $1 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for the same glass composition at 90°C and pH 8, measured on monolithic test coupons for which the reactive surface area was assumed equal to the geometric surface area. Taking the surface roughness into account typically results in a difference by a factor of 2 (Jaycock *et al.*, 1981).

The altered glass thickness after 7 days was estimated from NL(B) at $1.16 \mu\text{m}$. The silicon retention in the alteration products ranged from 5 to 10%, corresponding to the values measured by Advocat under initial rate conditions (Advocat *et al.*, 1991).

3.2 Static Tests at $S/V = 500 \text{ m}^{-1}$

The solution analysis data for the two static tests (ST1 and ST2) are indicated in **Table III** and **Table IV**. The pH values for both tests were identical, rising in a few days from the pH of pure water (about 6.5 at 90°C) to 8.9, then stabilizing at that value.

The alteration kinetics of the two glass specimens were very different, however, as shown by the normalized glass mass loss curves calculated from the boron concentrations (**Figure 1**) and the variation of the alteration rates over time (**Figure 2**). On completion of the test, the previously altered glass was 2.7 times as altered as the pristine glass. The differences were noted primarily between the first and 56th days (**Figure 2**): the alteration rate for both specimens diminished from the initial rate r_0 to about $r_0/5$ during the first day, but subsequently diminished much more slowly for the previously altered glass than for the initially pristine specimen. The initial state of the glass (pristine or previously altered) thus affects the mechanism controlling the diminishing alteration rate. After 56 days, the alteration rates in both cases were less than $10^{-3} \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (i.e. $r_0/1000$); the uncertainty on rates of such magnitude makes it impossible to identify any differences after 56 days.

The silicon concentrations were also very different in the two test media (**Figure 3**). At the first sampling interval, the Si concentration was twice as high for the ST2 test as for ST1, as were the concentrations of the tracer elements (B, Na, Li). Between 1 and 56 days the Si concentrations rose more quickly in the ST1 test medium. The concentrations stabilized after 56 days in both cases; the Si concentrations at the end of the experiment were twice as high for the previously altered glass (ST1) as for the pristine glass (ST2).

The ultrafiltered 84-day solution samples showed no significant differences in the concentrations of the dissolved species (**Table III** and **Table IV**), confirming the absence of colloids in the leachates.

3.3 Characterization of Alteration Films

Figure 4a shows a cross section through the alteration products formed during the flowing experiment. The gel ($1000 \pm 200 \text{ nm}$ thick) is clearly visible, as are the surface precipitates forming a rather heterogeneous layer about 100 nm thick. The morphology of the precipitates is characteristic of rare earth phosphates and phyllosilicates—the two phases generally described in this region (Noguès *et al.*, 1985). Localized analyses within the gel layer (**Figure 4b**) show a constant Si/O ratio of 0.26 in the gel, appreciably below the corresponding ratio in the pristine glass (0.47).

Figure 5 and **Figure 6** include images of the alteration products formed during the static tests. **Figure 5a** (test ST2) shows a gel layer 150 ± 50 nm thick together with a rather heterogeneous phyllosilicate layer about 40 nm thick. The Si/O ratio in the gel (0.37) was constant at the same value as in the pristine glass, and significantly higher than in the flowing experiment, suggesting that the gel network formed during the static tests was probably better cross-linked than the network formed during alteration under flowing conditions.

Figure 6a is a cross section of the alteration products that formed on the specimen leached successively under flowing and static conditions. Two regions can be distinguished within the total gel layer 1500 ± 200 nm thick: an inner region 400 nm thick and an outer region 1100 nm thick. The outer region corresponds to the gel formed during the flowing experiment, while the inner region was formed during static leaching. The Si/O profile (**Figure 6b**) indicates that this ratio gradually diminishes from the glass/gel interface, where it is the same as in the pristine glass (0.47), to the glass/solution interface, where it corresponds to the value measured in the gel formed under flowing conditions (0.26).

The ST1 experiment thus did not yield the same Si/O ratio in the gel formed during the flowing alteration phase. The result indicates that a fraction of the silicon hydrolyzed during the static experiment was retained in the nonprotective gel formed during the flowing experiment.

4. DISCUSSION

4.1 Experimental Findings

Analysis of the leachates from static test ST2 showed that between 0 and 0.17 day alteration occurred at the initial rate of $0.5 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ measured during the dynamic test. Over the same time interval, the previously altered glass dissolved at only half this rate. This behavior could be attributable to a partial diffusion barrier due to the preexisting gel layer. This behavior was transient, however, and after 1 day the trend was reversed, showing that a different limiting mechanism was involved at this stage of reaction progress.

During the time period corresponding to the transition from the initial rate to the final rate characteristic of a steady-state silicon concentration, static tests ST1 and ST2 show that the glass alteration kinetics were strongly influenced by the presence of the gel formed during the flowing experiment (**Figure 2**). The silicon fractions retained in the two types of gel (calculated from the differences between the boron and silicon flows) were not the same (**Table III** and **Table IV**), but this calculation provides no indication of the silicon distribution in the gel—and this is an essential point.

The leachate analysis results show that the steady-state silicon concentrations were also dependent on the initial system conditions. This observation can be interpreted only by considering that the steady-state dissolved silicon concentrations depends on the nature of the gel—i.e. it is not an inherent glass property. This is equivalent to asserting that the steady-state value does not correspond to the glass solubility, and that the difference between the silicon concentration at any given instant and the steady-state concentration is therefore not representative of the chemical affinity of the glass dissolution reaction. From this standpoint, these observations corroborate the results of other recent work in this area (Jégou, 1998; Gin *et al.*, 1999).

Although the silicon concentration in solution is not the parameter controlling the glass alteration kinetics, its role as a gel forming agent is fundamental. SON 68 glass alteration experiments in clay with strong complexation properties (Gin *et al.*, 2000b) have shown that the presence of silicon in the gel was necessary to constitute an effective diffusion barrier between the glass and solution. The presence of insoluble elements such as Zr or the rare earth elements favors cross-linkage in the gel and enhances its protective properties (Jégou, 1998), but this is possible only in a silicate network formed by recondensation of hydrolyzed silicon.

4.2 STEM Examination Results

STEM observation of the alteration films formed during static experiments ST1 and ST2 showed that a fraction of the silicon from the glass that was hydrolyzed during static alteration (ST1) migrated into the gel previously formed during the flowing experiment. The fact that Si/O ratios exceeding 0.25 were measured within the outer portion of the gel on this sample confirms that silicon migrated through the entire nonprotective gel layer. This further suggests that a fraction of the silicon hydrolyzed during the static test migrated completely into solution, and would account for the higher dissolved Si concentrations measured in test ST1 than in test ST2. Similar results were obtained for the Si/Fe, Si/Zr and Si/Nd ratios.

These observations, however, do not account for the fact that the glass was 2.7 times as altered in test ST1 as in test ST2.

The preceding observations indicate that silicon recondensation was relatively uniform (i.e. with a long diffusion distance before recondensation, compared with the thickness of the alteration film) rather than localized. The alteration products (nonprotective gel and/or phyllosilicates) that formed under flowing conditions thus exhibited the behavior of a silica pump comparable to the phenomena observed when glass is altered in the presence of clay (Gin *et al.*, 2000b). Saturation of the gel thus appears to be indispensable before it can become protective, and limit the kinetics of glass network dissolution.

4.3 Gel Density

Assuming glass dissolution is a constant-volume process, and considering that in experiment ST1 the gel formed under flowing conditions was not dissolved during the static phase, a material balance based on the silicon concentrations in the three gels in this series of experiments yields the following results (the gel thicknesses indicated are based on the observed normalized boron mass losses):

- On completion of the flowing experiment: $d_{\text{Si}} = 0.7$ Si atom per nm^3 of gel.
- After static leaching of the previously altered specimen (ST1): $d_{\text{Si}} = 2.6$ Si atoms per nm^3 of gel on average over the total thickness, taking into account the additional silicon corresponding to the dynamic and subsequent static alteration phases.
- After static leaching of the pristine glass specimen (ST2): $d_{\text{Si}} = 4.6$ Si atoms per nm^3 of gel.

The silicon profile in the gel on specimen ST1 reveals that near the glass/gel interface the Si/O ratio was the same as the value measured in the pristine glass, as in the case of specimen ST2. It may thus be assumed that the local silicon density near the reaction interface is 4.6 Si atoms per nm^3 of gel, as in the pristine glass. Moreover, the outer portion of the gel was not enriched in Si by comparison with the gel formed only during prior alteration under flowing conditions (Figure 4 and Figure 6). It can therefore also be assumed that the local silicon density in the outermost portion of the gel is 0.7 Si atom per nm^3 of gel, as in the gel formed under flowing conditions. This implies a density gradient between the reaction interface region and the outer portion of the gel. The distribution of the total quantity of silicon retained throughout the gel was calculated assuming a linear density gradient between the upper limit (4.6 Si atoms/ nm^3 of gel) and the lower limit (0.7 Si atom/ nm^3 of gel); the upper limit was reached to a depth of no more than 300 nm near the interface, and that at least 150 nm on the outer region of the gel showed no Si enrichment.

These results suggest the existence of a critical density above which the transport of glass species is sharply reduced, although further work will be necessary to substantiate this hypothesis. The critical density must be associated with a characteristic thickness to qualify the gel as "protective". In future work, we will focus on determining the possible relation between the protective gel density and thickness by examining alteration films formed at different stages of reaction progress.

4.4 Protective Gel Formation Conditions

For many years, it has been observed that increasing the S/V ratio of static alteration experiments tends to increase the solution pH, increase the dissolved silicon concentration, and diminish the altered glass thickness after a given time interval (Agida *et al.*, 1985; Ebert and Mazer, 1994): the higher the S/V ratio,

the faster the alteration rate diminishes. The classic interpretation of this observation is in terms of saturation. Increasing the S/V ratio allows solution saturation conditions to be reached sooner, hence the rate diminishes more quickly at higher S/V ratios. It is also acknowledged that a higher pH results in a greater apparent silica solubility of the glass. However, this interpretation breaks down in the case of a pristine glass specimen that dissolves at its initial rate r_0 as long as a protective gel has not been formed (Jégou, 1998; Gin *et al.*, 1999).

In the light of this work, the notion of solution saturation with respect to silica must be considered prudently, inasmuch as it apparently depends on the nature of the gel and thus on the specimen history (Vernaz and Gin, 2000). Experimental work carried out since 1990 on the effects of the glass composition has led some authors to suggest that the protective properties of the gel could increase with the S/V ratio (Feng *et al.*, 1990). The interpretation of our experimental data confirms this hypothesis and may explain the mechanisms involved.

The gel is formed by recondensation of hydrolyzed species. The recondensation rate depends primarily on the ratio between the number of recondensation sites and the concentration of species liable to recondense. When a pristine glass specimen is placed in pure water, the recondensation rate is low: the gel formed in the early stages of the reaction contains little silicon and its protective properties are very limited. Two hypotheses may be postulated at this point: ① the gel (or a fraction of the gel) must be saturated with respect to silicon in order to become protective, and ② an unsaturated gel (or phyllosilicate layer) constitutes a silicon pump. According to these hypotheses, the glass quantity that must be dissolved to saturate the gel depends on the mass of nonprotective gel—which is inversely proportional to the S/V ratio. The lower the S/V ratio, the greater the mass of unsaturated gel; this implies a major silica pump effect, hence a delay in the formation of a sufficient thickness of saturated, protective gel. The required minimum density necessary to obtain a protective gel thus accounts for the effect of the S/V ratio observed in the case of nuclear glasses.

It still remains to be understood why the nonprotective gel formed during the flowing experiment constitutes a pump for the silicon hydrolyzed during the static test. The “pump” must be located, by discriminating between the gel and the secondary rare-earth phosphate or phyllosilicate phases that precipitate at the gel/solution interface from the initial stages of the alteration process.

5. CONCLUSION

This study confirms that the notion of solution saturation with respect to silicon is not an inherent glass characteristic, since the steady-state concentrations depend on the gel formation conditions—and in particular on the capacity of the medium to provide or remove silicon. The degree of gel protection also depends on the experimental conditions. Nevertheless, it appears that the gel must reach a given silicon concentration before it becomes protective. The observations corroborating this hypothesis are consistent with the effects of the S/V ratio on the alteration kinetics of nuclear glass.

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Table I. SON 68 (R7T7-type) glass composition

Oxide	wt%	Element	wt%
SiO ₂	45.48	Si	21.26
Al ₂ O ₃	4.91	Al	2.60
B ₂ O ₃	14.02	B	4.35
Na ₂ O	9.86	Na	7.31
CaO	4.04	Ca	2.89
Li ₂ O	1.98	Li	0.92
ZnO	2.50	Zn	2.01
ZrO ₂	2.65	Zr	1.96
Fe ₂ O ₃	2.91	Fe	2.04
NiO	0.74	Ni	0.58
Cr ₂ O ₃	0.51	Cr	0.35
P ₂ O ₅	0.28	P	0.22
UO ₂	0.52	U	0.46
ThO ₂	0.33	Th	0.29
SrO	0.33	Sr	0.28
Y ₂ O ₃	0.20	Y	0.16
MoO ₃	1.70	Mo	1.13
MnO ₂	0.72	Mn	0.46
CoO	0.12	Co	0.09
Ag ₂ O	0.03	Ag	0.03
CdO	0.03	Cd	0.03
SnO ₂	0.02	Sn	0.02
Sb ₂ O ₃	0.01	Sb	0.01
TeO ₂	0.23	Te	0.18
Cs ₂ O	1.42	Cs	1.34
BaO	0.60	Ba	0.54
La ₂ O ₃	0.90	La	0.77
Ce ₂ O ₃	0.93	Ce	0.79
Pr ₂ O ₃	0.44	Pr	0.38
Nd ₂ O ₃	1.59	Nd	1.36
		O	45.21

Table II. Solution analysis data for the flowing experiment: concentrations *C* and normalized glass mass loss values *NL* calculated from Eqn (1); mean glass dissolution rate *r* (for *t* = 1 to 7 days) and standard deviation; silicon retention factor *f_{Si}* in the alteration products calculated from Eqn (2).

<i>t</i> (days)	Flow rate (ml·min ⁻¹)	pH at 90°C	<i>C</i> (Si) (mg·l ⁻¹)	<i>C</i> (B) (mg·l ⁻¹)	<i>C</i> (Na) (mg·l ⁻¹)	<i>C</i> (Li) (mg·l ⁻¹)	<i>C</i> (Al) (mg·l ⁻¹)	<i>C</i> (Ca) (mg·l ⁻¹)	<i>NL</i> (Si) (g·m ⁻²)	<i>NL</i> (B) (g·m ⁻²)	<i>NL</i> (Na) (g·m ⁻²)	<i>r</i> (B) (g·m ⁻² ·d ⁻¹)	<i>f_{Si}</i>
0.25	1.44	7.95	1.05	0.18	0.77	0.04	0.18	0.26	0.05	0.04	0.11	0.18	-0.17
1	1.98	7.95	2.33	0.45	1.08	0.07	0.22	0.74	0.62	0.59	0.84	0.73	-0.06
2	1.27	8.25	2.09	0.47	1.03	0.08	0.20	0.53	0.72	0.79	1.03	0.20	0.09
3	1.22	8.36	2.87	0.67	1.17	0.11	0.30	0.38	1.43	1.62	1.69	0.83	0.12
4	1.18	8.52	3.03	0.71	1.28	0.13	0.28	0.55	1.94	2.22	2.38	0.60	0.13
7	1.08	8.25	2.93	0.64	1.29	0.11	0.29	0.67	3.00	3.18	3.84	0.32	0.06
Mean <i>r</i> (B)												0.54	
Std. deviation												0.28	

Table III. Solution analysis data for static-mode experiment as $S/V = 500^{-1}$ with glass specimen ST1 (previously altered under flowing conditions): concentrations C and normalized glass mass loss values NL calculated from Eqn (1); silicon retention factor f_{Si} in the alteration products calculated from Eqn (2). Final test sample (*) corresponds to ultrafiltered solution (10000 Dalton).

t (days)	pH at 90°C	C(Si) (mg·l ⁻¹)	C(B) (mg·l ⁻¹)	C(Na) (mg·l ⁻¹)	C(Li) (mg·l ⁻¹)	C(Al) (mg·l ⁻¹)	C(Ca) (mg·l ⁻¹)	NL(Si) (g·m ⁻²)	NL(B) (g·m ⁻²)	NL(Na) (g·m ⁻²)	NL(Li) (g·m ⁻²)	f_{Si}
0.17	8.25	4.5	1.2	2.4	0.2	0.5	1.04	0.04	0.05	0.07	0.03	0.23
1	8.65	18.8	6.4	10.3	1.3	1.4	1.07	0.17	0.29	0.28	0.28	0.40
7	8.81	39.9	16.5	25.3	3.3	1.5	1.32	0.36	0.73	0.67	0.69	0.50
14	8.85	53.5	25.7	39.7	5.0	1.3	1.23	0.48	1.13	1.04	1.05	0.57
28	8.95	62.2	31.5	48.6	6.1	1.2	0.83	0.55	1.36	1.25	1.24	0.60
56	8.92	66.1	31.5	48.5	6.3	1.2	0.92	0.58	1.34	1.23	1.26	0.57
84	8.95	68.4	32.3	48.1	6.2	1.3	0.89	0.58	1.34	1.19	1.22	0.57
84*	8.95	64.5	31.1	45.3	6.3	0.8	0.81	0.55	1.29	1.12	1.24	0.58

Table IV. Solution analysis data for static-mode experiment as $S/V = 500^{-1}$ with pristine glass specimen ST2: concentrations C and normalized glass mass loss values NL calculated from Eqn (1); silicon retention factor f_{Si} in the alteration products calculated from Eqn (2). Final test sample (*) corresponds to ultrafiltered solution (10000 Dalton).

t (days)	pH at 90°C	C(Si) (mg·l ⁻¹)	C(B) (mg·l ⁻¹)	C(Na) (mg·l ⁻¹)	C(Li) (mg·l ⁻¹)	C(Al) (mg·l ⁻¹)	C(Ca) (mg·l ⁻¹)	NL(Si) (g·m ⁻²)	NL(B) (g·m ⁻²)	NL(Na) (g·m ⁻²)	NL(Li) (g·m ⁻²)	f_{Si}
0.17	8.3	8.0	2.1	4.4	0.4	0.9	1.9	0.08	0.10	0.12	0.09	0.22
1	8.64-8.69	18.0	5.3	9.8	1.1	1.6	2.3	0.17	0.24	0.26	0.23	0.31
7	8.81	25.5	8.2	14.7	1.7	1.7	2.8	0.23	0.36	0.39	0.35	0.36
14	8.85	28.5	9.3	16.4	1.9	1.9	2.5	0.26	0.41	0.43	0.40	0.37
28	8.85	30.2	9.9	17.8	2.2	1.7	2.3	0.27	0.43	0.46	0.44	0.38
56	9.03	34.5	11.3	19.6	2.4	1.7	2.0	0.30	0.48	0.50	0.49	0.37
84	8.75	36.8	11.9	20.8	2.6	1.7	2.1	0.31	0.49	0.51	0.51	0.37
84*	8.75	34.6	11.4	19.7	2.6	1.1	1.8	0.29	0.47	0.49	0.50	0.38

Table V. Altered glass thicknesses determined from boron concentrations in solution, thickness of alteration films observed by STEM, and from measured specimen mass loss.

Altered glass thickness	Dynamic test	Static test on previously altered glass (ST1)	Static test on pristine glass (ST2)
Solution analysis data			
Equivalent boron thickness (µm)	1.16	0.49 (+1.16)* = 1.65	0.18
STEM observation data			
Gel thickness (µm)	0.8-1.2	0.3-0.5 (+1.0-1.2)*	0.10-0.15
Precipitated thickness (µm)	≈ 0.1	≈ 0.2	≈ 0.04
Specimen mass loss data			
Gel thickness (µm)	1.0	1.5	unmeasurable

*gel previously formed under flowing conditions

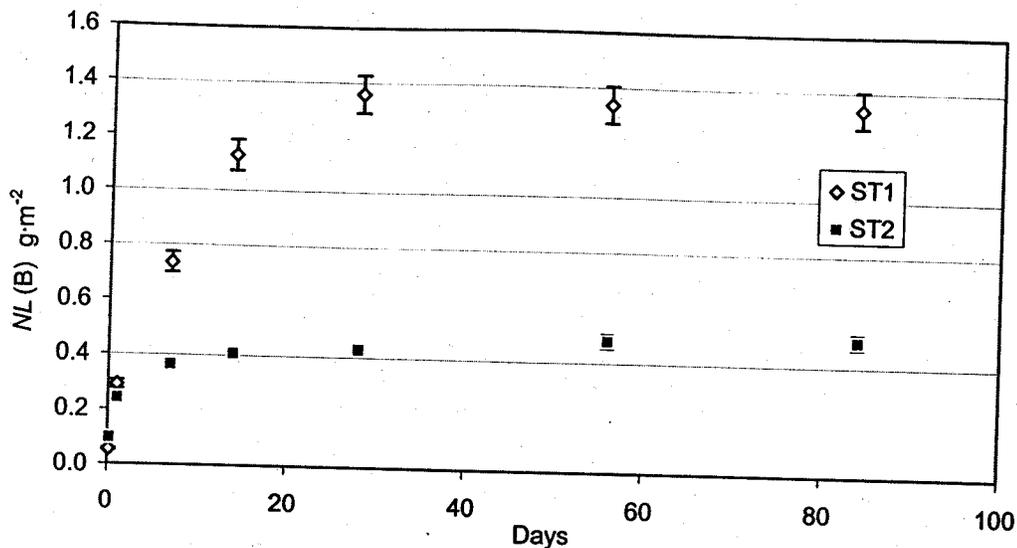


Figure 1. Normalized glass mass losses calculated from boron concentrations in static tests ST1 (glass specimen previously altered under flowing conditions) and ST2 (pristine glass coupon) versus time at 90°C and $S/V = 500 \text{ m}^{-1}$. Estimated uncertainty on normalized mass losses: 7%.

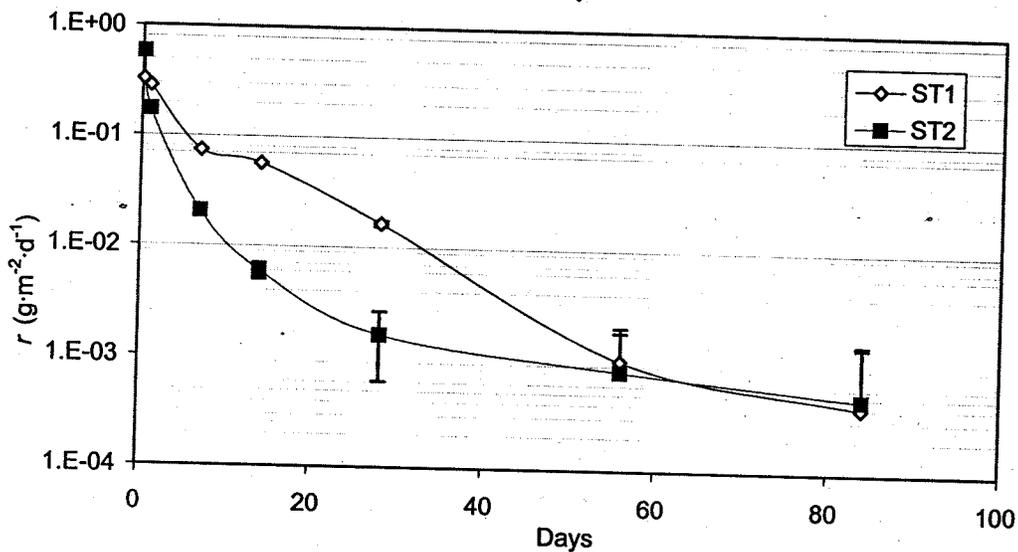


Figure 2. Glass alteration rates in static tests ST1 (glass specimen previously altered under flowing conditions) and ST2 (pristine glass coupon) versus time at 90°C and $S/V = 500 \text{ m}^{-1}$. Estimated uncertainty on alteration rates: $10^{-3} \text{ g·m}^{-2}\text{d}^{-1}$.

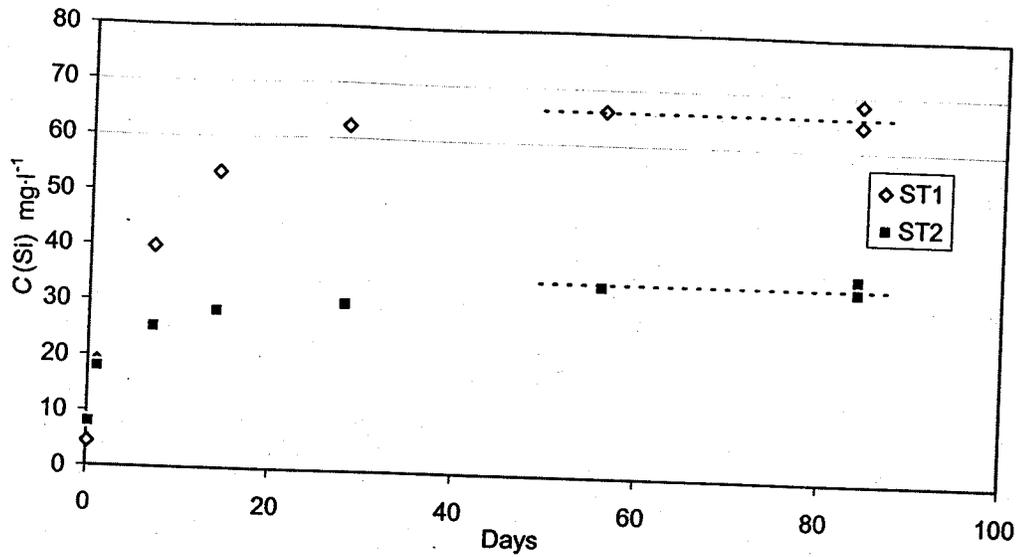


Figure 3. Dissolved silicon concentrations in static tests ST1 (glass specimen previously altered under flowing conditions) and ST2 (pristine glass coupon) versus time at 90°C and $S/V = 500 \text{ m}^{-1}$. Estimated uncertainty on concentrations: 3%.

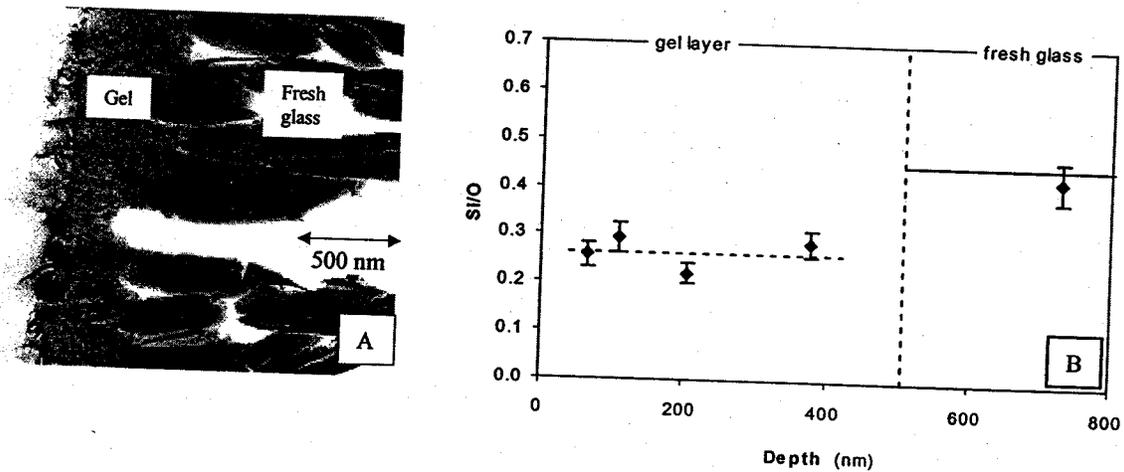


Figure 4. STEM characterization of alteration film formed during flowing experiment. (A) Morphology of alteration film showing (left to right): secondary phases precipitated at gel/solution interface (rare earth phosphates and phyllosilicates), gel layer formed by recondensation of silicate species, and pristine glass splinters (due to ultramicrotome). (B) Localized chemical analyses in gel and pristine glass. Solid line corresponds to theoretical Si/O ratio in pristine glass; broken line is a visual aid for clarity.

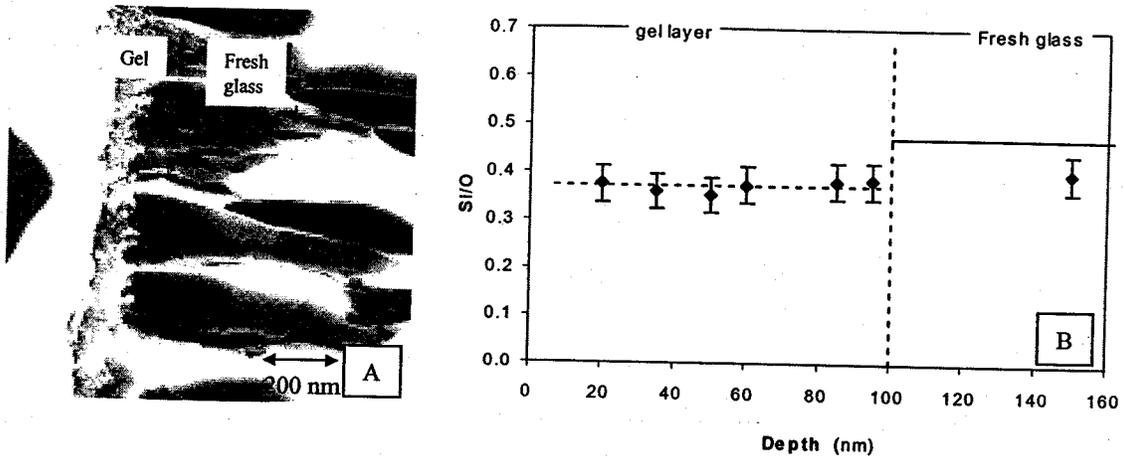


Figure 5. STEM characterization of alteration film formed during static alteration of pristine glass specimen (ST2). (A) Morphology of alteration film showing (left to right): gel layer formed by recondensation of silicate species, and pristine glass splinters (due to ultramicrotome). (B) Localized chemical analyses in gel and pristine glass. Solid line corresponds to theoretical Si/O ratio in pristine glass; broken line is a visual aid for clarity.

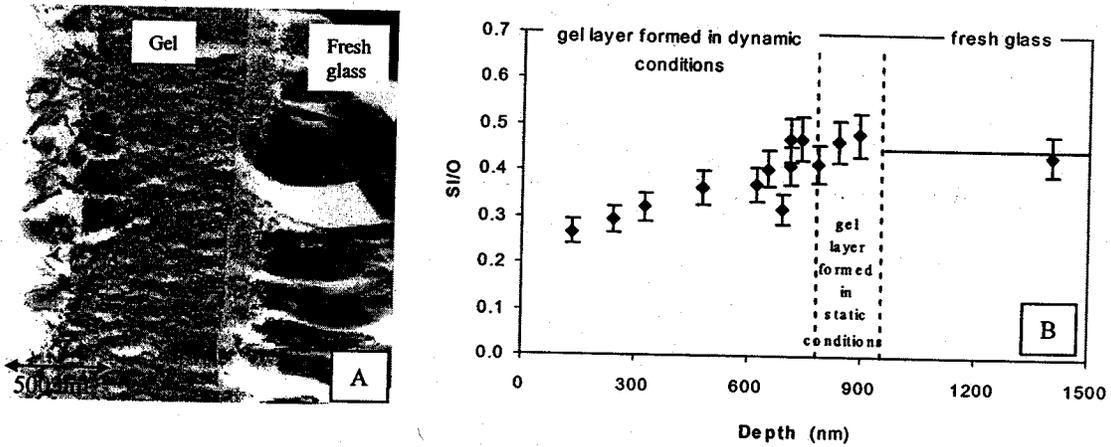


Figure 6. STEM characterization of alteration film formed by flowing and static alteration of glass specimen (ST1). (A) Morphology of alteration film showing (left to right): secondary phases precipitated at gel/solution interface (rare earth phosphates and phyllosilicates), gel layer formed by recondensation of silicate species (comprising gel formed during flowing experiment and gel formed during static test), and pristine glass splinters (due to ultramicrotome). (B) Localized chemical analyses in gel and pristine glass. Solid line corresponds to theoretical Si/O ratio in pristine glass; broken line is a visual aid for clarity.

APPENDIX II

Documents Listing

Primary Document

"A Strategy to Conduct and Analysis of the Long-Term Performance of Low-Activity Waste Glass in a Shallow Subsurface Disposal System at Hanford", PNNL- 11834, by B.P. McGrail, W.L. Ebert, D.H. Bacon and D.M. Strachan, draft- Feb. 1998.

Supporting Documents

- 1) "Measurement of Kinetic Rate Law Parameters on a Na-Ca-Al Borosilicate Glass for Low-Activity Waste", Journal of Nuclear Materials, B.P. McGrail, W.L. Ebert, A.J. Bakel and D.K. Peeler, Vol. 249, pp. 175-189 (1997).
- 2) "Accelerated Testing of Waste Forms Using a Novel Pressurized Unsaturated Flow (PUF) Method", Scientific Basis for Nuclear Waste Management XX, eds. W.J. Gray and I. Triay, Materials Research Society, Vol. 465, pp. 253-260, B.P. McGrail, P.F. Martin and C.W. Lindenmeier, (1997).
- 3) "Source Term Analysis for Hanford Low-Activity Tank Waste Using the Reaction-Transport Code AREST-CT", Scientific Basis for Nuclear Waste Management XX, eds. W.J. Gray and I. Triay, Materials Research Society, Vol. 465, pp. 1051-1058, Y. Chen, B.P. McGrail, and D.W. Engel (1997).
- 4) "Selection of a Computer Code for Hanford Low-Level Waste Engineered-System Performance Assessment", PNNL-10830- rev. 1, B.P. McGrail and D.H. Bacon, March 1998.