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Stirred-Reactor Coupon Analysis: An International Round Robin Study

September 2022

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Executive Summary

Previously in the nuclear waste performance community, the single-pass flow-through (SPFT) method ASTM C1662 (e.g., ASTM C1662-18 2018) has been the most common test chosen to evaluate waste form corrosion in dilute conditions. The test method consists of a target solution passed at a relatively low flow rate over a sample material (usually in particle form) and determining the dissolution rate by measuring the composition of the effluent by solution analyses. The typical analytical techniques for solution analyses have detection limits that can require lowering flow rates (and thus decreasing the dilution of the contacting solution) just so the concentration of ions in the resultant effluent is high enough to measure. This higher concentration impacts the resultant measured rate to the extent that extrapolations of multiple measurements must be made to estimate the dissolution rate in infinitely dilute conditions.

A new technique, termed the stirred-reactor coupon analysis (SRCA) method, has been developed to achieve dilute conditions through a large, well-mixed volume rather than via solute flow. In this method, monolithic glass coupons are partially masked with an inert material before undergoing corrosion in a large volume of solution with known chemistry and temperature for a pre-determined duration. After terminating the test, the mask is removed and the step height difference between the protected area under the mask and the exposed corroded portions of the sample coupon is measured to determine the extent of glass dissolution. The step height is converted to a rate measurement using the test duration and glass density.

The SRCA method presents many improvements over the SPFT method for measurements in dilute conditions. First, the direct measurement of the step height and straightforward conversion to dissolution rate is simpler, lower cost, and has lower uncertainty than doing the same from solution analysis data. The assumptions of surface area, surface area change, ion interactions with surfaces, and operating near the limits of detection combine to make the experimental uncertainty in SPFT measurements both relatively high and difficult to quantify. Second, the SRCA test maintains very dilute conditions through the entirety of the test duration, ensuring that any influence of ion activity in the solution is minimized. Third, the SRCA test is capable of simultaneous measurement of multiple glass samples. This enables direct comparison of different glasses in equivalent conditions or the ability to examine many replicates to improve test statistics.

With the laboratory testing success of the SRCA technique and potential use as a bulk measure of glass corrosion, it would be beneficial to establish a standard procedure recognized by an international consensus standards body such as ASTM International. Additionally, the successful use of the method by other respected laboratories would increase confidence in the technique's low uncertainty and ability to gather consistent glass corrosion data. The objective of this task was to determine the precision of the SRCA technique when used to determine the dilute condition corrosion rate. To this end, an interlaboratory round robin study was conducted per the ASTM procedures (ASTM D7778-15(2022)e1 2022, ASTM E691-22 2022) to measure the precision with which the SRCA test method can be conducted. The ASTM procedures recommend at least 6 labs participate in a round robin program testing the same 3 materials in the same conditions to determine precision. In this case, twelve independent labs from eleven different institutions each evaluated 12 independent tests (4 glass compositions in 3 different conditions. This was only possible in the time period available thanks to the multi-glass testing capability of the SRCA method.

A total of 114 duplicate pairs were used to calculate the repeatability of the tests, with the same glass tested in the same vessel, producing as identical conditions as possible for the replicates. These test results were closely clustered, with a median difference from the average dilute dissolution rate of the pair of 2.8%. Based on the calculations recommended in the ASTM E177-20 procedure (ASTM E177-20 2021) and the repeatability standard deviation (s_r) of 8.13%, **the test repeatability limit (*r*) was calculated to be precise within 21.8% of the expected value with 95% confidence level**.

The reproducibility limit (*R*) of the test was examined using 287 data points from the round robin, excluding the results from one major outlier test. Because of the differences in dissolution rates due to pH variability and intrinsically for the 12 conditions tested, the reproducibility limits for each condition and overall were calculated from the percent relative residual value for each test. The percent relative residual is the percent difference between the measured dissolution rate and the dissolution rate value predicted using a best linear pH vs. dissolution rate fit at the same pH value. The standard deviation for the percent relative residual was 19.0% for the entire dataset, with an average percent relative residual value of 23.8%, with only minor differences among the various glass/test condition sets. Using the ASTM calculations for reproducibility, **the SRCA test was calculated to be precise within 53.3% of the expected value with a 95% confidence level**.

Considering each of the 12 independent tests separately, the *R* values were remarkably consistent. The reproducibility limits for each test condition only ranged from 32% to 75% with an average of 50%. This is even more impressive considering that the pH measurements were performed at inconsistent intervals among the collaborating labs, with some achieving careful controls and others allowing extensive drift. It is evident that precise control and detailed knowledge of the test pH would produce even more consistent and accurately used measurements. The low variability highlights that it was appropriate to remove the outlier dataset. If those data were included, the R values for the four $\text{pH}_{(\text{RT})}$ = 10 and 70 °C tests ranged from 102% to 166% – a marked difference from the rest of the test results.

The SRCA repeatability and reproducibility limits were both significantly lower than those demonstrated with the round robin for the SPFT method and comparable to those for the PCT (ASTM C1285-21 2021) method. **This provides confidence that the SRCA method represents an improvement in precision over the standard method currently used for corrosion testing in dilute conditions, while providing enhanced sample throughput.** The success of this effort is expected to simplify a portion of the data collection to support waste form performance assessments worldwide by enabling rapid, reproducible measurements of corrosion in dilute conditions.

Acknowledgments

This work was completed as part of the ILAW Glass Testing for Disposal at the Hanford Integrated Disposal Facility (IDF) project. This project is supported by Washington River Protection *Solutions*, Inc. The testing could not have been completed without the assistance of scientists and students at the collaborating institutions. Specifically, we thank:

- Jean-Marc Delaye, CEA
- Jonathan Icenhower and Nick Stone-Weiss, Corning Inc.
- Junya Sato and Yuta Takahashi, JAEA
- Wenqing Xie, Myra Vu, and Thanh Nguyen, University of North Texas
- Pieter Schroeders and Ben Gielen, SCK CEN
- Ramya Ravikumar and Clare Thorpe, University of Sheffield
- Tracey Taylor, National Nuclear Laboratory
- Jessica Erickson and John Bussey, Washington State University

We also thank Jarrod Crum for his careful technical review and David MacPherson for his quality review. Richard Daniel and Alejandro Heredia-Langner provided reviews of the calculations in the report.

Acronyms and Abbreviations

%RSD	Percent relative standard deviation
APEL	Applied Process and Engineering Laboratory – at Pacific Northwest National Laboratory
ASTM	ASTM International
CCC	Canister centerline cooled profile
CEA	Commissariat à l'Énergie Atomique (Alternative Energies & Atomic Energy Commission)
CPC	Composition–parameter correlation
DIW	ASTM Type I water (ASTM D1193)
DOE	Department of Energy
EWG	Enhanced waste glass
FY	Fiscal year
GWB	The Geochemist's Workbench®
IDF	Integrated Disposal Facility, Hanford Site
ILAW	Immobilized low-activity waste
ISG	International Simple Glass
JAEA	Japan Atomic Energy Agency
LAW	Low-activity waste
LGS	Low-Activity Waste Glass Standards
LRM	Low-activity reference material
OP	Optical profilometry
PA	Performance assessment
$pH_{(RT)}$	pH value at room temperature (~25 °C)
PCT	Product consistency test (ASTM C1285)
PNNL	Pacific Northwest National Laboratory
QA	Quality assurance
SCK CEN	Studiecentrum voor Kernenergie Centre d'Etude de l'Énergie Nucléaire (the Belgian Nuclear Research Centre)
SEM	Scanning electron microscopy
SPFT	Single-pass flow-through (ASTM C1662)
SRCA	Stirred-reactor coupon analysis
TRIS	Tris(hydroxymethyl)aminomethane
TST	Transition state theory
VHT	Vapor hydration test (ASTM C1663)
WRPS	Washington River Protection *Solutions*, LLC
WTP	Waste Treatment and Immobilization Plant, Hanford Site
WWFTP	WRPS Waste Form Testing Program

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1.0 Introduction

A primary objective of radioactive waste immobilization is to retain radionuclides within a waste form matrix for long periods (thousands of years to geologic time scales). The chemical durability of the form, therefore, is a key parameter for its effectiveness no matter the material. Considering that vitrification has been declared the best demonstrated available technology for waste stabilization and its wide use throughout the world,(Federal Register 1990) the dissolution behavior of borosilicate glasses has been among the most extensively studied artificial materials when considering geologic time scales.(Lutze and Ewing 1988, Bourcier 1990, Cuunane et al. 1993, Bourcier 1994, Ebert and Mazer 1994, Van Iseghem et al. 2007, Van Iseghem et al. 2007) The only material/water interactions that have been more thoroughly studied are geologic or geochemical investigations into metasomatic mineral transformations. Regardless of the system, understanding long-term corrosion of ceramic or mineral materials in aqueous environments nearly always includes a study of how the material corrodes in dilute conditions.

This study serves to present results for a new test method for the corrosion of materials in dilute conditions. We summarize and discuss the results of a round-robin testing program that was designed and implemented to establish the precision of the newly developed Stirred Reactor Coupon Analysis (SRCA) test.(Ryan et al. 2021) This test will serve to increase glass corrosion testing specimens sample throughput in dilute conditions while providing a more repeatable result relative to other similar test methods.

The rest of this introduction details the uses of dilute condition corrosion testing and the development of the SRCA test. Section 2.0 of the report provides details on the glasses, method, and characterization for the round-robin effort. This section also describes how the results are used to calculate the precision of the technique. The round robin results are presented in Section 3.0. Section 4.0 goes into detail on the statistical evaluation of the collected data and the variances that can be attributed to the variables in the study. Finally, Section 5.0 discusses the overall findings of the study, including the precision statement for the SRCA test and a comparison to other test results.

1.1 Performance Assessment Representation of Glass Dissolution

In order to dispose of immobilized nuclear waste throughout the United States of America, the U.S. Department of Energy (DOE) Order 435.1 *Radioactive Waste Management* (DOE 2001) requires a performance assessment (PA) describing the potential long-term impacts on human health and the environment resulting from disposal of the particular wastes in the particular repository in question. Similar approaches are used in countries around the world for the evaluation of nuclear waste forms for disposal. These PAs must be performed to demonstrate that disposed waste forms meet environmental and health performance objectives before disposal site operation. To assess these risks, predictions of the long-term release of radionuclides and other contaminants of concern from the glass are required. The release rate of the radionuclides from the glass waste forms are calculated from models dependent on the dissolution rate of the glass and the disposal site infiltrating solution chemistry.

The evaluation of chemical durability is not limited to nuclear materials. Similar models are also used by industrial suppliers for commercial glass products, whether the corrosion in question is undesired or by design. In all cases, successful application of the glass material requires an accurate representation of corrosion in aqueous conditions.

Most glass corrosion models use at least in part a kinetic rate equation based on transition state theory (TST) arguments and assumptions (Åagaard and Helgeson 1982). In general, this theory assumes the displacement from pseudo-equilibrium drives the transformation of glass to more stable silicate materials. When used for glass materials such as developed by Grambow (1985), the activity of orthosilicic acid (H_4SiO_4) is usually taken as the species that governs the deviation from pseudo-equilibrium.

$$r = k_0 a_{\mathrm{H}^+}^{-\eta} \exp\left(\frac{-E_a}{RT}\right)\left[1-\left(\frac{Q}{K_g}\right)^{\sigma}\right] \qquad \text{Eq. 1-1}$$

where: r = glass dissolution rate (g-glass m^{-2} d^{-1})
k_0 = intrinsic rate constant (g-glass m^{-2} d^{-1})
$a_{\mathrm{H}+}$ = hydrogen ion activity
η = pH power law coefficient
E_a = activation energy (J mol^{-1})
R = gas constant (8.314 J $mol^{-1}\cdot K^{-1}$)
T = temperature (K)
Q = ion-activity product
K_g = pseudo-equilibrium constant for glass
σ = Temkin coefficient

The ion activity product, Q, is the variable that controls the rate evolution. In disposal calculations, Q must be computed by a numerical simulator as a function of time and space to evaluate how glass will dissolve in the local environment. The Temkin coefficient, σ, is the ratio of the rate of destruction of the activated complex involved in the rate-limiting reaction step to the overall dissolution rate. For glass corrosion, σ is assumed to be 1.(Lasaga 1995) The term inside the square brackets is commonly referred to as the chemical affinity term. In conditions far from equilibrium such as those discussed in this report (*i.e.*, dilute conditions where $Q << K_g$), the chemical affinity term is 1 and the glass dissolves at the maximum possible rate for the conditions. As the ionic concentration increases, different mechanisms control the glass corrosion rate and are the subject of much debate and research.(Kerisit et al. 2019, Frankel et al. 2021, Gin et al. 2021, Lenting and Geisler 2021)

In dilute conditions, the rate model reduces to

$$r = k_0 10^{\eta \times pH} \exp\left(\frac{-E_a}{RT}\right) \qquad \text{Eq. 1-2}$$

when the hydrogen ion activity is expressed in terms of pH (where pH $= (-log\ a_{\mathrm{H}^+})$). The logarithmic form of Eq. 1-2 can then be used to derive three parameters, η, E_a, and k_0, using a linear multivariate regression of glass dissolution rate data obtained at a range of pH/temperature combinations

$$\log(r) = \log(k_0) + \eta \times pH - \log(e)\frac{E_a}{R} \times \frac{1}{T} \qquad \text{Eq. 1-3}$$

These three parameters, i.e., pH power law coefficient (η), activation energy (E_a), and intrinsic rate constant (k_0), will be referred to hereafter as forward-rate model parameters. They have also been expressed elsewhere as dilute rate model parameters, kinetic parameters, or kinetic rate law parameters (Papathanassiu et al. 2017, Viragh et al. 2017, Viragh et al. 2018). For a chemical affinity rate model, these parameters are the typical parameter measurement goal for dilute condition testing of nuclear waste glass. Commercially, rapid dissolution behavior in dilute conditions is occasionally desired, such as for biological applications.

1.2 The Development of the SRCA Method

Previously in the nuclear waste performance community, the single-pass flow-through (SPFT) method (ASTM C1662-18 2018) has been the most common test chosen for dilute conditions. The test method consists of a target solution passed at a relatively low flow rate over a sample material (usually in particle form). The effluent from the test cell is then monitored by solution analyses, typically by exciting with an inductively coupled plasma (ICP) for optical emission spectroscopy (OES) or mass spectroscopy (MS). These techniques have detection limits that can require lower flow rates just to decrease the dilution of the resultant sample. This higher concentration impacts the resultant measured rate to the extent that extrapolations of multiple measurements must be made to estimate the dissolution rate in infinitely dilute conditions. Thus, it is always a balance between achieving fully dilute conditions and having a measurable result. Further, when acquiring glass dissolution parameters, a large number of conditions is necessary such that the throughput for the number of glass compositions tested is quite slow (i.e., it is relatively time consuming and costly). The ASTM C1220 (MCC-1) test (ASTM C1220-21 2021) and Soxhlet test (Delage and Dussossoy 1991) have also been used for dilute condition studies. Thus, there has been demand for a test method with higher throughput, operation in more dilute conditions, and without detection limit concerns. Such a test enables the parameterization of a large number of glass compositions in a shorter period of time that would provide ample data to support an assessment of a designed compositional space to improve both performance assessment flexibility and material development activities.

In FY16, efforts were initiated (Ryan et al. 2018) to develop a new technique to more efficiently determine dilute glass rate model parameters for large numbers of glass samples. Over the ensuing years, testing and optimization resulted in the attached stirred-reactor coupon analysis (SRCA) method (Appendix C). The method has two key components: a large, well-mixed reactor to ensure dilute conditions and a method to protect portions of the glass samples from corrosion. As shown in Figure 1-1, monolithic glass coupons are partially masked with an inert material before undergoing corrosion in a solution of known chemistry and temperature for a pre-determined duration. Based on the work of Icenhower and Steefel (Icenhower and Steefel 2015), who showed that interferometry could be used as a rapid throughput analysis method for glass corrosion, the step height difference between the masked and unmasked portions of the coupon is measured to determine the extent of glass dissolution. The step height can be converted to a rate measurement using the test duration and glass density. In contrast with SPFT, which measures glass constituent concentrations in solution, the SRCA method calculates rates based on bulk material loss from the glass thus alleviating challenges with solution detection limits to determine dissolution rates.

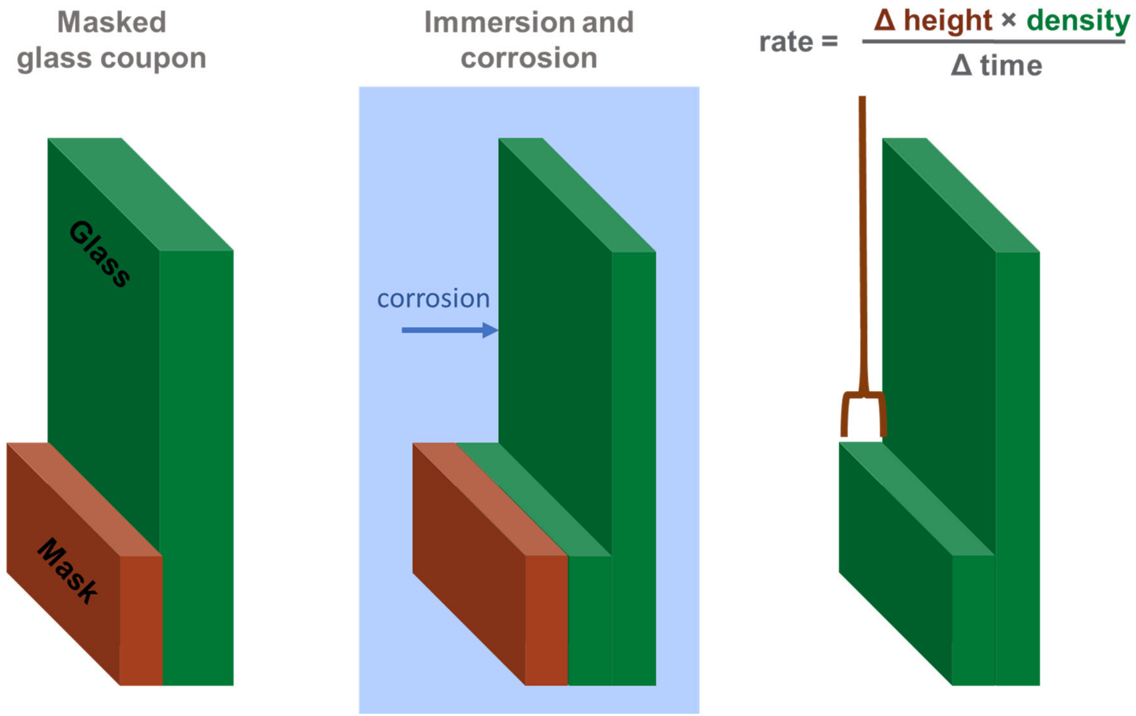


Figure 1-1. Schematic of glass coupon SRCA technique before corrosion (left), during corrosion (center), and during characterization (right).

As was detailed in (Ryan and Freedman 2016) a full set of forward-rate model parameters can be obtained by fitting the dissolution rate of the glass at a variety of test temperatures and pH values to a glass dissolution model such as (Eq. 1-2). In SPFT testing, the high flows that lead to the most dilute conditions can make it challenging to measure element concentrations in solution due to instrument detection limits. By using a coupon, the surface area of the glass exposed to the contacting solution is much smaller than with powder, making it easier to ensure dilute dissolution conditions while achieving a measurable result. Additionally, the surface area is a required parameter for SPFT and is difficult to measure or estimate consistently. With SRCA, the surface area is not required, and the dissolution extent is directly measured. Similar coupon-based approaches applied with a flow-through cell rather than a large solution volume found dissolution rates commensurate with SPFT for a high-level waste glass (Icenhower and Steefel 2015) and slightly lower than SPFT for a low-activity waste glass.(Neeway et al. 2017)

1.3 ASTM Method Development

With the laboratory testing success of the SRCA technique and potential use as a bulk measure of glass corrosion, it would be beneficial to establish a consensus standard procedure recognized by an international consensus standards body such as ASTM International. Additionally, the successful use of the method by other laboratories would increase confidence in the technique’s low uncertainty and ability to gather consistent glass corrosion data. The SRCA technique was used to parameterize a matrix of statistically designed glasses that provide broad coverage of an Enhanced Waste Glass (EWG) composition space (Ryan et al. 2021) for the Immobilized Low-Activity Waste (ILAW) glass performance evaluation program.(Ryan and Freedman 2016) The experience also led to a draft method statement in the style of an ASTM Standard Method.(Asmussen et al. 2017) The method and data were presented to the international community at glass conferences and to the International Workshop on Long-Term Glass Corrosion. The results were such that nearly all participating institutions in the Workshop expressed interest in evaluating the test for themselves.

This provided the initiative for the round robin effort documented here. ASTM methods require evaluations of the test precision to establish an understanding of the range of error that can be expected for the technique. The group of international glass corrosion experts highlighted in this report performed the same testing method on the same glasses in the same conditions using the same vessel design. Data from such a diverse group has enabled a statistically robust precision analysis(ASTM D7778-15(2022)e1 2022) for the test to assess intra- and interlaboratory variability and support establishment of SRCA as a consensus standard for the measurement of glass corrosion in dilute conditions. Further, input from the round robin participants have improved the clarity of the written method. The success of this effort is expected to simplify a portion of waste form performance assessments worldwide by assessing experimental uncertainty around the rates measured via SRCA to determine the dilute rate model parameters.

1.4 Quality Assurance

This work was conducted with funding from Washington River Protection *Solutions*, Inc. (WRPS) under contract 36437-161, ILAW Glass Testing for Disposal at IDF. The work was conducted as part of Pacific Northwest National Laboratory (PNNL) Project 77632, ILAW Glass Testing for Disposal at IDF.

The calculations in this work were performed in accordance with the WRPS Waste Form Testing Program (WWFTP) Quality Assurance Plan (QA-WWFTP-001) and associated QA procedures. The WWFTP QA program is based on the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008 Quality Assurance Requirements for Nuclear Facility Applications*, graded on the approach presented in NQA-1-2008, Part IV, Subpart 4.2, *Guidance on Graded Application of Quality Assurance (QA) for Nuclear-Related Research and Development*. This work was graded and performed as ‘applied research’.

The WWFTP QA Program supplements PNNL’s laboratory-level Quality Management Program, which is based upon the requirements as defined in the United States Department of Energy (DOE) Order 414.1D, *Quality Assurance,* and 10 CFR 830, *Nuclear Safety Management*, Subpart A, *Quality Assurance Requirements*. PNNL implements these requirements with a graded approach using the consensus standard ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications.*

The data collection efforts were performed in accordance with each institution’s best laboratory practices, but were not completed under the requirements of NQA-1-2008. While the quality of the data provided here can be used with confidence to evaluate the precision of this technique, **the data should not be deemed appropriate for inclusion to nuclear waste form performance analysis calculations or any other use where strict NQA-1 data traceability is required.**

2.0 Methods

The SRCA technique (Figure 2-1) is based off a simple premise: that a large volume of a well-mixed solution, provides sufficiently dilute conditions to allow glasses to corrode at the $Q = 0$ or "forward" rate (Eq. 1-1). In this section, we detail the round robin team, the glasses used in the study, the test parameters, the draft ASTM method, additional test instructions, and the post-test characterization. Finally, a brief description is given on the statistical methods used to evaluate test precision.

Figure 2-1. A photograph with cutaway schematic of the SRCA design for a large (11 L) stainless steel reactor.

2.1 Contributor Introductions

Out of the interested groups from the international workshop, two independent lab groups at PNNL and ten other external collaborating labs were identified for this round robin. For this report, the data is presented in anonymous fashion, with each of the twelve collaborating groups assigned a random letter designation from A to L. The participating groups and their lead scientists were as follows:

- Commissariat à l'Énergie Atomique (CEA) (Alternative Energies and Atomic Energy Commission) Marcoule, Dr. Stéphane Gin
- Corning, Inc., USA, Drs. Nicholas Smith and Jonathan Icenhower
- Japan Atomic Energy Agency (JAEA), Dr. Seiichiro Mitsui
- The University of Köln, Germany, Professor Christoph Lenting
- Kyushu University in Japan, Professor Yaohiro Inagaki
- National Nuclear Laboratory of the UK, Dr. Mike Harrison
- Pacific Northwest National Laboratory, Radiological Materials Group, Dr. Joseph Ryan
- Pacific Northwest National Laboratory, Earth Systems Science Group, Michelle Snyder
- University of North Texas, USA, Professor Jincheng Du
- Studecentrum voor Kernenerge Centre d'Etude de l'Énergie Nucléaire (SCK·CEN), the Belgian Nuclear Research Centre, Dr. Karine Ferrand
- University of Sheffield, UK, Professor Claire Corkhill
- Washington State University, USA, Professor John McCloy

Each collaborator was sent a package that included all items necessary to perform the SRCA test. The following items corresponding to the identification letters in Figure 2-2 were provided to each laboratory group:

Not shown: SRCA Reaction Vessel (10” diam by 10” deep, stainless steel)

A-D: Glass samples in four compositions (four polished coupons, four unpolished coupons, and a small amount of additional glass

E: Permatex RTV Silicone Sealant for masking samples

F: Stainless steel sample holding rods

G: Stainless steel clips to hold rods at correct height above stoppers

H: Neoprene stoppers

I: Silicone sampling port stopper

J: Teflon stir-shaft bushing

K: Stainless steel flexible coupler

L-M: Stainless steel stir shafts

N: Stainless steel propeller

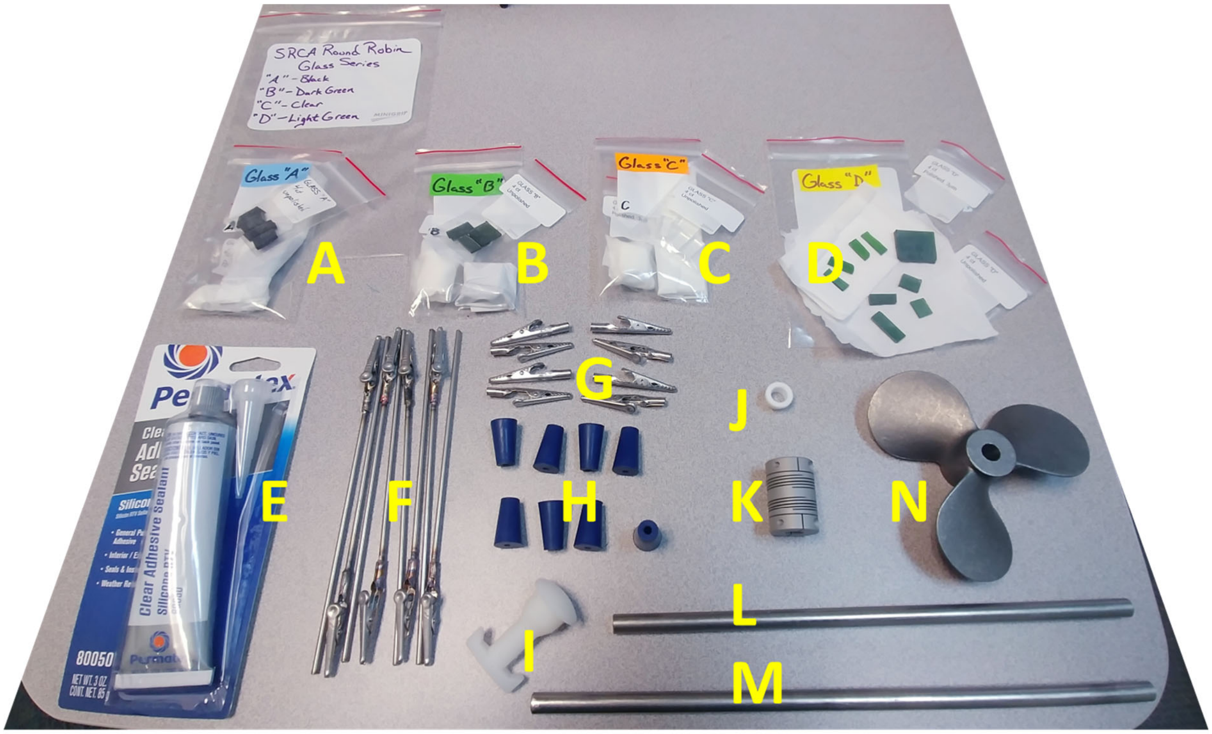


Figure 2-2 - Image of SRCA test apparatus component items shipped to collaborators to complete round robin testing. 10" diameter × 10" deep stainless-steel vessel and lid not shown.

2.2 Glass Design and Preparation

The four glass compositions for the round robin study (Table 2-1) were selected from standardized or otherwise well-characterized materials to, as much as is practical, both represent a variation in waste form materials and present a range of dissolution rates that would also be measurable given the designed test parameters. All glasses had been synthesized prior to this study for other purposes, but all were created in a bulk manner so that enough glass was available for all uses in the study. All glasses had also been annealed. In order to provide a blind test, the glasses were designated A, B, C, and D upon shipment to the collaborators. Only the originating lab (PNNL-APEL) was aware of the glass identities before testing.

Table 2-1 – As-measured glass compositions in mass % for glasses used in round robin testing:
LAWA44 (Meyer et al. 2020), LRM (Ebert and Wolf 2000)
ISG-2 (Ryan et al. 2022), and LGS19-03 (Crum et al. 2021)

	LAWA44 *“Glass A”*	***LRM*** *“Glass B”*	***ISG-2*** *“Glass C”*	***LGS19-03*** *“Glass D”*
Al_2O_3	6.01	9.51	5.96	6.92
B_2O_3	9.17	7.85	17.38	13.24
CaO	2.06	0.54	2.51	2.02
CdO	—	0.16	—	—
Cl	0.47	—	0.04	0.18
Cr_2O_3	0.02	0.19	—	0.49
F	0.01	0.86	—	0.4
Fe_2O_3	7.10	1.38	0.01	1.41
HfO_2	—	—	0.05	—
K_2O	0.50	1.5	0.01	4.75
La_2O_3	—	0.02	0.12	—
Li_2O	—	0.11	—	0.808
MgO	1.98	0.1	1.76	0.49
MnO_2	—	0.08	0.01	—
MoO3	0.09	0.1	—	—
Na_2O	20.91	20.03	12.10	16.22
NiO	—	0.19	—	—
P_2O_5	0.03	0.54	0.01	0.52
Re_2O_7	0.07	—	—	—
SiO_2	44.07	54.20	56.87	37.48
SnO_2	—	—	0.06	0.93
SO_3	0.12	0.30	0.01	0.6
TiO_2	1.98	0.10	0.01	0.5
V_2O_5	—	—	—	2.27
Y_2O_3	—	—	—	0.76
ZnO	3.07	—	—	3.57
ZrO_2	2.99	0.93	3.31	5.72
TOTALS	100.6	98.7	100.2	93.6

The LAWA44 glass composition is a baseline glass for the ILAW program (Pierce et al. 2004) and has been the subject of extensive testing. Dilute rates have been previously established for this composition using SPFT testing in multiple conditions.(Freedman et al. 2015) The samples used for this study were taken from bulk cylinders of the glass produced for a field lysimeter testing program. (Meyer et al. 2020)

A re-melt of the low-activity reference material (LRM) (Ebert and Wolf 2000) was chosen because the LRM glass was also used for the SPFT round-robin studies. Because the same pH_{RT}=11, 70°C condition was used in both the SPFT round robin and the SRCA round robin, the results can be directly compared.

The new composition of the International Simple Glass (ISG-2)(Ryan et al. 2022) was selected due to its acceptance as a baseline standard with the international nuclear waste glass waste forms community. It was fabricated in a very controlled manner and is exceptionally uniform. Both the composition and dissolution kinetics are similar to glasses designed for high-level waste form disposal. The replacement of half of the Ca in the original ISG composition with Mg results in a significantly higher dilute condition dissolution rate, which was a better fit relative to the other glasses in this study.

Finally, a composition from the 2019 Low-Activity Waste Glass Standards (LGS19) series produced for use as analysis standards for the Hanford Waste Treatment and Immobilization Plant (WTP) was selected.(Crum et al. 2021) The glasses were carefully produced in quantity. Of the seven LGS19 compositions, the LGS10-03 composition was found to have the highest nominal dilute corrosion rate in scoping tests and so was well suited for this study.

2.3 Test Matrix

The SRCA round robin tests were performed at a series of defined starting pH values and temperatures on the four chosen glass compositions. A test matrix was designed consisting of four pH, temperature, and sample configuration combinations, as detailed in Table 2-2. Nominally, eight glass coupons were placed in the reactor concurrently, with some samples polished by PNNL and others by the collaborator lab. Each experiment was to be run at least for the minimum duration. Since the step height between the masked and unmasked portions of the glass becomes larger and more accurately measured with longer exposure to the dilute solution, the collaborators were given discretion to run tests longer if possible.

Table 2-2 - Test conditions for each test number

Test number	pH	Temperature	Minimum duration
1 (req)	11	70 °C	1 day
2 (req)	10	70 °C	7 days
3 (req)	11	40 °C	9 days
4** (req)	11	70 °C	1 day

** For test four, it was requested that only one PNNL-polished and one collaborator-polished coupon each from **Glass "B" and Glass "D"** be included in the vessel. The remaining testing slots were filled with other materials provided by each collaborator to test. Alternatively, one or all of the remaining slots could remain empty, at the discretion of the collaborator. The test is designed to ensure consistent glass results even when other samples with other corrosion performance levels are tested in the same vessel.

2.4 ASTM Draft Method

The testing was done per the draft of the method description written for submission and balloting to ASTM International. The current version of this draft is given in Appendix C. Collaborator input has been incorporated into the draft test method based on their experiences, but the operational method items have not changed throughout the effort.

2.5 Additional Test Instructions

The experiments done by each collaborator followed the ASTM Draft Method (Appendix C) as well as the instructions in this section. Where the method was written to be generally applicable, these additional instructions were designed to make the performance of the tests as uniform as possible among collaborators. Data were recorded on experiment-specific data sheets covering each quality-affecting step of the work. Blank versions of these data sheets are provided in Appendix A.

These instructions detail the following general steps of a SRCA experiment:

- Prepare glass samples to be used in SRCA experiment
- Prepare the leachate solution
- Prepare clean vessel for testing
- Start SRCA experiment
- Monitor the SRCA experiment
- End SRCA alteration experiment and prepare coupons for analysis
- Perform post-alteration coupon analysis

i. Suggested verifications to be performed before conducting work

a) Balance calibration checks

It is suggested that performance checks of balances are performed each day they are used.

b) Pipette calibration check

It is suggested that pipettes used to volumetrically transfer chemicals in the preparation of buffer solutions be checked before use. If the mass is the controlling measurement being recorded (e.g., the liquid's mass is recorded even though the pipette may be used to transfer the solution), this check is not necessary.

c) pH meter calibration and calibration check

It is strongly recommended that pH meter calibrations and calibration checks be performed before each use.

d) Oven temperature check

It is suggested that calibrated thermocouples or thermometers be used to confirm the oven temperatures. The oven readout is not sufficient for this measurement. Placing the thermocouple or thermometer in a smaller vessel of water can produce a more accurate reading than those simply in the air space of the oven.

ii. Glass coupon preparation

a) Coupon polishing.

Samples should be cut to a dimension that can both be grasped by the sample holder clips, fit through the sample holes, and produce a long enough step length to accommodate several independent step height measurements.

Coupons are to be polished on at least one face. The recommended sequential finishes are 15 µm, 9 µm, and 3 µm using appropriate grinding media such as grinding paper, diamond metal grinding disks, or diamond suspension solutions on a polishing cloth. After polishing is complete, clean coupons to remove residual diamond suspensions and sample mounting adhesives. Use solvents that will not corrode the glass surface (e.g., acetone, ethanol, mineral spirits, etc.)

Coupons that have been previously subjected to SRCA testing may be repolished using the same procedure. In this case, it may be possible to use only the 3 µm polishing media.

b) Coupon masking

A portion of the polished surface of the coupon will be masked to protect an area of the surface from corrosion.

a. In order to avoid confusing the different glass coupons, place each coupon to be masked in a weigh boat (or similar suitable container) identified with the sample ID.
b. Apply silicone (using a toothpick or similar disposable applicator) to the polished side of the coupon. A line across the sample is common, but the mask should cover an area at minimum 2 mm × 2 mm on the glass surface.
c. Allow the silicone to cure before using the coupon in a SRCA glass corrosion test. Ideally, overnight curing at room temperature is the preferred method. However, drying in an oven can speed this process.

After curing of the silicone, coupons can be used for a SRCA glass corrosion test.

Figure 2-3. Examples of masked coupons before testing. The ruler scale is in centimeters.

iii. Solution preparation

Solutions at two different $pH_{(RT)}$ will be used for these experiments, each beginning with ASTM type I water (18MΩ+):

- Solutions at pH 10 will be buffered with 0.05 $mol \cdot L^{-1}$ TRIS adjusted to the desired pH with 15.8 $mol \cdot L^{-1}$ HNO_3 or 1 $mol \cdot L^{-1}$ LiOH.
- Solutions at pH 11 should be prepared to 0.019 $mol \cdot L^{-1}$ LiCl, and 0.001 $mol \cdot L^{-1}$ LiOH.

If solutions at other pH are to be used for follow-on testing, please identify the recipe clearly in a testing sheet.

All these solutions are made at room temperature. It will be assumed their density is 1 $kg \cdot L^{-1}$, thus for all solutions we assume $1\ L \approx 1\ kg$.

The volume of solution necessary for the SRCA vessels used for this round robin test is 8.8 L. Considering that there are three tests at pH 11, one can make a large batch to use for all three by simply multiplying the recipe below.

Although a lower volume could theoretically be used if the vessel had fewer than 8 samples, the mixing calculations were done for a full vessel and would be different for a different solution volume. Additionally, the solution is expected to be very dilute in either case, so the additional volume would not functionally change the experiment.

8.8 L of pH 10 solution:

- 8800.0 g **ASTM type 1 water**
- 53.309 g **TRIS**
- 440 µL **saturated HNO_3 (approx. 15.8 M)**

8.8 L of pH 11 solution:

- 8800.0 g **ASTM type 1 water**
- 7.0884 g **LiCl**
- 0.2108 g **LiOH**

The protocol to make solutions is as follows. A Solution Preparation Sheet is provided in Appendix A:

a. Label the container with the solution information
b. Add the components of the solution in the following order:
    i. First fraction of water (~1L)
    ii. All solids (MIX WELL)
    IMPORTANT: when adding solids, double check that the component added corresponds to the desired component and is not a hydrate of this component.
    iii. Remaining water
c. Stir the container regularly (shaking, using a stirring rod, using the test mixer, etc.) to ensure complete dissolution and mixing of the components.
d. Record all masses, volumes, and references for the components added as well as the measurement and testing equipment used on Solution Preparation Sheet
e. Take an aliquot and measure the $pH_{(RT)}$ of the solution
    i. Target a value between the target value and target + 0.3 (e.g., between pH 10 and 10.3).
    ii. If the pH **IS NOT** within this range, make the necessary adjustments (i.e., add **small amounts** of 15.8 $mol \cdot L^{-1}$ HNO_3 or 1 $mol \cdot L^{-1}$ LiOH solution), repeat the measurement until within range

iv. SRCA alteration test preparation

In order to initiate a SRCA alteration test, the following items must be gathered and prepared:

- SRCA vessel and accessories
- All the coupons of the glass(es) to be tested, previously masked at least 24 hours before the test.
- Sufficient solution at the target pH value for the test

a) Vessel cleaning

While the vessel requires a full cleaning the first time before use, as consecutive tests proceed, a limited cleaning of the vessel is sufficient. Per design, SRCA testing is conducted at very low S/V and will not cause extensive buildup of solution species, thus allowing a reduced cleanup of the alteration vessel.

1. Full cleaning of the alteration vessel.

Cleaning of the vessel and all solution-contacting parts should be recorded as “full cleaning” on the testing sheet.

a. These instructions are based on those in the PCT standard: Section 12 of ASTM C1285-21 (2021). The following changes have been made to make the procedure more feasible for such a large vessel:
    i. Vigorously wash the vessel using a detergent (e.g., dish soap, Micro-90, or the like) to degrease all machined parts.
    i. Ultrasonic cleaning is optional. Also, in order to minimize waste and hazards from solvents and acids, all cleaning with acetone, ethanol, and nitric acid will be performed at room temperature and in a fume hood, either by: (1) wiping surfaces with a towel soaked with the solvent; or, (2) by flowing a small amount of the solvent on the surface to clean.
    ii. Clean with either 99 % ethanol or absolute ethanol or another non-polar solvent like cyclohexane
    iii. Rinse with ASTM Type I water
    iv. Clean with 0.016 M HNO_3
    v. Rinse with ASTM Type I water
    vi. Fill with ASTM Type I water, with all baffles and sample rods in place, and hold in a 90+/- 10 C oven overnight.
    vii. Take an aliquot of the rinse solution and measure pH (pH strips acceptable). If the pH is not in the range 5.0 to 7.0, repeat steps v-vii. If still not within range, clean again from step i.
b. Rinse the reactor with several hundred mL of the solution at the same pH as the next experiment and discard.
c. Take care to ensure that the baffles, sample rods, and the mixing propeller/shaft are all cleaned thoroughly with the same procedure as the vessel.

2. Vessel rinse with ASTM Type 1 water (ASTM D1193-06(2018) 2018)

Cleaning of the vessel will be recorded as “rinse with DIW” on the Solution Preparation Sheet.

a. Rinse the reactor with several hundred mL to 1 L of ASTM Type 1 water.
b. Wipe the reactor with a disposable towel.
c. Repeat steps a and b.
d. Check the pH of the last rinse using pH strips or pH meter. If the pH is not in the range 5.0 to 7.0, repeat steps a-d. If still not within range, perform full clean.
e. Rinse the reactor with a several hundred mL of the solution at the same pH as the next experiment and discard.
f. Take care to ensure that the baffles, sample rods, and the mixing propeller/shaft are all cleaned thoroughly with the same procedure as the vessel.

b) Coupon preparation

Coupons should be polished and masked per instructions in Section ii. All the coupons must be placed on labeled sample rods to be inserted in the alteration vessels.

a. After curing, the mass of the coupon + silicone will be recorded on the Testing Sheet. Each coupon will be assigned a coupon ID in the following manner:

> **G-INST-POL-TD-#**
>
> where:
>
> - **G** is the glass designation: A, B, C, or D
> - **INST** is an identifier of the group doing the test (e.g., PNNL, CEA, UNT, etc.)
> - **POL** distinguishes samples polished at PNNL (pnl) and those polished by the collaborating group (col)
> - **TD** is the test designation based on Table 2-2
> - **#** is the position of the coupon in the vessel – determined by the number on the sample rod
>
> *Example: "C-WSU-pnl-3-5" would be a coupon of glass "C", polished by PNNL, in sample position 5 of Test 3 (40 °C and pH 11) performed by the group at Washington State University.*

b. Record the mass of the masked coupon on the Testing Sheet.
c. Record the brand and type of silicone masking material on the Notes area of the Testing Sheet.
d. Attach the coupon to the stainless steel alligator clip corresponding to the sample ID indicated on the Testing Sheet. As shown in Figure 2-4, the clip should not clamp the masked area and should be positioned as far as reasonably achievable from that masked area. The polished surface should be facing the impeller, i.e., oriented towards the center of the vessel, same as the flag.

Sample Rod Preparation

<table>
<tr><td>Clip coupons with the polished and masked face on the same side as the movable button of the clip.</td><td> </td></tr>
<tr><td colspan="2">Mark each sample rod with a small cross 1 cm from the end with the branch of the cross parallel to the length of the rod indicating the side on which the polished and masked face should be oriented towards. The branch of the cross perpendicular to the length of the rod is indicating the attachment location for the labeling clip so that samples are all inserted the same depth into the vessel.
</td></tr>
<tr><td colspan="2">Place a neoprene stopper on the sample holder rod and affix a label perpendicular to the cross marking. Make sure the polished and masked face is located on the flag's side of the sample rod.
 </td></tr>
</table>

Figure 2-4: Details for coupon placement attachment

c) Experiment initiation

Experiment initiation consists of three consecutive steps: solution addition in the vessel, temperature equilibration, coupon addition.

1. **Solution addition to the vessel**
   a. Target solution mass is 8800 grams. For each batch of solution used, record the mass of solution on the Testing Sheet:
   b. Measure pH of the solution.
      i. Take a 5 to 10 mL aliquot of the solution.
      ii. Measure room temperature pH of the solution. The $pH_{(RT)}$ must be within 0.15 pH units of the target value, if this is not the case, contact the cognizant scientist for mitigation.
      iii. Record the pH measurement, together with date and time on Testing Sheet
   c. Close the lid to the vessel with its corresponding lid with the impeller in place. Cover all coupon ports.
   d. Transfer the vessel to the oven.
   e. Mark the shaft such that the bottom of the impeller is ≈ 3 cm from the bottom of the vessel; mark at the top of the Teflon bushing. When attaching to the flexible coupler and the mixing head, take care that the propeller is at the proper height. To improve heat transfer in the oven, start the stirring motor at the speed on the Testing Sheet (60 rpm).
   f. If the test temperature is other than room temperature, wait at least 8 hours to allow the solution to reach the test temperature.

2. **Coupon insertion in the vessel.** For each added coupon:
   a. Record vessel temperature before opening the oven on the Testing Sheet.
   b. Insert each sample rod holding a coupon in the reaction vessel. Adjust as follows:
      i. The flag should point towards the center of the reactor.
      ii. The mark on the sample rod must be flush with the cap surface to ensure the samples are at the correct height.
      iii. Use tape or another stopper to close off any unused sample ports
   c. Record the Date and the Time that each coupon was put into the experiment vessel on the Testing Sheet. Time can be rounded to the nearest 5 minutes.

v. SRCA alteration test conduction

During the SRCA test, the following steps will be performed regularly:
- Oven temperature checks
- pH measurements of the solution in the alteration vessel
- Evaporation checks

a) Oven temperature monitoring

Check test temperature every working day and record on Testing Sheet. It is recommended to place a thermocouple in a small container of water near to the SRCA vessel so that short temperature excursions (due to, for example, brief door opening for pH sampling and test monitoring) do not impact the temperature monitoring. The oven display can be used as a less-accurate option if necessary.

b) pH monitoring

In addition to the measurement at the start and at the end of the experiment, the pH of the leachate will be measured twice a week for experiments lasting longer than one week. For tests of 1 week or less duration, it is only required that pH is measured at the start and end of the test. In all cases, more frequent testing will provide a more accurate representation of the evolution of solution pH contacting the glass samples.

All pH measurements will be recorded on the Testing Sheet. To measure pH:

a. Remove silicone cap over large sampling port
b. Sample ~5 mL of solution from the vessel with a transfer pipette into a scintillation vial.
c. Replace silicone cap
d. Allow the sample to equilibrate with room temperature.
e. Measure the pH of the solution with a calibrated pH meter.
f. Record pH value on Testing Sheet.
g. Dispose of the aliquot in the appropriate waste container.
h. It is not necessary to replace the volume lost in the test.

If, during testing, the pH has departed from the desired range, the solution can be adjusted as during the solution preparation step (i.e., add small amounts of 15.8 mol·L^{-1} HNO_3 or 1 mol·L^{-1} LiOH solution). The pH should be tested repeatedly after adjustment until a steady state value is maintained.

c) Evaporation check

Evaporation checks should be performed once a week for experiments lasting longer than a week, preferably at the same time a pH aliquot is withdrawn from the vessel. Using a probe stick, evaluate the level of solution relative to the start. If more than 10% of the solution has evaporated (~2 cm in these vessels), add more ASTM Type I water (ASTM D1193-06(2018) 2018) to refill to the original level.

vi. SRCA alteration test termination

Before opening the oven to terminate the test, record the oven temperature on the Testing Sheet.

a) Altered coupon retrieval

Before retrieving coupons, array some sample containers labeled with the coupon IDs.

Remove each of the coupons remaining in the vessel one-by-one as follows:

a. Remove a sample rod
b. Record the date and time the coupon was removed on the corresponding line of the Testing Sheet. Time rounded to the nearest 5 minutes is sufficient.
c. Rinse the coupon three times with ASTM Type 1 water (from a squirt bottle).
d. Rinse the coupon three times with ethanol (from a squirt bottle).
e. Place the rinsed coupon in the labelled container.
f. Check the "rinsed" checkbox on the corresponding line of the Testing Sheet.
g. Allow the coupons to dry by evaporating residual ethanol from the coupon surface: either at room temperature in a fume hood for at least 1 hour, or in a specialized ethanol evaporation oven at a maximum of 40 °C for 30 minutes or more.
h. Check the "dried" checkbox on the corresponding line of the Testing Sheet.
i. Take the mass of the altered coupon using a 0.0001 g precision laboratory balance **with the silicone mask still in place** and record the mass on the corresponding line of the Testing Sheet.
j. Place coupon back in its labeled container until analysis.

b) Experiment end (following coupon removal)

a. Turn off the mixer motor and oven.
b. Record the pH of the leachate at the end of the experiment.
c. Once the vessel has cooled to room temperature, remove the experiment vessel and record the final weight of solution remaining in the vessel. It may be necessary to subtract the tare of the vessel and/or the tare of its lid. Record the mass on the corresponding field on the Testing Sheet.
d. Dispose of solution in accordance with your laboratory procedures.

vii. Post-alteration coupon characterization and analysis

Techniques used to quantify coupon alteration after SRCA testing include, but are not limited to, optical profilometry, stylus profilometry, scanning electron microscopy, optical ellipsometry, and atomic force microscopy. Include details on the technique used. If there is a file generated by the technique, include it with your data package noting the relevant file numbers.

- Calibration of the technique is recommended
- Analyze the step height at several spots for each analyzed sample if possible

At a minimum, include the following information in the datasheets:

- Analysis technique name
- Instrument name and model
- Sample IDs for the analyzed sample
- Dates for measurements
- Files generated during the analysis (if any)
- Relevant notes

When all testing is done, please put the full dataset into a spreadsheet and perform the calculations necessary to obtain the dissolution rate for each sample. The calculation is simple:

$$\text{rate} = \frac{\Delta\ \text{height} \times \text{density}}{\Delta\ \text{time}}$$

You will notice that the density of the glass is a necessary parameter. Please use an established method for density determination at your laboratory. Buoyancy (ASTM C693-93(2019) 2019) or He pycnometry are both good options. If this is a hardship, the densities for the four glasses will be provided as determined at PNNL.

To complete the round robin, please do the following:

- Electronically forward copies of all data sheets
- Send a copy of the excel spreadsheet used to calculate the dissolution rates
- Send the four samples of each glass composition that were polished by PNNL back in the mail. We will analyze them using our optical profilometry system to standardize all results.
- Regarding “Test 4”, if you wish you do not need to identify the other samples chosen or send these samples to PNNL, but you will be asked to supply the observed corrosion rates so the approximate amount of ions released to solution is known. On the other hand, if you would like to compare step height measurement techniques, we would be glad to analyze them.
- The remaining glasses from the test are yours to keep.

viii. pH Definition for Test Solutions

All experimental pH values were recorded at room temperature ($pH_{(RT)}$), but pH at test temperatures ($pH_{Test\ T°C}$) were used for modeling. To calculate the pH over a range of temperatures, The Geochemist's Workbench® (GWB) software was used (Aqueous Solutions LLC, Champaign, IL, USA) with input data for the dissociation constant of TRIS from Bates and Hetzer (1961). The solution composition was input into the GWB software, and a pH was calculated at 25 °C. The modeled solution pH was adjusted to a target value with strong acid or base to within ± 0.05 pH units. Then, the temperature of the modeled system was varied, and the pH value at the target temperatures were noted. The GWB data were then imported into OriginPro software. For each $pH_{Test\ T°C} = f_{(T\ °C)}$, a third order polynomial fit was applied to the curve, and coefficients and fit parameters were obtained, as reported in Table 2-3**Error! Reference source not found.**.

Table 2-3 - $pH_{RT°C}$ to $pH_{Test\ T°C}$ recalculation parameters

Solution type	Intercept	B1	B2	B3
10-TRIS	10.46957	-0.02000	-1.03E-04	9.74E-07
11-LiOH	11.90679	-0.04119	1.78E-04	-3.45E-07

3.0 Experimental Results

Due to the design of the test, the round robin effectively produced twelve largely independent datasets representing the union of the four glass compositions and the three conditions. The summary data for each independent test are presented in this section while the overall summary is visually shown in Figure 3-1. It is important to understand that these are raw compilations of the data and do not yet consider competing variables, most notably pH. The pH effect is discussed in more detail in Section 0.

In general, the conditions ranked as expected from least to most aggressive: 40 °C/pH 11 < 70 °C/pH 10 < 70 °C/pH 11. This pattern was the same for all glasses in the study. Similarly, the glass compositions showed a consistent pattern from lowest to highest observed dissolution rates regardless of condition: LRM < ISG-2 < LAWA44 < LGS19-03

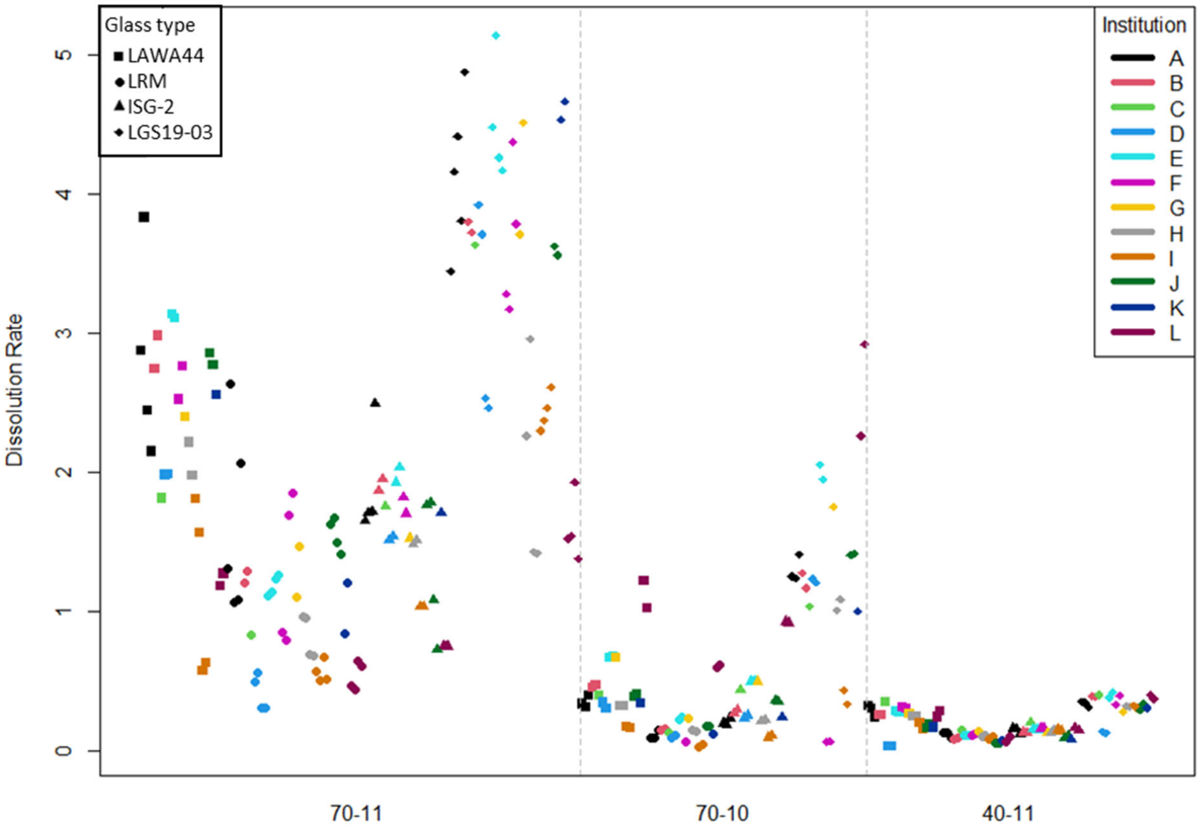


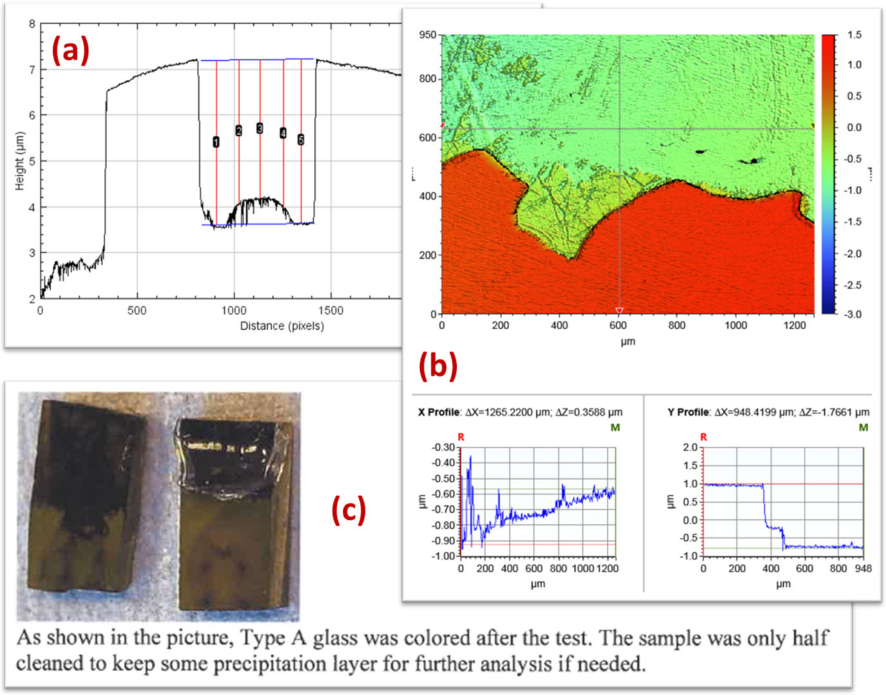
Figure 3-1 - Dilute dissolution rates ($g \cdot m^{-2} \cdot d^{-1}$) for all tests completed as part of the round robin test matrix. Nominal conditions are called out in the X-axis.

3.1 Experimental Observations

The collaborators completed the tests and reported general ease of the use for the method. The instructions were simple to understand and the process of masking was straightforward. There were two areas for attention that were commonly noted: pH stability and alteration layer formation.

The pH was reported as difficult to maintain by nearly every collaborator, particularly for the tests at an expected $pH_{(RT)}$ value of 11. In these experiments a persistent downward drift was observed for most studies. For some, this was corrected in a straightforward manner by the addition of LiOH solution to raise the pH. With careful monitoring, this would raise the pH back to the test starting point. Some collaborators noted that by taking some time to monitor and stabilize the solution before the test (1-3 days) that the drift rate was significantly reduced during testing. Although both approaches were used to successfully produce data for the round robin, all collaborators agreed that careful monitoring is required to understand the pH values being tested.

The second notable item was the formation of alteration layers on the surfaces of some glass samples. Particularly when tested in solutions with an expected $pH_{(RT)}$ value of 11, samples of LAWA44 (Glass A) and LGS19-03 (Glass D) exhibited iridescence after being removed from the solution. This was an obvious sign of an alteration layer with a different effective refractive index from the base glass. This was confirmed in the step height measurements where an intermediate step height was occasionally observed. The layers for both glasses were relatively fragile and were mostly removed in the process of cleaning off the mask material. Anecdotal evidence suggests that these layers are enriched in transition metals from these two compositions which are relatively insoluble in the testing conditions. Where measurable, the layers appeared to be about 10-25% the total thickness from the unaltered to most deeply altered area. The total thickness measurement was used for the analysis throughout. Care should be taken to remove the layers where possible before measurement and to measure the highest available step.



As shown in the picture, Type A glass was colored after the test. The sample was only half cleaned to keep some precipitation layer for further analysis if needed.

Figure 3-2 – Evidence of alteration layers from three collaborators following tests at $pH_{(RT)}=11$ and 70°C on (a) LGS19-03 glass (stylus profilometry), (b) LGS19-03 glass (optical profilometry), and (c) LAWA44 glass (optical picture and notes)

3.2 LAWA44 Glass (Glass A), $pH_{(RT)}$ 11, 70 °C

There were 23 reported tests (Table 3-1) of LAWA44 at 70 °C and a nominal $pH_{(RT)}$ value of 11, thanks in part to the composition being included as part of Test #4 by lab ”I” without knowing it was also “Glass A” of the round robin study. In this case, the glass did not have the same provenance as the rest of the study but is included in the statistical evaluations. Overall, the testing produced an average dissolution rate of 2.19 $g \cdot m^{-2} \cdot d^{-1}$with a standard deviation of 0.80 $g \cdot m^{-2} \cdot d^{-1}$ (36% of the average value). As with the other tests, much of this difference can be ascribed to the variations in pH between the tests.

Table 3-1 - A summary of data for tests nominally conducted on LAWA44 glass at 70 °C and a $pH_{(RT)}$ value of 11

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	9.64	70.81	2.88	2.873	8.16E-02
A	9.92	70.27	2.05	3.833	1.05E-01
A	9.57	70.34	2.86	2.443	4.16E-01
A	9.57	70.34	2.86	2.151	4.12E-01
B	9.64	68.95	1.00	2.741	5.06E-02
B	9.64	68.95	1.00	2.981	1.17E-01
C	9.54	70.00	1.00	1.815	N/A
D	9.05	73.85	1.06	1.982	1.45E-01
D	9.05	73.85	1.06	1.990	1.93E-01
E	9.72	69.95	1.00	3.135	7.60E-02
E	9.72	69.95	1.00	3.109	1.03E-01
F	9.54	70.65	1.00	2.524	9.22E-02
F	9.54	70.65	1.00	2.763	1.40E-01
G	9.67	70.53	1.01	2.395	6.45E-02
H	9.82	69.13	1.15	2.215	2.33E-02
H	9.82	69.13	1.15	1.978	1.89E-01
I	9.67	70.00	2.00	1.809	7.11E-02
I	9.67	70.00	2.00	1.565	5.39E-02
I	9.54	70.00	2.00	0.577	1.52E-01
I	9.54	70.00	2.00	0.631	1.73E-01
J	9.64	70.15	2.00	2.860	1.25E-01
J	9.64	70.15	2.00	2.774	1.10E-01
K	9.82	68.50	1.00	2.559	2.69E-02
L	9.37	70.00	1.00	1.182	5.32E-02
L	9.37	70.00	1.00	1.272	4.84E-02

3.3 LAWA44 Glass (Glass A), $pH_{(RT)}$ 11, 40 °C

There were 20 reported tests of LAWA44 at 40 °C and a nominal $pH_{(RT)}$ value of 11, as shown in Table 3-2. Overall, the testing produced an average dissolution rate of 0.233 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.087 $g \cdot m^{-2} \cdot d^{-1}$ (35% of the average value). As with the other tests, much of this difference can be ascribed to the variations in pH between the tests. In particular, the test by Lab "D" drifted from the target pH and produced a significantly lower dissolution rate.

Table 3-2 - A summary of data for tests nominally conducted on LAWA44 glass at 40 °C and a $pH_{(RT)}$ value of 11

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	10.30	40.65	11.78	0.325	1.32E-03
A	10.30	40.65	11.78	0.303	1.52E-02
A	9.99	40.60	11.78	0.243	5.28E-03
B	10.21	41.29	9.00	0.259	2.11E-03
B	10.21	41.29	9.00	0.256	2.99E-03
C	10.42	40.00	9.16	0.351	N/A
D	8.67	41.93	12.00	0.035	2.59E-03
D	8.67	41.93	12.01	0.036	N/A
E	10.55	39.07	9.02	0.283	5.04E-03
E	10.55	39.07	9.02	0.280	6.44E-03
F	10.21	41.77	9.00	0.315	8.28E-03
F	10.21	41.77	9.00	0.307	2.38E-02
G	10.56	39.95	9.00	0.266	3.81E-03
H	10.25	39.75	10.02	0.251	5.44E-03
H	10.25	39.75	10.02	0.251	2.21E-03
I	10.54	40.00	9.00	0.202	3.01E-03
I	10.54	40.00	9.00	0.159	1.05E-02
J	9.60	39.94	9.93	0.169	2.65E-03
J	9.60	39.94	9.93	0.189	9.78E-03
K	9.88	40.04	11.94	0.169	8.14E-03
L	9.70	40.00	9.00	0.244	1.05E-02
L	9.70	40.00	9.00	0.285	5.90E-03

3.4 LAWA44 Glass (Glass A), $pH_{(RT)}$ 10, 70 °C

There were 21 reported tests of LAWA44 at 70 °C and a nominal $pH_{(RT)}$ value of 10, as shown in Table 3-3. Overall, the testing produced an average dissolution rate of 0.471 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.265 $g \cdot m^{-2} \cdot d^{-1}$ (56% of the average value). While some of this difference can be ascribed to the variations in pH between the tests, outlier results impacted the overall statistics. All glasses tested by Lab "L" in these conditions exhibited rates several times higher than the other results. These data were so anomalous, in fact, that they had an outsized impact on both the best linear fit to pH and the overall precision statement for the condition. There were also some questions on the dataset, with two values that differed by a factor of 10 initially reported on different sheets. Due to these questions and the fact that the values were more than 300% the expected value for the condition, these data and the other values from Lab L taken at $pH_{(RT)} = 10$ and 70 °C were excluded from analysis. Additionally, the test done at Lab "F" in this condition produced low rates (for all glasses), to the point where the step was not measurable for the coupons of this glass.

Table 3-3 - A summary of data for tests nominally conducted on LAWA44 glass at 70°C and a $pH_{(RT)}$ value of 10

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	8.60	70.66	8.64	0.339	3.60E-03
A	8.60	70.66	8.63	0.316	4.77E-03
A	8.67	70.87	8.94	0.396	9.69E-03
B	8.84	68.80	7.00	0.456	7.31E-03
B	8.84	68.80	7.00	0.471	6.99E-03
C	8.84	70.00	6.99	0.398	N/A
D	8.64	70.80	7.22	0.348	9.14E-03
D	8.64	70.80	7.22	0.308	1.52E-02
E	8.92	69.78	7.00	0.668	1.46E-02
E	8.92	69.78	7.00	0.675	9.37E-03
G	8.89	70.45	7.00	0.669	4.59E-02
H	8.85	69.35	7.83	0.321	5.84E-03
H	8.85	69.35	7.83	0.322	8.18E-03
I	8.82	70.00	8.00	0.178	4.91E-03
I	8.82	70.00	8.00	0.163	6.75E-03
J	8.78	70.09	6.80	0.392	1.05E-02
J	8.78	70.09	6.80	0.411	8.24E-03
K	8.75	69.94	7.01	0.345	2.18E-02
L	8.71	70.00	7.00	1.220	5.37E-02
L	8.71	70.00	7.00	1.023	3.69E-02

3.5 LRM Glass (Glass B), $pH_{(RT)}$ 11, 70 °C

There were 34 reported tests of LRM at 70 °C and a nominal $pH_{(RT)}$ value of 11, as shown in Table 3-4. Due to the inclusion of the glass in Test #4, there are significantly more tests for this glass in this condition (38) than all other except for LGS19-03 in the same conditions. Overall, the testing produced an average dissolution rate of 1.03 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.52 $g \cdot m^{-2} \cdot d^{-1}$ (51% of the average value). The pH dependence was stronger with this glass/condition combination than any other, accounting for much of this difference between test values.

Table 3-4 - A summary of data for tests nominally conducted on LRM glass at 70 °C and a $pH_{(RT)}$ value of 11 (continued next page)

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	9.64	70.81	2.88	1.310	3.58E-02
A	9.92	70.27	2.04	2.640	1.52E-01
A	9.57	70.34	2.86	1.063	1.48E-01
A	9.57	70.34	2.86	1.087	3.61E-02
A	9.95	70.21	2.04	2.063	7.14E-02
B	9.64	68.95	1.00	1.21E+00	1.08E-02
B	9.64	68.95	1.00	1.29E+00	5.29E-02
C	9.54	70.00	1.00	0.836	N/A
D	9.05	73.85	1.06	0.501	2.80E-02
D	9.05	73.85	1.06	0.565	1.40E-02
D	9.11	70.80	1.84	0.310	1.48E-02
D	9.11	70.80	1.85	0.309	6.93E-02
E	9.72	69.95	1.00	1.116	4.39E-02
E	9.72	69.95	1.00	1.138	4.76E-02
E	9.62	69.90	1.00	1.238	5.87E-02
E	9.62	69.90	1.00	1.267	3.69E-02
F	9.54	70.65	1.00	0.856	3.35E-02
F	9.54	70.65	1.00	0.792	1.49E-01
F	9.89	69.45	1.00	1.697	1.28E-01
F	9.89	69.45	1.00	1.852	1.91E-01
G	9.67	70.53	1.01	1.109	4.50E-02
G	9.85	70.28	1.00	1.468	1.63E-02
H	9.82	69.13	1.15	0.965	4.11E-02
H	9.82	69.13	1.15	0.953	2.26E-02
H	9.74	67.80	1.71	0.696	9.54E-03
H	9.74	67.80	1.71	0.681	2.08E-02

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
I	9.67	70.00	2.00	0.571	1.27E-01
I	9.67	70.00	2.00	0.505	1.49E-02
I	9.54	70.00	2.00	0.676	2.94E-02
I	9.54	70.00	2.00	0.520	9.23E-02
J	9.64	70.15	2.00	1.628	1.44E-01
J	9.64	70.15	2.00	1.671	9.93E-02
J	9.56	70.34	1.03	1.49E+00	1.14E-01
J	9.56	70.34	1.03	1.41E+00	6.85E-02
K	9.82	68.50	1.00	0.844	2.56E-02
K	9.67	69.85	1.00	1.210	1.21E-01
L	9.37	70.00	1.00	0.468	3.90E-02
L	9.37	70.00	1.00	0.438	3.71E-02
L	9.09	70.00	1.00	0.642	2.49E-02
L	9.09	70.00	1.00	0.605	5.59E-02

3.6 LRM Glass (Glass B), $pH_{(RT)}$ 11, 40 °C

There were 18 reported tests of LRM at 40 °C and a nominal $pH_{(RT)}$ value of 11, as shown in Table 3-5. This combination produced the lowest observed average dissolution rate of all the test combinations: 0.105 $g{\cdot}m^{-2}{\cdot}d^{-1}$with a standard deviation of 0.027 $g{\cdot}m^{-2}{\cdot}d^{-1}$ (26% of the average value). This particular combination was one of the most consistent of all the test combinations, although the pH effect on rate was still evident. In particular, the test by Lab "D" drifted far from the target and produced a significantly lower dissolution rate that was measurable but was excluded for being below the instrument limit.

Table 3-5 - A summary of data for tests nominally conducted on LRM glass at 40 °C and a $pH_{(RT)}$ value of 11

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g{\cdot}m^{-2}{\cdot}d^{-1}$)	Coupon rate standard deviation
A	10.30	40.65	11.78	0.129	4.52E-03
A	10.30	40.65	11.78	0.132	7.83E-03
A	9.99	40.60	11.78	0.098	2.17E-03
B	10.21	41.29	9.00	0.090	3.89E-03
B	10.21	41.29	9.00	0.100	4.29E-03
C	10.42	40.00	9.16	0.152	N/A
E	10.55	39.07	9.02	0.113	4.29E-03
E	10.55	39.07	9.02	0.118	8.08E-03
F	10.21	41.77	9.00	0.112	1.15E-02
F	10.21	41.77	9.00	0.126	2.54E-02
G	10.56	39.95	9.00	0.138	9.34E-04
H	10.25	39.75	10.02	0.106	3.91E-03
H	10.25	39.75	10.02	0.115	1.90E-03
I	10.54	40.00	9.00	0.088	5.91E-03
I	10.54	40.00	9.00	0.103	8.19E-03
J	9.60	39.94	9.93	0.057	7.16E-03
J	9.60	39.94	9.93	0.059	4.56E-03
K	9.88	40.04	11.94	0.073	2.14E-03
L	9.70	40.00	9.00	0.068	4.19E-03
L	9.70	40.00	9.00	0.103	3.71E-03

3.7 LRM Glass (Glass B), pH$_{(RT)}$ 10, 70 °C

There were 21 reported tests (Table 3-6) of LRM at 70 °C and a nominal pH$_{(RT)}$ value of 10. Overall, the testing produced an average dissolution rate of 0.183 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.153 $g \cdot m^{-2} \cdot d^{-1}$ (84% of the average value). While some of this difference can be ascribed to the variations in pH between the tests, outlier results impacted the overall statistics. All glasses tested by Lab “L” in these conditions exhibited rates several times higher than the other results. These data were so anomalous, in fact, that they had an outsized impact on both the best linear fit to pH and the overall precision statement for the condition. There were also some questions on the dataset, with two values that differed by a factor of 10 initially reported on different sheets. Due to these questions and the fact that the values were more than 400% the expected value for the condition, these data and the other values from Lab L taken at pH$_{(RT)}$ = 10 and 70 °C were excluded from analysis. Conversely, the test done at Lab “F” in this condition produced anomalously low rates (for all glasses), to the point where the step was not measurable for one of the coupons of this glass. Similarly low rates were observed by lab “I”, although both coupons were measurable in this case.

Table 3-6 - A summary of data for tests nominally conducted on LRM glass at 70 °C and a pH$_{(RT)}$ value of 10

Institution short name	Average pH$_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	8.60	70.66	8.64	0.100	2.14E-02
A	8.60	70.66	8.63	0.098	1.07E-02
A	8.67	70.87	8.94	0.150	1.65E-03
B	8.84	68.80	7.00	0.150	6.18E-03
B	8.84	68.80	7.00	0.158	2.77E-03
C	8.84	70.00	6.99	0.130	N/A
D	8.64	70.80	7.22	0.092	6.04E-03
D	8.64	70.80	7.23	0.114	1.22E-02
E	8.92	69.78	7.00	0.227	4.14E-03
E	8.92	69.78	7.00	0.240	7.56E-03
F	8.74	70.68	7.00	0.068	3.51E-03
G	8.89	70.45	7.00	0.231	1.41E-02
H	8.85	69.35	7.83	0.151	4.24E-03
H	8.85	69.35	7.83	0.146	9.74E-03
I	8.82	70.00	8.00	0.033	4.84E-03
I	8.82	70.00	8.00	0.044	6.94E-03
J	8.78	70.09	6.80	0.183	5.74E-03
J	8.78	70.09	6.80	0.180	6.51E-03
K	8.75	69.94	7.00	0.128	6.33E-03
L	8.71	70.00	7.00	0.604	2.45E-02
L	8.71	70.00	7.00	0.621	4.84E-03

3.8 ISG-2 Glass (Glass C), $pH_{(RT)}$ 11, 70 °C

There were 23 reported tests of ISG-2 at 70 °C and a nominal $pH_{(RT)}$ value of 11, as shown in Table 3-7. Overall, the testing produced an average dissolution rate of 1.52 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.41 $g \cdot m^{-2} \cdot d^{-1}$ (29% of the average value). This particular combination was one of the most consistent of all the test combinations. Predictably, even the small differences between results showed a statistically significant pH dependence.

Table 3-7 - A summary of data for tests nominally conducted on ISG-2 glass at 70 °C and a $pH_{(RT)}$ value of 11

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	9.64	70.81	2.88	1.653	2.76E-02
A	9.57	70.34	2.86	1.706	4.76E-02
A	9.57	70.34	2.86	1.716	2.78E-02
A	9.95	70.21	2.04	2.492	8.77E-02
B	9.64	68.95	1.00	1.868	9.30E-02
B	9.64	68.95	1.00	1.952	3.67E-02
C	9.54	70.00	1.00	1.754	N/A
D	9.05	73.85	1.06	1.511	7.51E-02
D	9.05	73.85	1.06	1.542	2.34E-02
E	9.72	69.95	1.00	1.926	4.26E-02
E	9.72	69.95	1.00	2.035	5.32E-02
F	9.54	70.65	1.00	1.820	7.02E-02
F	9.54	70.65	1.00	1.702	2.26E-02
G	9.67	70.53	1.01	1.527	1.23E-01
H	9.82	69.13	1.15	1.483	2.81E-02
H	9.82	69.13	1.15	1.514	2.55E-02
I	9.67	70.00	2.00	1.038	3.04E-02
I	9.67	70.00	2.00	1.035	1.36E-01
J	9.64	70.15	2.00	1.762	2.57E-02
J	9.64	70.15	2.00	1.783	6.80E-02
J	9.56	70.34	1.03	1.080	1.39E-01
J	9.56	70.34	1.03	0.726	3.29E-02
K	9.82	68.50	1.00	1.708	2.47E-02
L	9.37	70.00	1.00	0.756	2.74E-02
L	9.37	70.00	1.00	0.749	4.23E-02

3.9 ISG-2 Glass (Glass C), $pH_{(RT)}$ 11, 40 °C

There were 18 reported tests of ISG-2 at 40 °C and a nominal $pH_{(RT)}$ value of 11, as shown in Table 3-8. Overall, the testing produced an average dissolution rate of 0.142 $g \cdot m^{-2} \cdot d^{-1}$ with very little differences between results and a standard deviation of 0.029 $g \cdot m^{-2} \cdot d^{-1}$ (21% of the average value). Even with such small differences, the variations in pH between tests resulted in measurable differences in rate. The pH drift in the test by lab "D" produced such small steps that, while measurable, they were excluded for being below the instrument limit.

Table 3-8 - A summary of data for tests nominally conducted on ISG-2 glass at 40 °C and a $pH_{(RT)}$ value of 11

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	10.30	40.65	11.78	0.163	1.21E-02
A	10.30	40.65	11.78	0.157	6.75E-03
A	9.99	40.60	11.78	0.122	7.58E-03
B	10.21	41.29	9.00	0.133	1.48E-02
B	10.21	41.29	9.00	0.127	1.73E-03
C	10.42	40.00	9.16	0.202	N/A
E	10.55	39.07	9.02	0.154	4.49E-03
E	10.55	39.07	9.02	0.151	4.61E-03
F	10.21	41.77	9.00	0.162	1.11E-02
F	10.21	41.77	9.00	0.164	1.47E-02
G	10.56	39.95	9.00	0.132	2.08E-03
H	10.25	39.75	10.02	0.127	1.11E-02
H	10.25	39.75	10.02	0.143	1.80E-03
I	10.54	40.00	9.00	0.153	4.16E-03
I	10.54	40.00	9.00	0.141	1.56E-03
J	9.60	39.94	9.93	0.093	2.89E-03
J	9.60	39.94	9.93	0.104	3.24E-03
K	9.88	40.04	11.94	0.082	5.21E-03
L	9.70	40.00	9.00	0.169	6.04E-03
L	9.70	40.00	9.00	0.145	5.93E-03

3.10 ISG-2 Glass (Glass C), $pH_{(RT)}$ 10, 70 °C

There were 20 reported tests (Table 3-9) of LRM at 70 °C and a nominal $pH_{(RT)}$ value of 10. Overall, the testing produced an average dissolution rate of 0.354 $g \cdot m^{-2} \cdot d^{-1}$ with a standard deviation of 0.229 $g \cdot m^{-2} \cdot d^{-1}$ (65% of the average value). As with the other $pH_{(RT)}$ 10, 70 °C tests, much of this difference can be ascribed outlier tests. As with the other coupons in this condition, the test done at Lab "F" produced such low rates that the steps could not be used for analysis and the tests from Lab "I" also showed significantly lower rates at the pH reported relative to the other test data. The significantly higher test results in this condition from Lab "L" again would have had by far the largest impact on the test statistics. These data were so anomalous, in fact, that they had an outsized impact on both the best linear fit to pH and the overall precision statement for the condition. There were also some questions on the dataset, with two values that differed by a factor of 10 initially reported on different sheets. Due to these questions and the fact that the values were more than 300% the expected value for the condition, these data and the other values from Lab L taken at $pH_{(RT)}$ = 10 and 70 °C were excluded from analysis.

Table 3-9 - A summary of data for tests nominally conducted on ISG-2 glass at 70 °C and a $pH_{(RT)}$ value of 10

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	8.60	70.66	8.63	0.198	5.73E-03
A	8.60	70.66	8.63	0.186	9.22E-03
A	8.67	70.87	8.93	0.237	1.12E-02
B	8.84	68.80	7.00	0.268	6.63E-03
B	8.84	68.80	7.00	0.298	8.16E-03
C	8.84	70.00	6.99	0.439	N/A
D	8.64	70.80	7.23	0.237	3.31E-02
D	8.64	70.80	7.23	0.256	1.35E-02
E	8.92	69.78	7.00	0.497	1.22E-02
E	8.92	69.78	7.00	0.505	8.59E-03
G	8.89	70.45	7.00	0.499	3.25E-02
H	8.85	69.35	7.83	0.215	3.38E-03
H	8.85	69.35	7.83	0.221	3.23E-03
I	8.82	70.00	8.00	0.097	1.05E-02
I	8.82	70.00	8.00	0.109	6.18E-03
J	8.78	70.09	6.81	0.365	1.64E-02
J	8.78	70.09	6.81	0.355	7.57E-03
K	8.75	69.94	7.00	0.243	8.90E-03
L	8.71	70.00	7.00	0.928	1.41E-02
L	8.71	70.00	7.00	0.918	7.36E-02

3.11 LGS19-03 Glass (Glass D), $pH_{(RT)}$ 11, 70 °C

There were 36 reported tests of LGS19-03 at 70 °C and a nominal $pH_{(RT)}$ value of 11, with the data shown in Table 3-10. Due to the inclusion of the glass in Test #4, there are significantly more tests for this glass in this condition than all other test combinations except for LRM in the same conditions. Overall, the testing produced the highest observed dissolution rate with an average of 3.29 $g \cdot m^{-2} \cdot d^{-1}$ and a standard deviation of 1.11 $g \cdot m^{-2} \cdot d^{-1}$ (34% of the average value). The pH dependence likely is responsible for much of this difference between test values.

Table 3-10 - A summary of data for tests nominally conducted on LGS19-03 glass at 70 °C and a $pH_{(RT)}$ value of 11 (continued next page)

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
A	9.64	70.81	2.88	3.446	4.68E-01
A	9.92	70.27	2.04	4.163	1.11E-01
A	9.57	70.34	2.86	4.414	2.00E-01
A	9.57	70.34	2.87	3.808	2.09E-01
A	9.95	70.21	2.04	4.877	5.42E-01
B	9.64	68.95	1.00	3.80E+00	2.08E-01
B	9.64	68.95	1.00	3.72E+00	2.17E-01
C	9.54	70.00	1.00	3.632	N/A
D	9.05	73.85	1.06	3.924	1.46E-01
D	9.05	73.85	1.06	3.710	2.05E-01
D	9.11	70.80	1.85	2.534	5.78E-02
D	9.11	70.80	1.85	2.461	1.64E-01
E	9.72	69.95	1.00	4.478	5.57E-01
E	9.72	69.95	1.00	5.139	6.46E-02
E	9.62	69.90	1.00	4.262	7.68E-01
E	9.62	69.90	1.00	4.171	5.72E-01
F	9.54	70.65	1.00	3.283	2.19E-01
F	9.54	70.65	1.00	3.171	1.33E-01
F	9.89	69.45	1.00	4.374	2.98E-01
F	9.89	69.45	1.00	3.786	3.97E-01
G	9.67	70.53	1.01	3.710	5.42E-02
G	9.85	70.28	1.00	4.513	4.97E-02
H	9.82	69.13	1.15	2.262	5.85E-01
H	9.82	69.13	1.15	2.960	3.67E-01
H	9.74	67.80	1.71	1.429	4.12E-02
H	9.74	67.80	1.71	1.420	1.78E-02
I	9.67	70.00	2.00	2.300	1.22E-01

Institution short name	Average $pH_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation
I	9.67	70.00	2.00	2.372	2.29E-01
I	9.54	70.00	2.00	2.460	1.92E-02
I	9.54	70.00	2.00	2.611	1.14E-01
J	9.64	70.15	2.00	3.625	3.58E-02
J	9.64	70.15	2.00	3.562	7.45E-02
K	9.82	68.50	1.00	4.535	7.00E-01
K	9.67	69.85	1.01	4.665	1.62E-01
L	9.37	70.00	1.00	1.525	4.95E-02
L	9.37	70.00	1.00	1.546	5.24E-02
L	9.09	70.00	1.00	1.928	6.86E-02
L	9.09	70.00	1.00	1.381	4.06E-02

3.12 LGS19-03 Glass (Glass D), pH$_{(RT)}$ 11, 40 °C

There were 20 reported tests (see Table 3-11) of LGS19-03 at 40 °C and a nominal pH$_{(RT)}$ value of 11. Overall, the testing produced an average dissolution rate of 0.326 g·m^{-2}·d^{-1} with a standard deviation of 0.077 g·m^{-2}·d^{-1} (23% of the average value). As with the other tests, much of this difference can be ascribed to the variations in pH between the tests. In particular, the test by Lab "D" drifted far from the target pH value and produced a significantly lower dissolution rate.

Table 3-11 - A summary of data for tests nominally conducted on LGS19-03 glass at 40 °C and a pH$_{(RT)}$ value of 11

Institution short name	Average pH$_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation
A	10.30	40.65	11.78	0.354	2.04E-02
A	10.30	40.65	11.78	0.348	3.34E-02
A	9.99	40.60	11.78	0.318	4.57E-02
B	10.21	41.29	9.00	0.394	4.13E-02
B	10.21	41.29	9.00	0.393	2.70E-02
C	10.42	40.00	9.16	0.404	N/A
D	8.67	41.93	12.00	0.139	1.16E-02
D	8.67	41.93	12.00	0.130	9.12E-03
E	10.55	39.07	9.02	0.384	5.55E-02
E	10.55	39.07	9.02	0.425	1.01E-02
F	10.21	41.77	9.00	0.335	2.43E-02
F	10.21	41.77	9.00	0.398	2.27E-02
G	10.56	39.95	9.00	0.282	2.99E-03
H	10.25	39.75	10.02	0.325	1.34E-02
H	10.25	39.75	10.02	0.319	1.50E-02
I	10.54	40.00	9.00	0.326	2.33E-02
I	10.54	40.00	9.00	0.310	2.97E-02
J	9.60	39.94	9.93	0.294	1.04E-02
J	9.60	39.94	9.93	0.338	6.08E-03
K	9.88	40.04	11.94	0.311	4.32E-02
L	9.70	40.00	9.00	0.407	1.11E-02
L	9.70	40.00	9.00	0.374	5.28E-02

3.13 LGS19-03 Glass (Glass D), pH$_{(RT)}$ 10, 70 °C

There were 22 reported tests of LGS19-03 at 70 °C and a nominal pH$_{(RT)}$ value of 10, as shown in Table 3-12. Overall, the testing produced an average dissolution rate of 1.26 g·m^{-2}·d^{-1-1} with a standard deviation of 0.68 g·m^{-2}·d^{-1} (54% of the average value). As with the rest of the glasses in the same conditions, the data was heavily impacted with outlier results. The tests done at Labs “F” and ”I” again produced low rates relative to those observed at other labs, although the relatively high rate of the LGS19-03 glass allowed all measurements to be within detectability limits. Conversely, the results from Lab “L” were again substantially higher than those from any of the other labs. While the data for glass D from this test condition were closer to the expected values than the other glasses tested in the same vessel, they were still 200-300% the expected value for the condition. There were also some questions on the dataset, with two values that differed by a factor of 10 initially reported on different sheets. For consistency, these data were excluded from analysis along with the other values from Lab L taken at pH$_{(RT)}$ = 10 and 70 °C.

Table 3-12 - A summary of data for tests nominally conducted on LGS19-03 glass- at 70 °C and a pH$_{(RT)}$ value of 10

Institution short name	Average pH$_{T°C}$	Average T °C or target value	Duration (d)	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation
A	8.60	70.66	8.63	1.255	9.59E-03
A	8.60	70.66	8.63	1.242	4.80E-03
A	8.67	70.87	8.93	1.409	3.50E-03
B	8.84	68.80	7.00	1.280	9.86E-02
B	8.84	68.80	7.00	1.169	3.58E-02
C	8.84	70.00	6.99	1.038	N/A
D	8.64	70.80	7.23	1.235	1.17E-02
D	8.64	70.80	7.23	1.210	2.06E-02
E	8.92	69.78	7.00	2.053	5.77E-02
E	8.92	69.78	7.00	1.953	7.03E-02
F	8.74	70.68	7.00	0.068	6.13E-03
F	8.74	70.68	7.00	0.069	8.29E-03
G	8.89	70.45	7.00	1.750	2.65E-02
H	8.85	69.35	7.83	1.007	5.95E-02
H	8.85	69.35	7.83	1.088	1.06E-02
I	8.82	70.00	8.00	0.440	4.94E-03
I	8.82	70.00	8.00	0.336	2.65E-02
J	8.78	70.09	6.81	1.406	3.98E-02
J	8.78	70.09	6.81	1.419	2.43E-02
K	8.75	69.94	7.00	1.004	4.47E-03
L	8.71	70.00	7.00	2.263	8.49E-02
L	8.71	70.00	7.00	2.920	7.58E-02

4.0 Statistical Evaluation

By design, the twelve distinct tests allowed for separate determinations of SRCA repeatability. As expected, there were different rate ranges for each of the glasses and conditions. The differences in pH impact on dissolution with glass composition were evident in the study.

4.1 Discussion of Intratest Repeatability

Because of the design of the round robin study, nearly all of the experiments were performed in duplicate. There were 114 individual instances where the experiment had two coupons of the same glass that produced measurable step heights in the same vessel. Because the instances were duplicates rather than higher multiples, standard deviation cannot be used to compare the measurements. Instead, we have analyzed the relative distance of each datapoint from the average of the pair to achieve a determination of how consistent measurements of different coupons of the same glass in the same vessel can be expected. This method was used so that all results could be considered together, regardless of glass type or solution conditions.

Complicating this analysis was the fact that most of these pairs (89 of the 114) consisted of instances where one of the duplicates was provided polished while the other was to be polished by the collaborating institution. Overall (Table 4-1), the polishing did not make a statistically evident difference, with the provided polished samples producing a higher rate 49% of the time and a lower rate 51% of the time relative to the sample in the same test polished by the participating institution in question. When comparing to individual institutions, there were only 10-14 instances for each of seven labs. These small sample sizes make any conclusions inferring a persistent bias unsubstantiated. Thus, all sample pairs were evaluated in the same manner.

Table 4-1 – Results showing the relative impact of polish location (provided by PNNL vs. polished at another institution) as to which sample exhibited the higher dissolution rate in the same conditions

	Total	**Lab B**	**Lab E**	**Lab F**	**Lab H**	**Lab I**	**Lab J**	**Lab L**
Sample polished at PNNL exhibited higher rate	44	**5**	5	6	7	9	6	6
Sample polished at PNNL exhibited lower rate	45	**7**	9	5	7	5	8	4

Each result from the median pair of coupons (Figure 4-1) deviated by less than 3% from the average of the two coupons. More than two-thirds of the pairs exhibited less than 5% deviation from the average measured value and more than 90% of the pairs exhibited less than 9% difference from the pair average. Only 3 pairs deviated by more than 15% from their average, and in several of those cases the discrepancy highlighted an issue with the step measurements such as one value not agreeing with the others. This compares favorably to previous studies where multiple glass coupons in the same vessel produced results that differed by 3, 4, and 4% from the average.(Ryan et al. 2021)

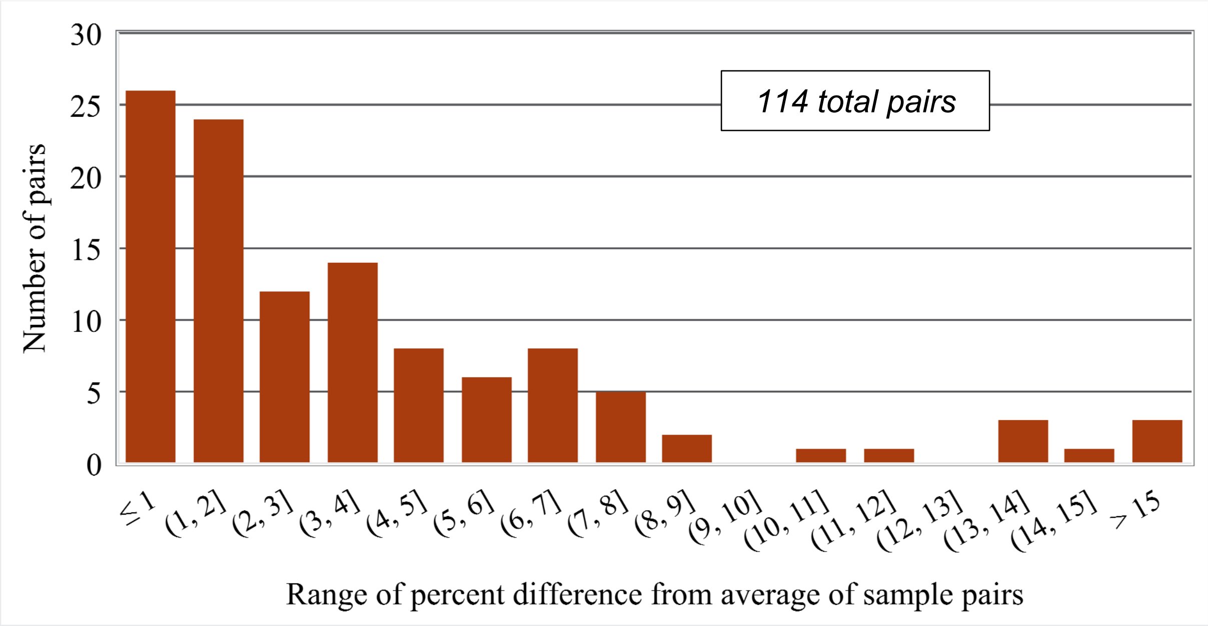


Figure 4-1 - Histogram of percent difference from average value for all duplicate tests in all conditions.

4.2 Discussion of Temperature Impact

Test temperature was an obviously impactful variable in the study. The drop in rate due to a temperature change from 70 °C to 40 °C at the same pH was larger in all samples than the drop in $pH_{(RT)}$ from 11 to 10 at the same 70 °C temperature. The temperature variable, however, proved much easier to control than the pH. Over the testing done, only two measurements were ever greater than 2 °C away from the target and these appeared only at test initiation, suggesting perhaps a measurement made before the oven was back up to temperature after loading samples. The average standard deviation of the temperature measurements among participants was a scant 0.34 °C, which is only a little over 1% of the difference between 70 °C and 40 °C. Suffice to say that careful attention to temperature control can neutralize this variable within testing programs.

4.3 Discussion of pH Impact

It has been long known that solution pH has a strong impact on glass dissolution in all stages.(Hench 1975, Grambow 1985, Hamilton et al. 2001, Gislason and Oelkers 2003, Pierce et al. 2008, Vienna et al. 2018) The η term in the affinity rate model (Eq. 1-1 specifically accounts for this effect. It was no surprise, then, when pH represented the variable with the strongest observed effect on the corrosion rate, as shown in Figure 4-2.

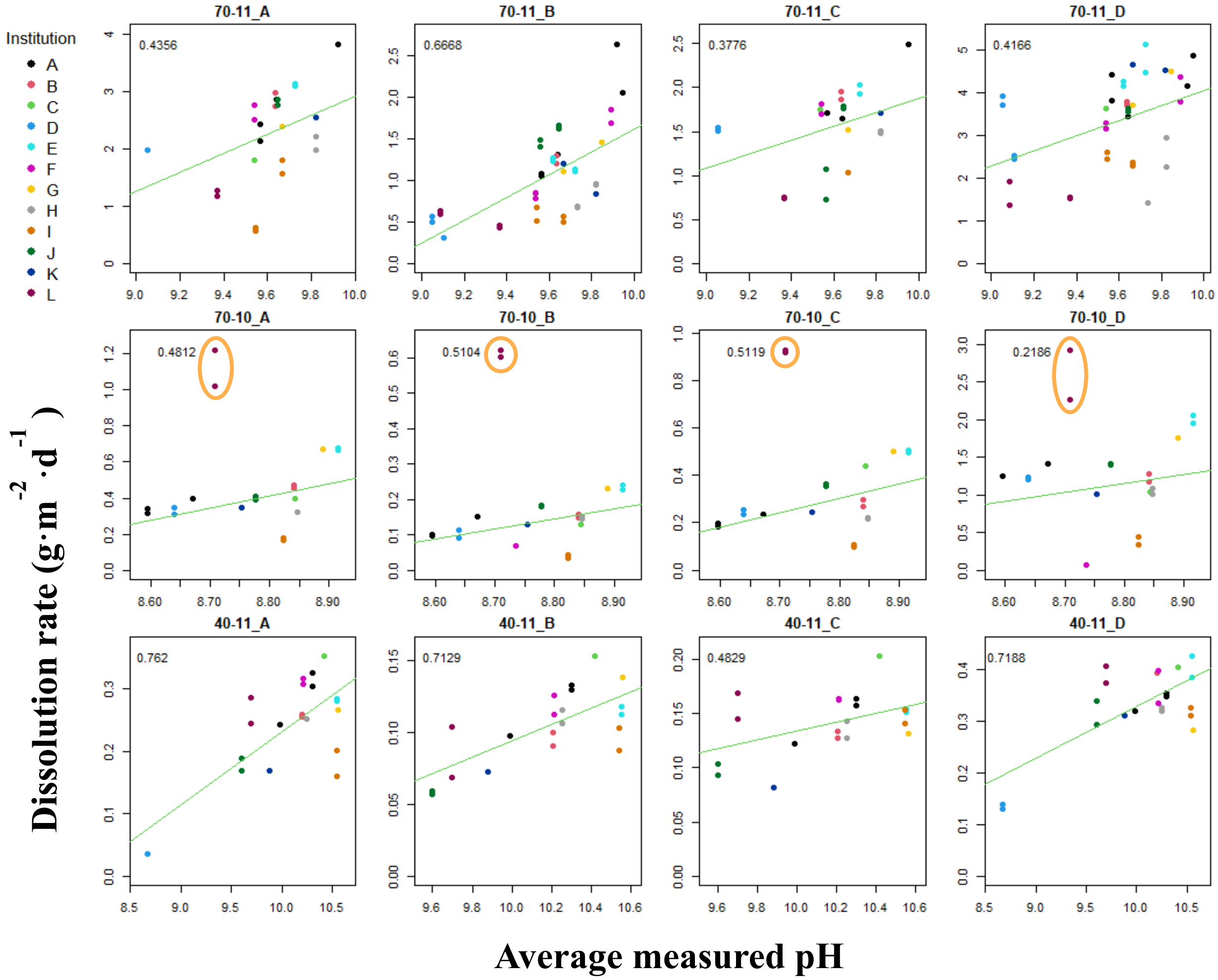


Figure 4-2 - Average dissolution rate as a function of pH for each test in all conditions. For each condition, a linear fit is presented with the R^2 value in the upper left of each plot. Outlier data points from the $\mathrm{pH}_{(\mathrm{RT})}$ = 10 and 70 °C conditions that were excluded from further analysis are circled in orange.

The correlation of dissolution rate with pH allows a more nuanced interpretation of the SRCA precision. For each glass/condition set, a best linear fit of dissolution rate as a function of pH was calculated. The data can then be evaluated by the distance of each data point from this line. While each linear fit is not expected to be a particularly accurate determination of the pH dependence, the fits are improvements over a non-correlated consideration. As mentioned earlier, the data from the outlier test at $\mathrm{pH}_{(\mathrm{RT})}$ = 10 and 70 °C (circled in orange in Figure 4-2), were excluded both from the calculation of the linear fir to pH and the statistical evaluation of precision. The extent of the outlying nature of these results is evident in the figure. Using this approach, the percentage deviation of each data point from the best linear fit for each glass/condition set is given in Figure 4-3. Again, the degree of separation of the excluded outlier data points (circled in orange) is evident, with percent relative residual values running from 100% to nearly 500% for those data points.

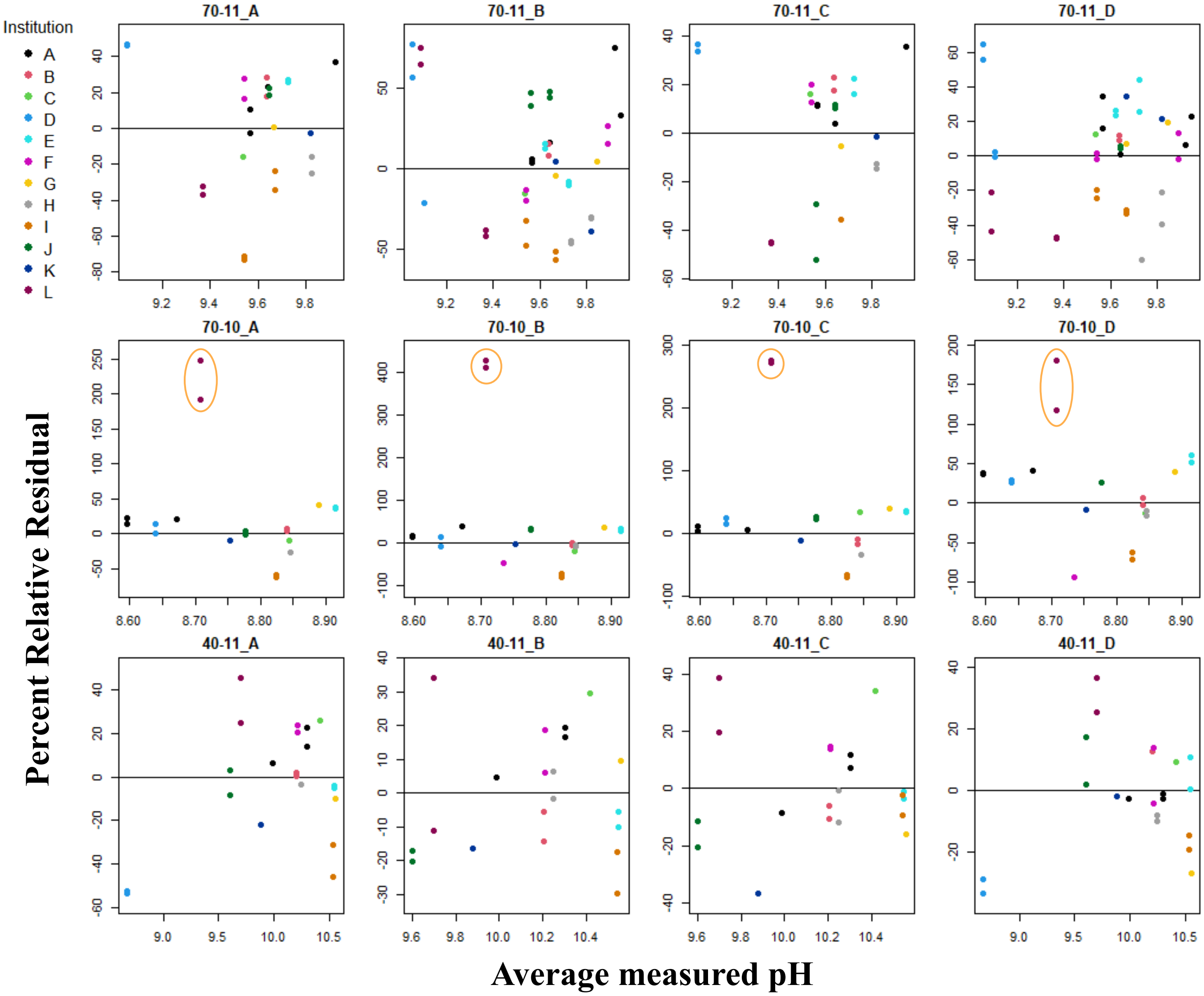


Figure 4-3 - Plot of the departure in % of value from the best linear fit of pH dependence in the given condition as a function of pH. Outlier data points from the $pH_{(RT)}$ = 10 and 70 °C conditions that were excluded from further analysis are circled in orange.

4.4 Comparison of Full Round Robin Dataset

The main advantage of an approach using percent relative residual values is that all datapoints in the entire study can be compared directly, regardless of testing conditions or glass composition. While the relative residuals can be positive or negative, taking the absolute value of the results gives a single positive number for each test that represents how far the result is from expected. Thus, a general understanding of difference from expected can be calculated and applies as an expectation of precision for the method. The relative residual values can also then be applied to examine the impact of the other variables in the study.

The full dataset of the round robin resulted in 287 individual coupon rates, which were then subtracted from the rate calculated at their conditions from the best linear fit for rate vs. pH for that particular glass-condition set. Taking the absolute value of that difference and dividing it into the best fit rate, the fractional relative residual is calculated. When expressing the value as a percent, that is termed the percent relative residual.

As expected, the range of percent relative residual values observed roughly followed a half-normal distribution as shown in Figure 4-4. The median percent relative residual for the full data set was found to be 19.4% while the average value was pulled slightly higher (23.8%) by a small number of samples that deviated strongly from the expected values.

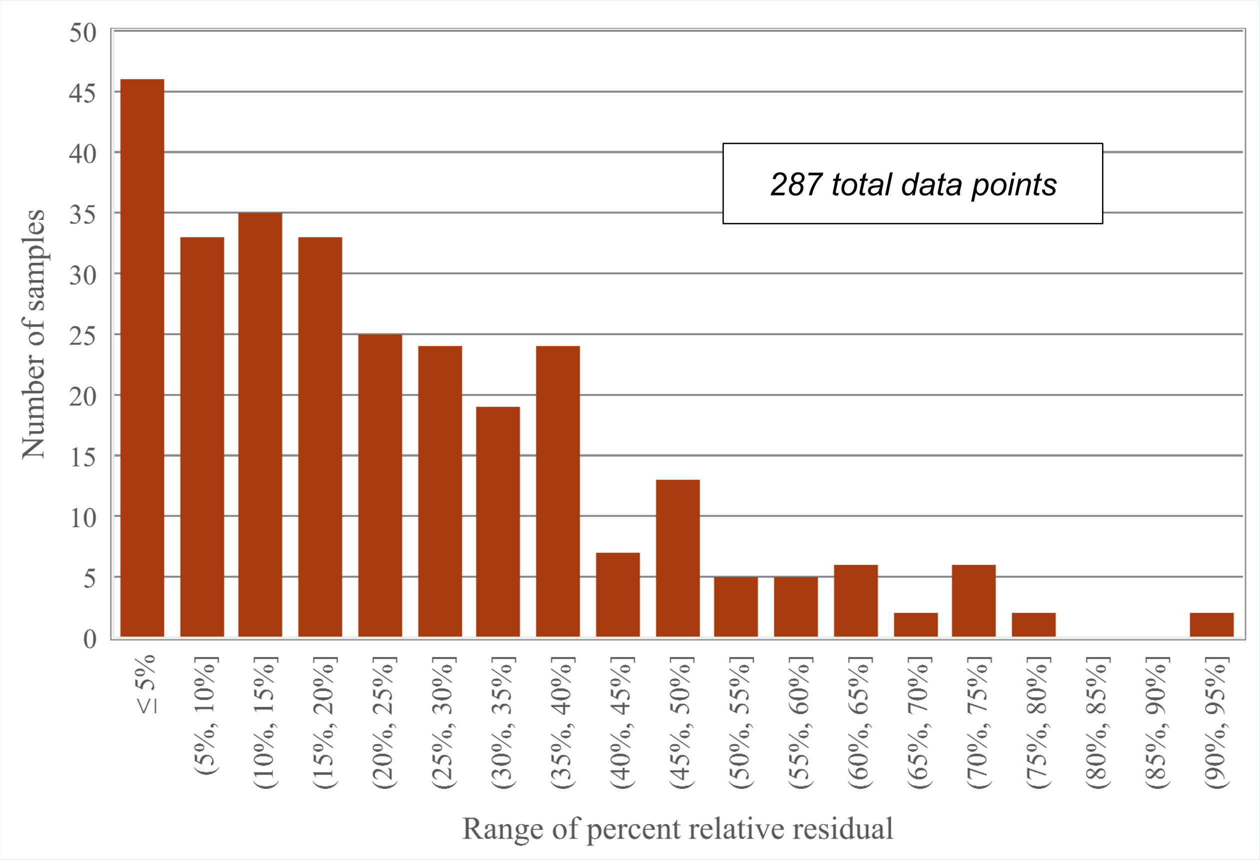


Figure 4-4 – Distribution of percent relative residuals over the full round robin dataset

4.5 Discussion of Impact of Condition Studied

The overall dataset is sufficient to establish precision of the SRCA method, but the dataset can be further explored to evaluate the other variables in the study. The variable with the most impact on the observed percent relative residual was the test conditions themselves. This result was consistent across glass compositions. As described in Table 2-2, there were four nominal tests requested in the round robin instructions.

Test 1 requested the participant to test two samples of each of the four included glass compositions in a solution with a $pH_{(RT)}$ value of 11 and a temperature of 70 °C. Test 1 accounted for 87 of the 287 total tests, and the distribution largely mirrored the overall results. The test results differed from the best-fit line for the conditions by 24.0% on average.

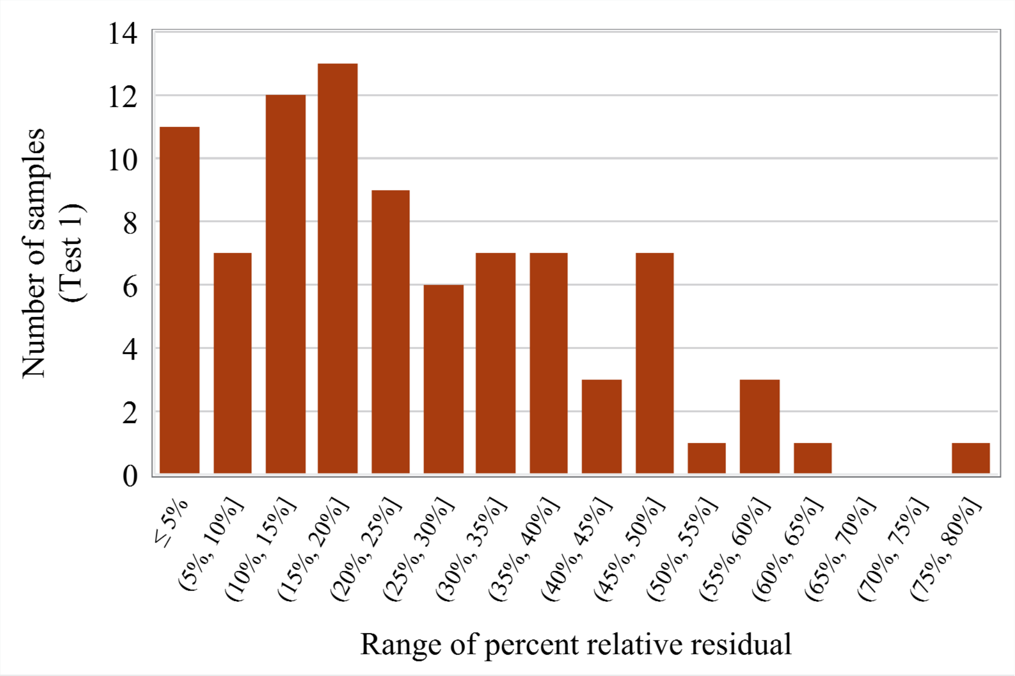


Figure 4-5 – The distribution of percent relative residual values for all Test 1 samples ($pH_{(RT)} = 11$, 70 °C)

Test 2 was the outlier of the group. The 75 tests were also in a 70 °C solution, but this time in a solution buffered with TRIS to a nominal $pH_{(RT)}$ value of 10. The median of this set was 25.7%, slightly higher than the overall numbers. The distribution of values was skewed as shown in Figure 4-6, with 7 of the 12 data points in the study greater than 65% relative residual exhibited by tests in this condition. This condition simply seemed to be a difficult one to run consistently.

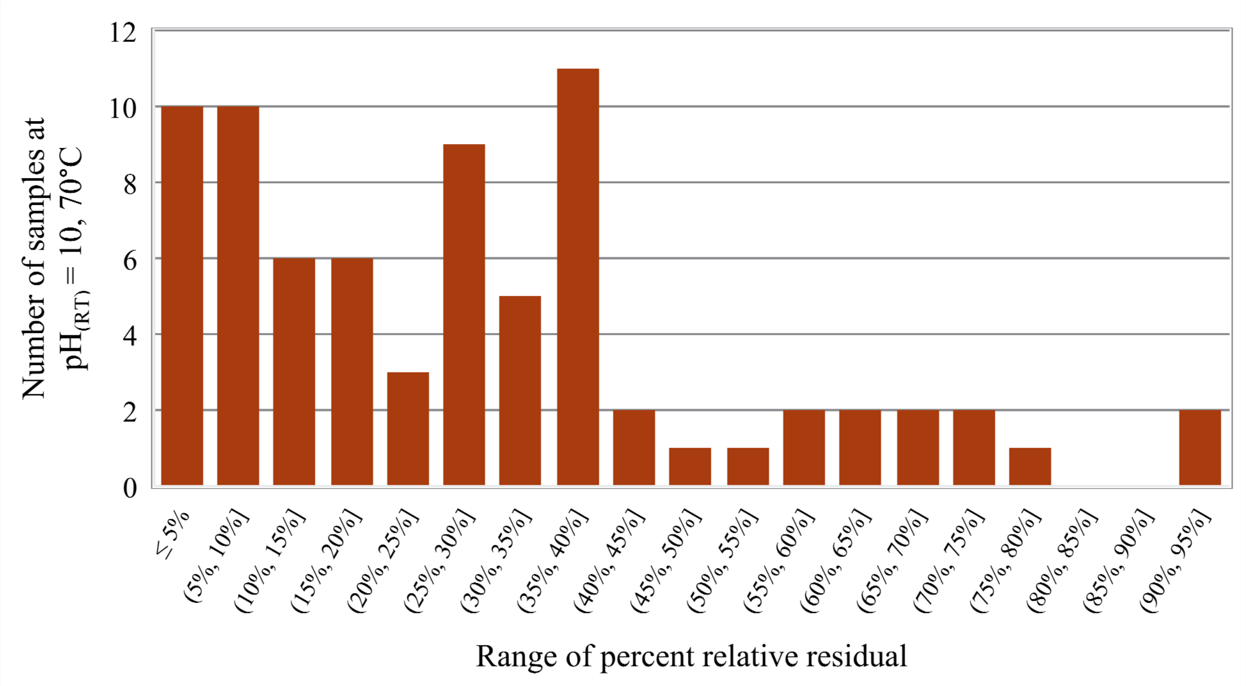


Figure 4-6 – The distribution of percent relative residual values for all samples tested at $pH_{(RT)} = 10$, 70 °C

In contrast to Test 2, the 84 samples of Test 3 exhibited the lowest relative residual values with a median of 12.4% and only four samples with 40-60% relative residual. In addition, the distribution of residual values as shown in Figure 4-7 is a good example of half-normal statistics, suggesting an even distribution around a well-predicted expected value. The test, run in solutions with a nominal $pH_{(RT)}$ value of 11 and a temperature of 40 °C, produced the slowest dissolution rates of the round robin. This shows that the wider distribution of results in Test 2 was not simply because of lower average observed dissolution rates.

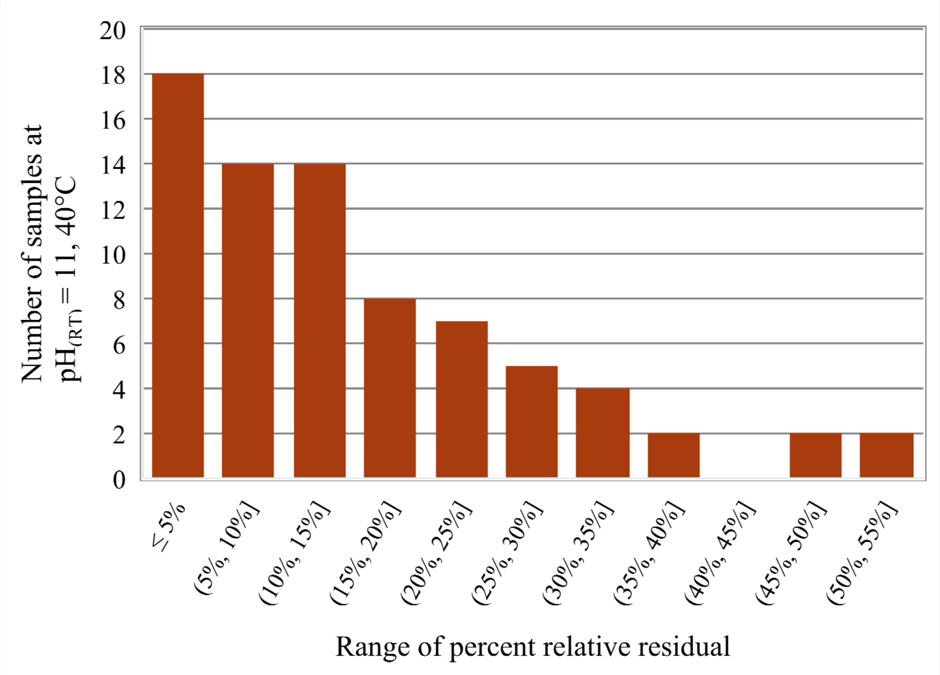


Figure 4-7 – The distribution of percent relative residual values for all samples tested at $pH_{(RT)} = 11$, 40 °C

Similar to the Test 1 samples, Test 4 were also exposed to solutions with a nominal $pH_{(RT)}$ value of 11 and a temperature of 70 °C. The difference was that in these datasets, the testing institution was to only examine the LRM and LGS19-03 glasses. In the other positions, the lab was given leeway to include any other sample (or none). For the 10 Test 4s that were completed, 6 added other glasses, 2 added at least some ceramic materials, and 1 left the other positions blank. In some instances, the blind nature of the testing led the participant to include a glass composition from the study unintentionally in the extra spots, resulting in more data for that composition. Although the data were too sparse to examine individual impact, the average (32.5%) and median values (27.8%) were increased slightly relative to the results in Test 1 and the results were distrusted more evenly than a typical half-normal distribution. The impact was statistically significant, but slight, and more research is recommended into the co-testing of different material types. The differences were not enough to warrant caution in co-testing, however.

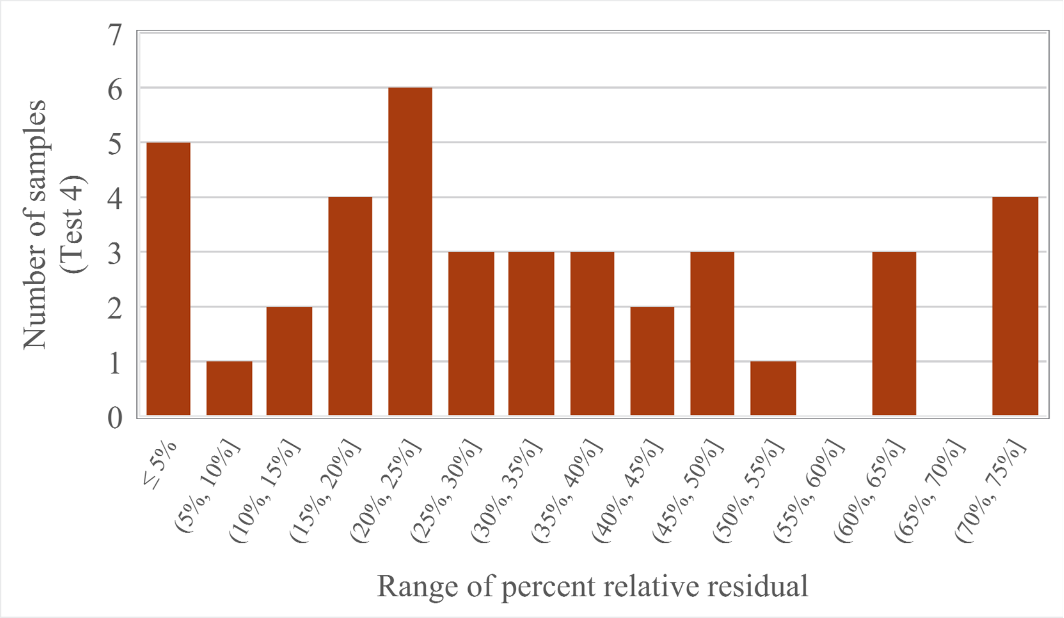


Figure 4-8 – The distribution of percent relative residual values for all Test 4 samples ($pH_{(RT)}$ = 11, 70 °C)

4.6 Discussion of Impact of Glass Type and Polish

In contrast to the impact of condition, the glass type did not have a statistically significant effect on the percent relative residual values (Table 4-2). This is not to say that the four glasses behave the same. In the same conditions, the average observed dissolution rate from the slowest glass (LRM) was only ~30% that of the fastest glass (LGS19-03). The SRCA method is designed to be applicable to any glass composition and this result confirms that most glasses can be tested alone or together without interferences.

Table 4-2 – The statistical percent relative residual values for all tests performed on each of the four glass types

Glass	Average	Median	St. dev	Min	Max	# of coupons
A	23.2%	22.2%	18.0%	0.3%	73.4%	65
B	25.9%	18.7%	20.1%	1.4%	78.5%	79
C	21.2%	16.1%	15.4%	0.7%	69.5%	63
D	24.5%	20.2%	21.3%	0.3%	93.7%	80
Overall	23.8%	19.4%	19.0%	0.3%	93.7%	287

Similarly, the institution where each sample was polished was evaluated as a potential impactful variable. The result confirmed the findings discussed as part of the study of duplicates (Section 4.1). The 181 samples polished by PNNL and the 106 samples polished at other institutions had a median percent relative residual very similar to each other and the overall numbers, with 20.0% and 18.7%, respectively. These values are not significant and point to polish location as an inefficacious variable

4.7 Discussion of Impact of Institution

There was one obvious outlier in percent relative residual when analyzed by participating institution, as shown in Table 4-3. All institutions except three had reasonably similar average and median percent relative residual values. This was often because of particularly different dissolution rates in their Test 2 ($pH_{(RT)}$=10, 70 °C) study. For institution L, their Test 2 data were such an outlier (>300% relative residual) that they were removed from the overall dataset. If they were included, the outliers would have raised the average percent relative residual for institution L to 74.4% as well as raising the values for most other data from Test 2 by skewing the linear fit to pH. This shows how one test that is particularly troublesome combined with the relatively small number of coupons evaluated in each case can shift the expected spread in the data.

Table 4-3 – The statistical percent relative residual values for all tests performed by each of the twelve institutions that participated in the round robin study

Institution	**Average**	**Median**	**St. dev**	**Min**	**Max**	**# of coupons**
A	17.5%	14.4%	15.0%	0.7%	74.6%	42
B	10.3%	9.1%	7.1%	0.3%	28.3%	24
C	19.3%	16.0%	8.9%	9.2%	34.0%	12
D	31.8%	28.4%	21.1%	0.8%	76.7%	24
E	22.0%	23.0%	15.8%	0.3%	59.7%	28
F	22.5%	15.6%	24.5%	1.3%	93.7%	23
G	18.6%	13.1%	15.1%	0.8%	41.7%	14
H	21.7%	16.2%	17.1%	0.7%	60.4%	28
I	42.6%	35.8%	21.9%	2.2%	78.5%	30
J	21.4%	20.4%	14.9%	1.2%	52.5%	28
K	15.1%	10.6%	13.5%	1.5%	38.5%	14
L	38.7%	38.3%	14.7%	11.1%	74.2%	20
Overall	23.8%	19.4%	19.0%	0.3%	93.7%	287

5.0 Discussion and Conclusions

The objective of this task was to determine the precision of the SRCA technique when used to determine the dilute condition corrosion rate. This interlaboratory study was conducted per the instructions in (ASTM E691-22 2022) to measure the precision with which the SRCA test method can be conducted. Twelve independent labs from eleven different institutions each evaluated four glass compositions in three different conditions. In essence, the multi-glass testing capability of the SRCA test enabled the simultaneous evaluation of twelve different test conditions over the course of the study. The ASTM procedures recommend at least 6 labs participate in a round robin testing the same 3 materials in the same conditions to determine precision. In this case, 12 labs each performed 12 independent tests.

5.1 Precision Statement for ASTM

A total of 114 duplicate pairs were used to calculate the repeatability of the tests, with the same glass tested in the same vessel, producing as identical conditions as possible for the replicates. These test results were quite closely clustered, with a median difference from the average value of the pair of 2.8%. Based on the calculations recommended in the ASTM E177-20 procedure (ASTM E177-20 2021) and the repeatability standard deviation (s_r) of 8.13%, **the test repeatability limit (*r*) was calculated to be within 21.8% of the expected value with 95% confidence level**. In this case, the troublesome $pH_{(RT)}$ = 10 and 70 °C test series that was excluded from analysis did not impact the overall numbers because although the values of the tests may have been inconsistent relative to the other tests, they were still just as consistent as other tests within the same vessel.

The reproducibility limit (*R*) of the test was examined using all 287 data points from the round robin. Because of the differences in dissolution rates due to pH variability and intrinsically for the 12 conditions tested, the reproducibility limits for each condition and overall were calculated from the percent relative residual value for each test. As discussed earlier, this is the percent difference of a value from the value predicted using a best linear pH vs. dissolution rate fit at the same pH value. These results were calculated for all 12 glass/condition sets, as shown in Table 5-1.

The overall reproducibility limit was determined from all 287 test datapoints by applying a factor of 2.8 to the reproducibility standard deviation, s_R, per the instructions in the ASTM methods.(ASTM E177-20 2021, ASTM D7778-15(2022)e1 2022, ASTM E691-22 2022) Based on the full dataset, **the SRCA test is expected to be precise within 53.3% of the expected value with a 95% confidence level**.

Considering each glass/condition separately, the *R* values were remarkably consistent. The separate reproducibility limits only ranged from 32% to 75% with an average of 50%. The tests performed at a $pH_{(RT)}$ of 11 and a temperature of 70 °C exhibited the lowest R values while the tests performed at $pH_{(RT)}$ = 10 and 70 °C exhibited the highest. This is even more impressive considering that the pH measurements were performed at inconsistent intervals among the collaborating labs, with some achieving careful controls and others allowing extensive drift. It is evident that precise control and detailed knowledge of the test pH would produce even more consistent and accurately used measurements. The low variability highlights that it was appropriate to remove the outlier Test 2 data from Lab L. If those data were included, the R values for the four $pH_{(RT)}$ = 10 and 70 °C tests ranged from 102% to 166% – a marked difference from the rest of the test results.

Table 5-1 – Table of statistical analyses for the 12 independent tests done within the round robin, including the repeatability limit (*r*) reproducibility limit (*R*) to a 95% confidence level

Glass	Condition	# of coupons	Average	Median	Min	Max	Standard Deviation	s_r	*r*	s_R	*R*
LAWA44	70-11	25	27.3%	24.9%	0.8%	73.4%	18.0%	7.413	20.76	16.82	**47.09**
LRM	70-11	40	31.3%	30.2%	3.8%	76.7%	21.2%	11.845	33.17	11.85	**33.17**
ISG-2	70-11	25	22.5%	17.6%	1.5%	52.5%	14.2%	6.106	17.10	12.31	**34.48**
LGS19-03	70-11	38	24.1%	21.3%	0.7%	64.5%	18.7%	6.406	17.94	11.42	**31.98**
LAWA44	70-10	18	22.3%	18.0%	1.1%	61.9%	18.8%	4.643	13.00	18.43	**51.62**
LRM	70-10	19	25.7%	17.4%	1.4%	78.5%	22.1%	10.091	28.25	22.46	**62.88**
ISG-2	70-10	18	27.5%	25.9%	4.4%	69.5%	18.3%	5.202	14.57	18.34	**51.36**
LGS19-03	70-10	20	37.5%	32.3%	2.4%	93.7%	27.3%	7.492	20.98	26.93	**75.41**
LAWA44	40-11	22	19.4%	17.2%	0.3%	53.4%	17.2%	6.303	17.65	18.46	**51.69**
LRM	40-11	20	14.7%	15.4%	1.7%	34.2%	9.1%	6.379	17.86	22.05	**61.74**
ISG-2	40-11	20	14.0%	11.5%	0.7%	38.8%	11.2%	9.057	25.36	15.62	**43.74**
LGS19-03	40-11	22	13.3%	11.8%	0.3%	36.6%	10.9%	9.188	25.73	18.62	**52.13**
All	**All**	**287**	**23.8%**	**19.4%**	**0.3%**	**93.7%**	**19.0%**	**7.792**	**21.82**	**19.03**	**53.28**

5.2 Comparison to Other Studies

The LRM glass (Glass B) used in this study was selected partly because of its similar use to evaluate the precision of both the PCT (ASTM C1285-21 2021) and SPFT (ASTM C1662-18 2018) test methods in round robin testing.(Ebert 2005, Ebert 2005, Ebert 2006) The SPFT test is particularly noteworthy because it has been one of the most popular methods to evaluate dissolution under dilute conditions. As with test conditions #1 and #4 in this study, the precision studies for the SPFT test using LRM glass were also performed at a nominal temperature of 70 ºC and in a LiCl/LiOH solution with a $pH_{(RT)}$ near 11.(Ebert 2005) Although data were provided by 7 participants, only the data sets provided by 5 participants were sufficient to determine the forward rates by linear regression of the rates measured at steady-state Si concentrations below about 30 mg/L. The forward rate was also determined from the combined rates from all participants at steady-state Si concentrations below about 10 mg/L.

For the intralaboratory SPFT tests, three values were used to measure a repeatability limit of 1.29 ± 0.39 $g \cdot m^{-2} \cdot d^{-1}$ at the 95 % confidence level, or 30% of the average value. The SRCA *r* value was based on far more tests and still resulted in a significantly smaller repeatability limit. Additionally, the SRCA method does not require multiple tests to establish a linear extrapolation to 0% Si in solution. Similarly, seven values were used to determine the reproducibility limit (*R*) of 1.64 ± 1.80 $g \cdot m^{-2} \cdot d^{-1}$ at the 95% confidence level, or 110% of the average value. The SRCA round robin used 287 measurements to again establish an *R* value of 53.3% of the average value.

Although it is not a dilute condition test, the PCT (ASTM C1285-21 2021) has been used effectively as a test for evaluating the corrosion behavior of nuclear waste materials. As mentioned, the LRM composition was included in the precision study for the PCT method as well. The repeatability and reproducibility were evaluated slightly differently for those tests, with a percent relative standard deviation (%RSD) reported separately for both the intralaboratory (repeatability) and interlaboratory (reproducibility) aspects of the study. By the same metric, the SRCA test showed a very similar intralaboratory repeatability with a 2.8% where the PCT exhibited 2.4%. The interlaboratory study showed more scatter in the SRCA test (%RSD of 31.5%) relative to the PCT test (%RSD of 9.5%), but still lower than the SPFT test.

It is clear that the SRCA test is less complicated, can allow for more samples, and is more repeatable than the SPFT test. The SRCA test is well within the precision level of other widely used ASTM Test Methods. The operator should take care to carefully control and document the conditions of the experiment, particularly with regard to pH and temperature. Given the differences observed in this study between tests done in solutions using two different buffering systems, care should also be taken to examine the impact of the buffer system on the dissolution behavior of the tested materials.

It should be noted, however, that the SRCA test has not been evaluated for use in conditions where the silica concentration in solution is not dilute. Until this use is demonstrated, the SPFT test is still necessary to evaluate the feedback between solution ions and glass corrosion.

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Appendix A – Data Sheet Templates

2022 SRCA Round Robin Testing **Testing Sheet**

Test ID:

Vessel setup & Test conditions

Vessel Cleaning	☐ Full Clean ☐ Rinsed with DIW	**Target T °C/pH$_{(RT)}$**	____ °C, pH ____
Solution Equilibration Time		**Solution mass (g):**	At test start: At test end:
Stir set speed (rpm)	60	**Solution ID**	
pH measurement	At test start: At test end:	**Oven Temp**	At test start: At test end:

Coupon Information

Coupon ID	Initial mass of masked coupon (g)	Date and time started	Date and time ended	Rinse? Dry?	Final mass of coupon with mask (g)
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	
				R☐ D☐	

Entries made by (initial/date): ____

Technical Data Review performed by: _________________________ Date: ___________

Testing Sheet (pH and notes page)

Test ID:

pH meter:			**Thermometer:**		
Date	**$pH_{(RT)}$**	**Initials**	**Date**	**Temp (°C)**	**Initials**

Notes: (Date & initial each entry)

FY22 – SRCA Testing

Post-alteration characterization sheet

Instrument name and model number:________________________________
Instrument calibrated before measurement? ___ Yes ___ No

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Entries made by (initial/date): ____

Technical Data Review performed by: _______________________ Date: __________

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Sample ID		**Meas. Date:**	
Spot#	**Filename**	**Nominal Step Height (nm)**	**Notes?**
1			☐
2			☐
3			☐
			☐
			☐

Notes: Date & initial each entry. Indicate sample ID and spot # when appropriate.

Appendix B – Data Summary

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average pH$_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation (g·m^{-2}·d^{-1})
A	1	11	70	9.64	70.8	A	2.885	OpticalProf	2.873	0.082
A	4	11	70	9.92	70.3	A	2.045	OpticalProf	3.833	0.105
A	1	11	70	9.57	70.3	A	2.861	OpticalProf	2.443	0.416
A	1	11	70	9.57	70.3	A	2.863	OpticalProf	2.151	0.412
C	1	11	70	9.54	70.0	A	1.003	StylusProf	1.815	NA
D	1	11	70	9.05	73.9	A	1.056	OpticalProf	1.982	0.145
D	1	11	70	9.05	73.9	A	1.056	OpticalProf	1.990	0.193
E	1	11	70	9.72	70.0	A	1.000	VSI	3.135	0.076
E	1	11	70	9.72	70.0	A	1.000	VSI	3.109	0.103
F	1	11	70	9.54	70.7	A	1.000	Confocal	2.524	0.092
F	1	11	70	9.54	70.7	A	1.000	Confocal	2.763	0.140
G	1	11	70	9.67	70.5	A	1.010	OpticalMicro	2.395	0.064
H	1	11	70	9.82	69.1	A	1.146	StylusProf	2.215	0.023
H	1	11	70	9.82	69.1	A	1.146	StylusProf	1.978	0.189
I	1	11	70	9.67	70.0	A	2.000	OpticalProf	1.809	0.071
I	1	11	70	9.67	70.0	A	2.000	OpticalProf	1.565	0.054
I	4	11	70	9.54	70.0	A	2.000	OpticalProf	0.577	0.152
I	4	11	70	9.54	70.0	A	2.000	OpticalProf	0.631	0.173
J	1	11	70	9.64	70.1	A	2.000	OpticalProf	2.860	0.125
J	1	11	70	9.64	70.1	A	2.000	OpticalProf	2.774	0.110
K	1	11	70	9.82	68.5	A	1.000	OpticalProf	2.559	0.027
L	1	11	70	9.37	70.0	A	1.000	StylusProf	1.182	0.053
L	1	11	70	9.37	70.0	A	1.000	StylusProf	1.272	0.048
A	1	11	70	9.64	70.8	B	2.883	OpticalProf	1.310	0.036
A	4	11	70	9.92	70.3	B	2.044	OpticalProf	2.640	0.152
A	1	11	70	9.57	70.3	B	2.863	OpticalProf	1.063	0.148
A	1	11	70	9.57	70.3	B	2.863	OpticalProf	1.087	0.036
A	4	11	70	9.95	70.2	B	2.037	OpticalProf	2.063	0.071
C	1	11	70	9.54	70.0	B	1.003	StylusProf	0.836	NA

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $pH_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average $(g \cdot m^{-2} \cdot d^{-1})$	Coupon rate standard deviation $(g \cdot m^{-2} \cdot d^{-1})$
D	1	11	70	9.05	73.9	B	1.056	OpticalProf	0.501	0.028
D	1	11	70	9.05	73.9	B	1.056	OpticalProf	0.565	0.014
D	4	11	70	9.11	70.8	B	1.844	OpticalProf	0.310	0.015
D	4	11	70	9.11	70.8	B	1.847	OpticalProf	0.309	0.069
E	1	11	70	9.72	70.0	B	1.000	VSI	1.116	0.044
E	1	11	70	9.72	70.0	B	1.000	VSI	1.138	0.048
E	4	11	70	9.62	69.9	B	1.000	VSI	1.238	0.059
E	4	11	70	9.62	69.9	B	1.000	VSI	1.267	0.037
F	1	11	70	9.54	70.7	B	1.000	Confocal	0.856	0.034
F	1	11	70	9.54	70.7	B	1.000	Confocal	0.792	0.149
F	4	11	70	9.89	69.5	B	1.000	Confocal	1.697	0.128
F	4	11	70	9.89	69.5	B	1.000	Confocal	1.852	0.191
G	1	11	70	9.67	70.5	B	1.010	OpticalMicro	1.109	0.045
G	4	11	70	9.85	70.3	B	1.000	OpticalMicro	1.468	0.016
H	1	11	70	9.82	69.1	B	1.146	StylusProf	0.965	0.041
H	1	11	70	9.82	69.1	B	1.146	StylusProf	0.953	0.023
H	4	11	70	9.74	67.8	B	1.708	StylusProf	0.696	0.010
H	4	11	70	9.74	67.8	B	1.708	StylusProf	0.681	0.021
I	1	11	70	9.67	70.0	B	2.000	OpticalProf	0.571	0.127
I	1	11	70	9.67	70.0	B	2.000	OpticalProf	0.505	0.015
I	4	11	70	9.54	70.0	B	2.000	OpticalProf	0.676	0.029
I	4	11	70	9.54	70.0	B	2.000	OpticalProf	0.520	0.092
J	1	11	70	9.64	70.1	B	2.000	OpticalProf	1.628	0.144
J	1	11	70	9.64	70.1	B	2.000	OpticalProf	1.671	0.099
J	4	11	70	9.56	70.3	B	1.031	OpticalProf	1.494	0.114
J	4	11	70	9.56	70.3	B	1.031	OpticalProf	1.408	0.068
K	1	11	70	9.82	68.5	B	1.000	OpticalProf	0.844	0.026
K	4	11	70	9.67	69.9	B	1.000	OpticalProf	1.210	0.121
L	1	11	70	9.37	70.0	B	1.000	StylusProf	0.468	0.039
L	1	11	70	9.37	70.0	B	1.000	StylusProf	0.438	0.037
L	4	11	70	9.09	70.0	B	1.000	StylusProf	0.642	0.025
L	4	11	70	9.09	70.0	B	1.000	StylusProf	0.605	0.056

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $pH_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average $(g \cdot m^{-2} \cdot d^{-1})$	Coupon rate standard deviation $(g \cdot m^{-2} \cdot d^{-1})$
A	1	11	70	9.64	70.8	C	2.879	OpticalProf	1.653	0.028
A	1	11	70	9.57	70.3	C	2.862	OpticalProf	1.706	0.048
A	1	11	70	9.57	70.3	C	2.865	OpticalProf	1.716	0.028
A	4	11	70	9.95	70.2	C	2.036	OpticalProf	2.492	0.088
C	1	11	70	9.54	70.0	C	1.003	StylusProf	1.754	NA
D	1	11	70	9.05	73.9	C	1.059	OpticalProf	1.511	0.075
D	1	11	70	9.05	73.9	C	1.059	OpticalProf	1.542	0.023
E	1	11	70	9.72	70.0	C	1.000	VSI	1.926	0.043
E	1	11	70	9.72	70.0	C	1.000	VSI	2.035	0.053
F	1	11	70	9.54	70.7	C	1.000	Confocal	1.820	0.070
F	1	11	70	9.54	70.7	C	1.000	Confocal	1.702	0.023
G	1	11	70	9.67	70.5	C	1.010	OpticalMicro	1.527	0.123
H	1	11	70	9.82	69.1	C	1.146	StylusProf	1.483	0.028
H	1	11	70	9.82	69.1	C	1.146	StylusProf	1.514	0.025
I	1	11	70	9.67	70.0	C	2.000	OpticalProf	1.038	0.030
I	1	11	70	9.67	70.0	C	2.000	OpticalProf	1.035	0.136
J	1	11	70	9.64	70.1	C	2.003	OpticalProf	1.762	0.026
J	1	11	70	9.64	70.1	C	2.003	OpticalProf	1.783	0.068
J	4	11	70	9.56	70.3	C	1.028	OpticalProf	1.080	0.139
J	4	11	70	9.56	70.3	C	1.028	OpticalProf	0.726	0.033
K	1	11	70	9.82	68.5	C	1.000	OpticalProf	1.708	0.025
L	1	11	70	9.37	70.0	C	1.000	StylusProf	0.756	0.027
L	1	11	70	9.37	70.0	C	1.000	StylusProf	0.749	0.042
A	1	11	70	9.64	70.8	D	2.878	OpticalProf	3.446	0.468
A	4	11	70	9.92	70.3	D	2.042	OpticalProf	4.163	0.111
A	1	11	70	9.57	70.3	D	2.863	OpticalProf	4.414	0.200
A	1	11	70	9.57	70.3	D	2.865	OpticalProf	3.808	0.209
A	4	11	70	9.95	70.2	D	2.037	OpticalProf	4.877	0.542
C	1	11	70	9.54	70.0	D	1.003	StylusProf	3.632	NA
D	1	11	70	9.05	73.9	D	1.059	OpticalProf	3.924	0.146
D	1	11	70	9.05	73.9	D	1.059	OpticalProf	3.710	0.205
D	4	11	70	9.11	70.8	D	1.847	OpticalProf	2.534	0.058

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $\text{pH}_{T^\circ C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation (g·m^{-2}·d^{-1})
D	4	11	70	9.11	70.8	D	1.847	OpticalProf	2.461	0.164
E	1	11	70	9.72	70.0	D	1.000	VSI	4.478	0.557
E	1	11	70	9.72	70.0	D	1.000	VSI	5.139	0.065
E	4	11	70	9.62	69.9	D	1.000	VSI	4.262	0.768
E	4	11	70	9.62	69.9	D	1.000	VSI	4.171	0.572
F	1	11	70	9.54	70.7	D	1.000	Confocal	3.283	0.219
F	1	11	70	9.54	70.7	D	1.000	Confocal	3.171	0.133
F	4	11	70	9.89	69.5	D	1.000	Confocal	4.374	0.298
F	4	11	70	9.89	69.5	D	1.000	Confocal	3.786	0.397
G	1	11	70	9.67	70.5	D	1.010	OpticalMicro	3.710	0.054
G	4	11	70	9.85	70.3	D	1.000	OpticalMicro	4.513	0.050
H	1	11	70	9.82	69.1	D	1.146	StylusProf	2.262	0.585
H	1	11	70	9.82	69.1	D	1.146	StylusProf	2.960	0.367
H	4	11	70	9.74	67.8	D	1.708	StylusProf	1.429	0.041
H	4	11	70	9.74	67.8	D	1.708	StylusProf	1.420	0.018
I	1	11	70	9.67	70.0	D	2.000	OpticalProf	2.300	0.122
I	1	11	70	9.67	70.0	D	2.000	OpticalProf	2.372	0.229
I	4	11	70	9.54	70.0	D	2.000	OpticalProf	2.460	0.019
I	4	11	70	9.54	70.0	D	2.000	OpticalProf	2.611	0.114
J	1	11	70	9.64	70.1	D	2.003	OpticalProf	3.625	0.036
J	1	11	70	9.64	70.1	D	2.003	OpticalProf	3.562	0.074
K	1	11	70	9.82	68.5	D	1.000	OpticalProf	4.535	0.700
K	4	11	70	9.67	69.9	D	1.007	OpticalProf	4.665	0.162
L	1	11	70	9.37	70.0	D	1.000	StylusProf	1.525	0.049
L	1	11	70	9.37	70.0	D	1.000	StylusProf	1.546	0.052
L	4	11	70	9.09	70.0	D	1.000	StylusProf	1.928	0.069
L	4	11	70	9.09	70.0	D	1.000	StylusProf	1.381	0.041
A	2	10	70	8.60	70.7	A	8.637	OpticalProf	0.339	0.004
A	2	10	70	8.60	70.7	A	8.631	OpticalProf	0.316	0.005
A	2	10	70	8.67	70.9	A	8.940	OpticalProf	0.396	0.010
B	2	10	70	8.84	68.8	A	7.000	OpticalMicro	0.456	0.007
B	2	10	70	8.84	68.8	A	7.000	OpticalMicro	0.471	0.007

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average pH$_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation (g·m^{-2}·d^{-1})
C	2	10	70	8.84	70.0	A	6.990	StylusProf	0.398	NA
D	2	10	70	8.64	70.8	A	7.222	OpticalProf	0.348	0.009
D	2	10	70	8.64	70.8	A	7.222	OpticalProf	0.308	0.015
E	2	10	70	8.92	69.8	A	7.003	VSI	0.668	0.015
E	2	10	70	8.92	69.8	A	7.003	VSI	0.675	0.009
G	2	10	70	8.89	70.5	A	7.000	OpticalMicro	0.669	0.046
H	2	10	70	8.85	69.4	A	7.833	StylusProf	0.321	0.006
H	2	10	70	8.85	69.4	A	7.833	StylusProf	0.322	0.008
I	2	10	70	8.82	70.0	A	8.000	OpticalProf	0.178	0.005
I	2	10	70	8.82	70.0	A	8.000	OpticalProf	0.163	0.007
J	2	10	70	8.78	70.1	A	6.802	OpticalProf	0.392	0.010
J	2	10	70	8.78	70.1	A	6.802	OpticalProf	0.411	0.008
K	2	10	70	8.75	69.9	A	7.010	OpticalProf	0.345	0.022
L	2	10	70	8.71	70.0	A	7.000	StylusProf	1.220	0.054
L	2	10	70	8.71	70.0	A	7.000	StylusProf	1.023	0.037
A	2	10	70	8.60	70.7	B	8.636	OpticalProf	0.100	0.021
A	2	10	70	8.60	70.7	B	8.630	OpticalProf	0.098	0.011
A	2	10	70	8.67	70.9	B	8.938	OpticalProf	0.150	0.002
B	2	10	70	8.84	68.8	B	7.000	OpticalMicro	0.150	0.006
B	2	10	70	8.84	68.8	B	7.000	OpticalMicro	0.158	0.003
C	2	10	70	8.84	70.0	B	6.990	StylusProf	0.130	NA
D	2	10	70	8.64	70.8	B	7.222	OpticalProf	0.092	0.006
D	2	10	70	8.64	70.8	B	7.226	OpticalProf	0.114	0.012
E	2	10	70	8.92	69.8	B	7.003	VSI	0.227	0.004
E	2	10	70	8.92	69.8	B	7.003	VSI	0.240	0.008
F	2	10	70	8.74	70.7	B	7.000	Confocal	0.068	0.004
G	2	10	70	8.89	70.5	B	7.000	OpticalMicro	0.231	0.014
H	2	10	70	8.85	69.4	B	7.833	StylusProf	0.151	0.004
H	2	10	70	8.85	69.4	B	7.833	StylusProf	0.146	0.010
I	2	10	70	8.82	70.0	B	8.000	OpticalProf	0.033	0.005
I	2	10	70	8.82	70.0	B	8.000	OpticalProf	0.044	0.007
J	2	10	70	8.78	70.1	B	6.802	OpticalProf	0.183	0.006

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average pH$_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average (g·m^{-2}·d^{-1})	Coupon rate standard deviation (g·m^{-2}·d^{-1})
J	2	10	70	8.78	70.1	B	6.802	OpticalProf	0.180	0.007
K	2	10	70	8.75	69.9	B	7.000	OpticalProf	0.128	0.006
L	2	10	70	8.71	70.0	B	7.000	StylusProf	0.604	0.024
L	2	10	70	8.71	70.0	B	7.000	StylusProf	0.621	0.005
A	2	10	70	8.60	70.7	C	8.634	OpticalProf	0.198	0.006
A	2	10	70	8.60	70.7	C	8.626	OpticalProf	0.186	0.009
A	2	10	70	8.67	70.9	C	8.935	OpticalProf	0.237	0.011
B	2	10	70	8.84	68.8	C	7.000	OpticalMicro	0.268	0.007
B	2	10	70	8.84	68.8	C	7.000	OpticalMicro	0.298	0.008
C	2	10	70	8.84	70.0	C	6.990	StylusProf	0.439	NA
D	2	10	70	8.64	70.8	C	7.226	OpticalProf	0.237	0.033
D	2	10	70	8.64	70.8	C	7.226	OpticalProf	0.256	0.014
E	2	10	70	8.92	69.8	C	7.003	VSI	0.497	0.012
E	2	10	70	8.92	69.8	C	7.003	VSI	0.505	0.009
G	2	10	70	8.89	70.5	C	7.000	OpticalMicro	0.499	0.032
H	2	10	70	8.85	69.4	C	7.833	StylusProf	0.215	0.003
H	2	10	70	8.85	69.4	C	7.833	StylusProf	0.221	0.003
I	2	10	70	8.82	70.0	C	8.000	OpticalProf	0.097	0.010
I	2	10	70	8.82	70.0	C	8.000	OpticalProf	0.109	0.006
J	2	10	70	8.78	70.1	C	6.806	OpticalProf	0.365	0.016
J	2	10	70	8.78	70.1	C	6.806	OpticalProf	0.355	0.008
K	2	10	70	8.75	69.9	C	7.000	OpticalProf	0.243	0.009
L	2	10	70	8.71	70.0	C	7.000	StylusProf	0.928	0.014
L	2	10	70	8.71	70.0	C	7.000	StylusProf	0.918	0.074
A	2	10	70	8.60	70.7	D	8.633	OpticalProf	1.255	0.010
A	2	10	70	8.60	70.7	D	8.627	OpticalProf	1.242	0.005
A	2	10	70	8.67	70.9	D	8.933	OpticalProf	1.409	0.004
B	2	10	70	8.84	68.8	D	7.000	OpticalMicro	1.280	0.099
B	2	10	70	8.84	68.8	D	7.000	OpticalMicro	1.169	0.036
C	2	10	70	8.84	70.0	D	6.990	StylusProf	1.038	NA
D	2	10	70	8.64	70.8	D	7.226	OpticalProf	1.235	0.012
D	2	10	70	8.64	70.8	D	7.226	OpticalProf	1.210	0.021

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $pH_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average ($g \cdot m^{-2} \cdot d^{-1}$)	Coupon rate standard deviation ($g \cdot m^{-2} \cdot d^{-1}$)
E	2	10	70	8.92	69.8	D	7.003	VSI	2.053	0.058
E	2	10	70	8.92	69.8	D	7.003	VSI	1.953	0.070
F	2	10	70	8.74	70.7	D	7.000	Confocal	0.068	0.006
F	2	10	70	8.74	70.7	D	7.000	Confocal	0.069	0.008
G	2	10	70	8.89	70.5	D	7.000	OpticalMicro	1.750	0.026
H	2	10	70	8.85	69.4	D	7.833	StylusProf	1.007	0.059
H	2	10	70	8.85	69.4	D	7.833	StylusProf	1.088	0.011
I	2	10	70	8.82	70.0	D	8.000	OpticalProf	0.440	0.005
I	2	10	70	8.82	70.0	D	8.000	OpticalProf	0.336	0.026
J	2	10	70	8.78	70.1	D	6.806	OpticalProf	1.406	0.040
J	2	10	70	8.78	70.1	D	6.806	OpticalProf	1.419	0.024
K	2	10	70	8.75	69.9	D	7.000	OpticalProf	1.004	0.004
L	2	10	70	8.71	70.0	D	7.000	StylusProf	2.263	0.085
L	2	10	70	8.71	70.0	D	7.000	StylusProf	2.920	0.076
A	3	11	40	10.30	40.6	A	11.785	OpticalProf	0.325	0.001
A	3	11	40	10.30	40.6	A	11.783	OpticalProf	0.303	0.015
A	3	11	40	9.99	40.6	A	11.782	OpticalProf	0.243	0.005
C	3	11	40	10.42	40.0	A	9.163	StylusProf	0.351	NA
D	3	11	40	8.67	41.9	A	11.997	OpticalProf	0.035	0.003
D	3	11	40	8.67	41.9	A	12.007	OpticalProf	0.036	NA
E	3	11	40	10.55	39.1	A	9.021	VSI	0.283	0.005
E	3	11	40	10.55	39.1	A	9.021	VSI	0.280	0.006
F	3	11	40	10.21	41.8	A	9.003	Confocal	0.315	0.008
F	3	11	40	10.21	41.8	A	9.003	Confocal	0.307	0.024
G	3	11	40	10.56	40.0	A	9.000	OpticalMicro	0.266	0.004
H	3	11	40	10.25	39.8	A	10.021	StylusProf	0.251	0.005
H	3	11	40	10.25	39.8	A	10.021	StylusProf	0.251	0.002
I	3	11	40	10.54	40.0	A	9.000	OpticalProf	0.202	0.003
I	3	11	40	10.54	40.0	A	9.000	OpticalProf	0.159	0.011
J	3	11	40	9.60	39.9	A	9.927	OpticalProf	0.169	0.003
J	3	11	40	9.60	39.9	A	9.927	OpticalProf	0.189	0.010
K	3	11	40	9.88	40.0	A	11.938	OpticalProf	0.169	0.008

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $\mathrm{pH}_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average $(g \cdot m^{-2} \cdot d^{-1})$	Coupon rate standard deviation $(g \cdot m^{-2} \cdot d^{-1})$
L	3	11	40	9.70	40.0	A	9.000	StylusProf	0.244	0.010
L	3	11	40	9.70	40.0	A	9.000	StylusProf	0.285	0.006
A	3	11	40	10.30	40.6	B	11.783	OpticalProf	0.129	0.005
A	3	11	40	10.30	40.6	B	11.782	OpticalProf	0.132	0.008
A	3	11	40	9.99	40.6	B	11.780	OpticalProf	0.098	0.002
C	3	11	40	10.42	40.0	B	9.163	StylusProf	0.152	NA
E	3	11	40	10.55	39.1	B	9.021	VSI	0.113	0.004
E	3	11	40	10.55	39.1	B	9.021	VSI	0.118	0.008
F	3	11	40	10.21	41.8	B	9.003	Confocal	0.112	0.012
F	3	11	40	10.21	41.8	B	9.003	Confocal	0.126	0.025
G	3	11	40	10.56	40.0	B	9.000	OpticalMicro	0.138	0.001
H	3	11	40	10.25	39.8	B	10.021	StylusProf	0.106	0.004
H	3	11	40	10.25	39.8	B	10.021	StylusProf	0.115	0.002
I	3	11	40	10.54	40.0	B	9.000	OpticalProf	0.088	0.006
I	3	11	40	10.54	40.0	B	9.000	OpticalProf	0.103	0.008
J	3	11	40	9.60	39.9	B	9.927	OpticalProf	0.057	0.007
J	3	11	40	9.60	39.9	B	9.927	OpticalProf	0.059	0.005
K	3	11	40	9.88	40.0	B	11.938	OpticalProf	0.073	0.002
L	3	11	40	9.70	40.0	B	9.000	StylusProf	0.068	0.004
L	3	11	40	9.70	40.0	B	9.000	StylusProf	0.103	0.004
A	3	11	40	10.30	40.6	C	11.781	OpticalProf	0.163	0.012
A	3	11	40	10.30	40.6	C	11.781	OpticalProf	0.157	0.007
A	3	11	40	9.99	40.6	C	11.779	OpticalProf	0.122	0.008
C	3	11	40	10.42	40.0	C	9.163	StylusProf	0.202	NA
E	3	11	40	10.55	39.1	C	9.021	VSI	0.154	0.004
E	3	11	40	10.55	39.1	C	9.021	VSI	0.151	0.005
F	3	11	40	10.21	41.8	C	9.003	Confocal	0.162	0.011
F	3	11	40	10.21	41.8	C	9.003	Confocal	0.164	0.015
G	3	11	40	10.56	40.0	C	9.000	OpticalMicro	0.132	0.002
H	3	11	40	10.25	39.8	C	10.021	StylusProf	0.127	0.011
H	3	11	40	10.25	39.8	C	10.021	StylusProf	0.143	0.002
I	3	11	40	10.54	40.0	C	9.000	OpticalProf	0.153	0.004

Institution identifier	Condition number	Nominal pH	Nominal temperature (°C)	Average $pH_{T°C}$	Average T°C or target value	Glass	Duration (days)	Step height characterization technique	Coupon rate average ($g·m^{-2}·d^{-1}$)	Coupon rate standard deviation ($g·m^{-2}·d^{-1}$)
I	3	11	40	10.54	40.0	C	9.000	OpticalProf	0.141	0.002
J	3	11	40	9.60	39.9	C	9.931	OpticalProf	0.093	0.003
J	3	11	40	9.60	39.9	C	9.931	OpticalProf	0.104	0.003
K	3	11	40	9.88	40.0	C	11.944	OpticalProf	0.082	0.005
L	3	11	40	9.70	40.0	C	9.000	StylusProf	0.169	0.006
L	3	11	40	9.70	40.0	C	9.000	StylusProf	0.145	0.006
A	3	11	40	10.30	40.6	D	11.780	OpticalProf	0.354	0.020
A	3	11	40	10.30	40.6	D	11.779	OpticalProf	0.348	0.033
A	3	11	40	9.99	40.6	D	11.778	OpticalProf	0.318	0.046
C	3	11	40	10.42	40.0	D	9.163	StylusProf	0.404	NA
D	3	11	40	8.67	41.9	D	12.003	OpticalProf	0.139	0.012
D	3	11	40	8.67	41.9	D	12.003	OpticalProf	0.130	0.009
E	3	11	40	10.55	39.1	D	9.021	VSI	0.384	0.055
E	3	11	40	10.55	39.1	D	9.021	VSI	0.425	0.010
F	3	11	40	10.21	41.8	D	9.003	Confocal	0.335	0.024
F	3	11	40	10.21	41.8	D	9.003	Confocal	0.398	0.023
G	3	11	40	10.56	40.0	D	9.000	OpticalMicro	0.282	0.003
H	3	11	40	10.25	39.8	D	10.021	StylusProf	0.325	0.013
H	3	11	40	10.25	39.8	D	10.021	StylusProf	0.319	0.015
I	3	11	40	10.54	40.0	D	9.000	OpticalProf	0.326	0.023
I	3	11	40	10.54	40.0	D	9.000	OpticalProf	0.310	0.030
J	3	11	40	9.60	39.9	D	9.931	OpticalProf	0.294	0.010
J	3	11	40	9.60	39.9	D	9.931	OpticalProf	0.338	0.006
K	3	11	40	9.88	40.0	D	11.944	OpticalProf	0.311	0.043
L	3	11	40	9.70	40.0	D	9.000	StylusProf	0.407	0.011
L	3	11	40	9.70	40.0	D	9.000	StylusProf	0.374	0.053

Appendix C – ASTM Method – current state

Standard Test Method for

Measurement of Glass Dissolution Rate Using Stirred Dilute Reactor Conditions on Monolithic Samples[1]

This standard is issued under the fixed designation X XXXX; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method describes a test method in which the dissolution rate of a homogenous silicate glass, including nuclear waste glasses, is measured through corrosion of monolithic samples in stirred dilute conditions.

1.2 Various test solutions can be used at temperatures less than 100 °C. While the durability of the glass can be impacted by dissolving species from the glass, and thus the test can be conducted in dilute conditions or concentrated condition to determine the impact of such species, care must be taken to avoid or account for the production of alteration layers which may confound the step height measurements.

1.3 The dissolution rate measured by this test is, by design, an average of all corrosion that occurs during the test. In dilute conditions, glass is assumed to dissolve congruently and the dissolution rate is assumed to be constant.

1.4 Tests are carried out via the placement of the monolithic samples in a large well-mixed volume of solution, achieving a high volume to surface area ratio resulting in dilute conditions with agitation of the solution.

1.5 This test method excludes test methods using powdered glass samples, or in which the reactor solution saturates with time. Glass fibers may be used without a mask if the diameter is known to high accuracy prior to the test.

1.6 Tests may be conducted with ASTM Type I water, chemical solutions (buffered solutions, simulated groundwater), or actual groundwater.

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[1] This test method is under the jurisdiction of ASTM Committee and is the direct responsibility of Subcommittee .
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1.7 Tests are conducted with monolithic glass samples with at least a single flat face. Although having two plane-parallel faces is helpful for certain step height measurements, it is not required. The geometric dimensions of the monolith are not required to be known. The reacted monolithic sample is to be analyzed following the reaction to measure a corroded depth to determine dissolution rate.

1.8 Tests may be performed with radioactive samples. However, safety concerns working with radionuclides are not addressed in this test method.

1.9 Data from these tests can be used to determine the value of kinetic rate model parameters needed to predict glass corrosion behavior over long periods of time. For an example, see Test method C1662, section 9.5.

1.10 This test method must be performed in accordance with all quality assurance requirements for acceptance of the data.

1.11 The values stated in SI units are regarded as the standard. Any values given in parentheses are for information only.

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C693: Test Method for Density of Glass by Buoyancy

C859: Standard terminology relating to nuclear materials.

C1174: Standard Guide for Evaluation of the Long-Term Behavior of Materials Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste.

C1220: Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste

C1662: Standard Test method for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method

D859: Test Method for Silica in Water

D1129: Terminology Relating to Water

D1193: Specification for Reagent Water

D1293: Test Methods for pH of Water

3. Terminology

3.1 *Definitions:*

3.1.1 *Chemical durability, n* – the resistance of a glass to dissolution under particular test conditions.

3.1.2 *Forward glass dissolution rate, n* – the rate at which glass dissolves into solution at specific values of the temperature and pH in the absence of back reactions.

3.1.3 *glass coupon, n-* a mechanically sectioned monolith of glass containing at least one flat surface. The flat surface should be polished to a finish of 3000 nm or better.

3.1.4 *Gravimetric, adj* – measured by change in mass

3.1.5 *Intrinsic rate constant, n* – the component of the forward rate constant that depends only on the glass composition.

3.1.6 *Reaction vessel, n* – a sealed container made of an inert material containing the contacting solution and glass sample.

3.1.7 *Step height, n* – the difference in height between an un-corroded portion of a glass monolith sample and the bulk corroded surface.

3.1.8 *Test solution, n* – the solution contacting the glass during the experiment.

3.2 Definitions not listed here can be found in C859.

4. Summary of Test Method

4.1 Based on C1220, C1662, and the work of Icenhower and Steefel (2015), monolithic glass specimens are contacted by a solution by suspending the glass coupon in a well-agitated reaction vessel at a low surface area to volume ratio, to maintain dilute conditions. A portion of the glass coupon surface is masked with an inert material during the solution exposure. Following the exposure, the inert material is removed from the surface or accounted for in the height measurement. The height difference between the protected, un-corroded surface and the receded corroded surface is then measured. This step height is used to calculate the dissolution rate of the glass by using Eq. 1:

$$rate = \frac{h \times \rho}{t}$$

Eq.1

where rate is the dissolution rate of the glass (in $g/m^2 \cdot d$), h is the depth of surface recession in m, ρ is the density of the glass in g/m^3, and t is the experimental duration in days (d).

The step height measurements are to be collected from samples where the dilution of species dissolving from the glass remain at concentration below which they can impact the dissolution of the glass. In doing so, the forward glass dissolution rate at infinite dilution can be determined.

5. Significance and Use

5.1 This test method provides a description of the design of the SRCA apparatus and identifies aspects of the performance of the SRCA tests and interpretation of the test results that must be addressed by the experimenter to provide confidence in the measured dissolution rate.

5.2 The SRCA methods described in this test method can be used to characterize several aspects of glass corrosion that can be included in mechanistic models of long-term durability of glasses, including nuclear waste glasses.

5.3 Depending on the test parameters investigated, the SRCA results can be used to measure the intrinsic glass dissolution rate, as well as the effects of conditions such as temperature, pH, and solution chemistry on the dissolution rate.

5.4 Due to the scalable nature of the method, it is particularly applicable to studies of the impact of glass composition on dilute-condition corrosion. Testing glass composition matrices can parameterize models of glass behavior using quantitative structure-property relationships.

5.5 The step heights present on the corroded sample can be measured by a variety of techniques including profilometry (optical or stylus), atomic force microscopy, interferometry or other techniques capable of determining relative depths on a sample surface. The sample can also be interrogated with other techniques such as scanning electron microscopy to characterize the corrosion behavior. These further analyses can determine if the sample corroded homogenously and possible formation of secondary phases or leached layers. Occurrence of these features may impact the accuracy of glass dissolution. This test method does not address these solid-state characterizations.

6. Procedure

6.1 Sample preparation

6.1.1 Monolithic glass samples are used in SRCA testing and require at least one flat face for surface recession measurements. The dimensions and shape of the monolith are irrelevant, although the coupon must be able to fit though the sample ports of the reaction vessel. A coupon size of ~15 mm x 5 mm x 2 mm has been found to be convenient.

6.1.2 The surface finish of the flat face(s) of the monolith is important and should be polished to ensure that the surface recession will not be hidden within the polishing lines. A final polish of 3 µm or better is recommended. The procedure for polishing the monolith samples shall be documented with the tests. An example preparation procedure for monolithic glass samples is given in Test Method C1220.

6.1.3 Following polishing of the face, a mask will be applied to the flat surface of the monolith. The mask shall be made of an inert material and is used to protect the area below the mask from dissolution. Suggested masks include room temperature vulcanizing silicone and sputter deposited chromium metal. Before use of a mask material, a control test to determine the stability of the mask material in the solution of interest shall be performed and documented.

6.1.3.1 When using a removable mask material, such as silicone, post-reaction treatment of the masked area shall be consistent. The mask shall be removed manually to expose the protected surface. Additional cleaning of the protected area may be required to remove any residual mask material. For example, isopropyl alcohol with light agitation from a cotton swab has been shown to be sufficient for removing residual silicone.

6.1.3.2 For use of more permanent masking materials, such as sputtered Cr, no post reaction treatment is required. The mask will remain undisturbed during the test and can be analyzed as is. The thickness of such films should be documented and subtracted from the analyzed step height.

6.1.4 If a leached layer is observed on the monolith following the reaction, the impact of such a layer on glass dissolution should be investigated.

6.2 Dilute Condition Reactor

6.2.1 In order for forward rate conditions to be present, the contacting solution for the monolithic glass sample must be representative of an infinitely dilute solution. Figure 1 shows a schematic of a dilute reactor SRCA design. Alternative designs that achieve a dilute, well-mixed condition can be used as well. Section 7.1 and ANNEX A.1 should be used to guide reactor design.

6.2.2 A reservoir of solution is contained within an appropriately sized vessel made of an inert material (example: polytetrafluoroethylene (PTFE) or stainless steel). The monolithic glass sample are then suspended within the vessel. The vessel can be placed within an oven or water bath to attain steady temperature within the vessel.

6.2.3 Preparation of the monolith samples shall be performed using the steps outlined in section 6.1.

6.2.4 The volume of solution to use should be determined based on the resulting concentration of species that can influence glass dissolution if the entire inventory of glass in the reactor were to dissolve. A ratio of glass surface area 5 cm^2 to 1 L of solution is recommended. A resulting concentration of < 1 ppm Si if the entire glass inventory dissolved is recommended.

6.2.5 An aliquot may be collected from the dilute reaction vessel at the conclusion of each test for measurement to ensure chemical concentrations remained at dilute conditions.

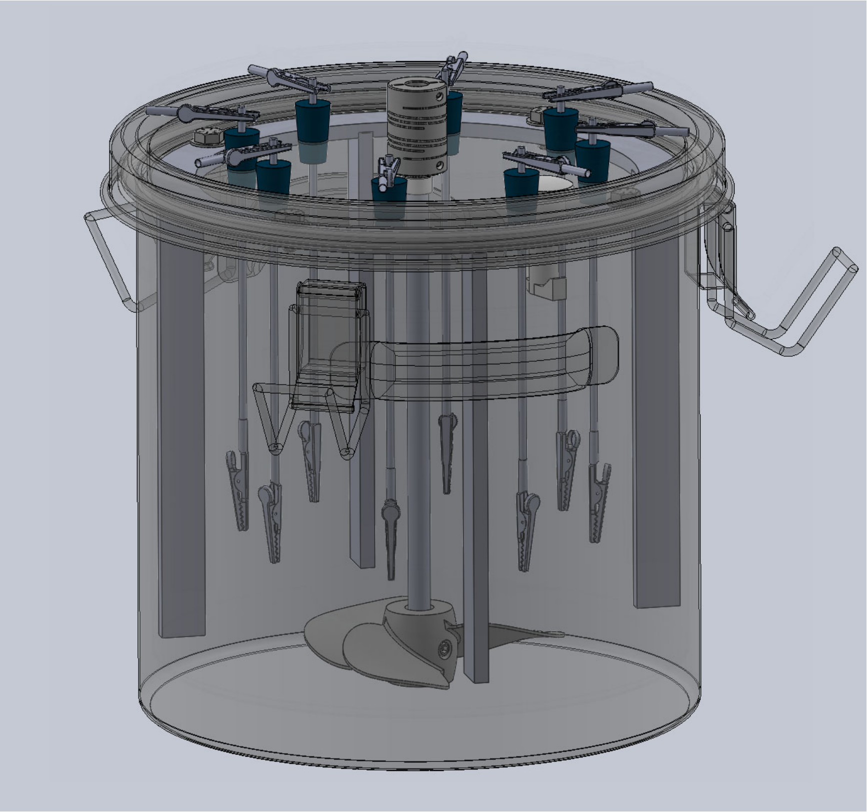

Figure 6-1 - Schematic of a the dilute reactor SRCA design used for the precision round robin studies

7. Requirements of the Apparatus

7.1 Requirements for SRCA vessel design

7.1.1 It is important to use a vessel that maintains dilute and well mixed solution conditions. It is also important that the solution not interact with the vessel. Examples of inert vessel materials may include polypropylene, polytetrafluoroethylene (PTFE), or stainless steel, but the vessel material should be chosen to be inert with respect to the individual solution/glass combination to be tested.

7.1.2 The solution volume should be such that at least 1L of solution will be present for every 5 cm^2 of exposed glass surface area for all samples. An exact measurement is not required, with conservatism suggested to ensure that the limit is not reached. The vessel size should be chosen such that with typical coupon sizes (15 mm x 5 mm x 2 mm), the volume required to fulfill the requirement can be safely contained with a reasonable head space to allow for safe handling of the vessel.

7.1.3 The vessel should be designed such that turbulent mixing is achieved. Mixing calculations to aid in this design are found in ANNEX A.1

7.2 Requirements for test solution and monitoring

7.2.1 The test solution should not interact with any part of the test apparatus, including sample hangers, baffles, and the mixing apparatus. If a change in material of the system components is made, a control test to ensure no interactions occur must be performed. Any interactions leading to a change in system material shall be documented.

7.2.2 The solutions may be purged with an inert gas, such as N_2, to prevent drifting of the pH due to ingress of CO_2.

7.2.3 If a pH series is being done, it is recommended that the effect of any change in buffering agent over the series should be evaluated by performing measurements at the same pH with both buffering agents.

7.2.4 The temperature of the reaction vessel solution shall be measured and monitored with a thermocouple or similar device. Within a large oven, a representative solution in a separate vessel may be monitored if there are concerns about thermocouple materials interacting with the test solution. At a minimum, temperature should be recorded at the beginning of the test immediately prior to glass addition and at the conclusion of the test prior to removal of the glass samples. For longer tests, a daily temperature check regimen or online monitoring is suggested. Temperatures shall be within 2 °C of the desired temperature of the test throughout the duration.

7.2.5 Aliquots of solution collected for analysis shall be stored in sealed containers. If pH is to be measured per D1293, it shall be measured no later than 1 hour following collection.

7.2.6 The solution within the reaction vessel requires light agitation through use of an impeller, ensuring turbulent flow (Reynold’s number > 10000), but preventing vortex formation in the reactor to disturb any potential diffusion layers near the glass monolith surface.

7.2.7 At higher temperatures, evaporation of the solution is possible. It suggested that the solution level be monitored through manual observation. Suggested methods include comparing level to a known mark in the chamber, an inert dipstick, or the use of a sight tube. Lost solution can be replaced with ASTM Type I water. Unreplaced evaporation of >10% of the original volume shall result in termination of the test.

8. Test Method

8.1 *Stirred reactor test protocol*

8.1.1 The reactor parts (vessel, baffles, sample holders, agitator), shall be cleaned by rinsing with dilute nitric acid (~0.1 M) and demineralized water, in that order, prior to use.

8.1.2 Add the calculated volume of reaction solution to the reaction vessel.

8.1.3 Place reactor vessel in oven or water bath, if being used, to establish consistent temperature prior to glass sample introduction. Temperature shall be monitored by a thermocouple or other temperature recording device.

8.1.4 Begin agitation of the reaction vessel solution.

8.1.5 When the target temperature has been reached, measure solution pH (D1293).

8.1.6 Suspend the masked glass monolith samples in the reaction vessel solution with an inert rigid hanging system or placement on a rack made of inert material.

8.1.6.1 Monolithic glass samples are to be suspended such that 100% of the surface to be investigated for height recession is exposed to the contacting solution. Attachment with a hanging design made of an inert material is recommended, Figure 2, but this can also be achieved by placement of the monolith on a rack made of inert material.

8.1.7 During testing, particularly for tests lasting longer than 2 days, the temperature and pH (D1293) of the contacting solution should be monitored on a regular basis. The pH should be measured with a recently calibrated pH meter on an aliquot of solution removed from the vessel and discarded following measurement to avoid any contamination from the pH meter. The aliquot can be cooled to room temperature to maintain a consistent baseline temperature for pH monitoring. If solution pH drifts, careful adjustment of the pH with the same buffer system is allowed.

8.1.8 Following the set test time, measure solution pH (D1293) and remove the masked glass monolith sample. Treat sample according with Section 8.2. Removing subsets of the sample group and allowing the rest to continue is allowed, but the solution pH should be measured at each sample termination.

8.1.9 If re-use of the solution is desired, collect a sample of the reaction vessel solution and place into a clear, tared bottle labelled with the test identification information and submit for analysis (by ICP-OES or similar solution analysis technique) for crucial components such as Si (D859) and Al. If ion concentrations are below a determined concentration, the solution inside the reaction vessel can be re-used for subsequent tests.

8.1.10 Properly dispose of reaction solution. Clean the vessel with rinses of dilute nitric acid followed by demineralized water.

8.2 *Treatment of Glass Monolith Samples.*

8.2.1 Remove the glass monolith from solution and immediately rinse three times with demineralized water. Shake to remove excess water between rinses. Next rinse the glass monolith three times with ethanol, shaking to remove excess between rinses.

8.2.2 Immediately following the ethanol rinse, place the glass monolith in an oven set between 20 °C and 50 °C to allow the ethanol to evaporate. This temperature is selected as to not alter any hydrated gel layers present on the glass monolith.

8.2.3 For a removable mask for which no baseline measurement was made prior to corrosion, manually remove the mask from the glass sample using tweezers or other method determined to not harm the glass sample or the step produced by corrosion. Solvents that are not expected to alter the sample specimen such as ethanol or acetone, are permitted, as is gentle wiping such as with a cotton swab.

8.2.4 For a mask which a baseline height measurement was taken, such as sputter deposited metal, visually inspect to ensure mask remained intact.

8.2.5 Analyze the step height which exists between the protected and corroded surfaces of the glass monolith. Techniques such as profilometry, atomic force microscopy, white light interferometry, or confocal laser microscopy are suggested for such measurements, depending on the depth resolution required. Microscopy of a sample cross section is another potential method, although care must be taken to avoid damage to the step during sample preparation.

8.2.6 Following step height analysis, the glass monolith sample can be polished again and used in further tests.

9. Calculation or Interpretation of Results

9.1 Calculations related to effluent collection and analyses are covered in Test Method C1662 section 9.0.

9.2 *Determination of Glass Dissolution Rate from Step Height*

9.2.1 The dissolution rate is determined from the recession of the glass surface over a period of exposure using Equation 1. This method overcomes challenges in selecting proper element tracers for glass dissolution.

9.2.2 Tabulate the measured step heights of the samples (m) and the start time and sampling time of the monolithic sample.

9.2.3 Subtract the sampling time from the starting time to determine the duration of the test.

9.2.4 Determine the dissolution rate, in g/m^2 per unit time using equation 1.

9.2.5 The intrinsic rate constant can be determined using Equation 2:

$$rate = k_o \cdot 10^{\eta pH} \cdot exp\left(-\frac{E_a}{RT}\right) \cdot \left(1 - \frac{Q}{K}\right) \quad \text{Eq.2}$$

where k_0 is the intrinsic rate constant, η is the pH dependence, E_a is the activation energy, R is the gas constant, and T is absolute temperature. The method of solving for the intrinsic rate constant are discussed in section 9.5 of C1662.

10. Possible Complications

10.1 *Phase Separated Glasses* – The dissolution rate measured for a phase separated glass may be incorrectly influenced by preferential dissolution of a single phase. Section of the glass monolith would then recede farther than others, and if not observed prior to measurement lead to an incorrect step height. Imaging the protected:corroded interface at a lower magnification prior to step height measurement will aid in identifying such separation.

10.2 *Alteration Layer Formation* – Some glasses in some conditions may form alteration layers during testing. Some step height measurement techniques may not be sensitive to alteration layers and may return an artificially low step height. If the total step height is desired, efforts should be undertaken to remove any alteration layer before measurement. If solution feedback was part of the test, solid characterization must be performed such that the height of the alteration layer and the corrosion step can be determined and considered separately.

10.3 *Sloped Interfaces* – The protected:corroded interface may not in all cases be a steep step. If the dissolution of the glass undercuts the mask material, a sloped surface may exist between the receded surface and the protected region. If the bottom of the step is not properly identified, the step height calculation will be incorrect. Imaging the protected:corroded interface at a lower magnification prior to step height measurement will aid in identifying a sloped surface.

11. Report

11.1 Report the test conditions including

11.1.1 Glass composition, from measured or as-batched.

11.1.2 Composition and pH of contacting test solution during test.

11.1.3 Temperature of reaction vessel during test.

11.1.4 Initial mask step height if applicable.

11.1.5 Table of measured step heights, experimental start and end times.

11.2 Report the calculated values

11.2.1 Table of calculated experiment durations.

11.2.2 Table of calculated dissolution rates.

11.2.3 Plot of dissolution rate versus pH.

11.3 Report any deviations from the test method and discuss the expected effects on the results.

12. Precision and Bias

12.1 An interlaboratory study was conducted per the instructions in (ASTM E691-22 2022) to measure the precision with which the SRCA test method can be conducted. Twelve independent labs from eleven different institutions each evaluated four glass compositions in three different conditions.

12.2 All studies examined the dissolution rate of four different borosilicate glasses, LAWA44, LRM, ISG-2, and LGS19-03, with density values of 2.694, 2.557, 2.475, and 2.710 g/cm^3, respectively. The four glasses were selected to provide a range of glass dissolution rates for evaluation. All sample coupons were polished to a 3000 nm finish and RTV silicone was used as the masing material.

12.3 The SRCA round robin tests were performed at a series of defined starting pH values and temperatures on the four chosen glass compositions. A test matrix was designed consisting of four pH, temperature, and sample configuration combinations, as detailed in Table 1. Each experiment was to be run at least for the minimum duration. Since the step height between the masked and unmasked portions of the glass becomes larger and more accurately measured with longer exposure to the dilute solution, the collaborators were given discretion to run tests longer if possible.

Table 6-1 - Test conditions for each test number

Test number	pH	Temperature	Minimum duration
1	11	70 °C	1 day
2	10	70 °C	7 days
3	11	40 °C	9 days
4**	11	70 °C	1 day

** For test four, it was requested that only one PNNL-polished and one collaborator-polished coupon each of the LRM and LGS19-03 compositions be included in the vessel. The remaining testing slots were filled with other materials provided by each collaborator or left empty, at the discretion of the collaborator.

12.4 Initially, a single lab study at $pH_{(RT)}$=11 and 70C tested 10 samples of the LRM glass composition in the same vessel with differing polish levels, showing that all polish levels better than 3000 nm behaved similarly (Figure 3) with an average value (1.15 g/m^2d) within the range of the others reported in the SPFT interlaboratory study.

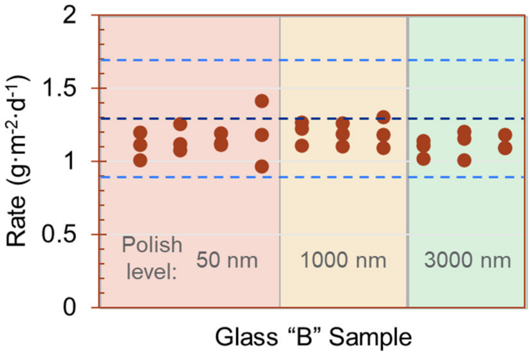

Figure 6-2 - Single vessel replicates of Glass"B" showing repeatability and no impact of polish quality on results.

12.5 For the interlaboratory tests, total of 114 duplicate pairs were used to calculate the repeatability of the tests, with the same glass tested in the same vessel, producing as identical conditions as possible for the replicates. These test results were quite closely clustered, with a median difference from the average value of the pair of 2.8%.

12.6 Based on the calculations recommended in the ASTM E177-20 procedure (ASTM E177-20 2021) and the repeatability standard deviation (sr) of 8.13%, **the test repeatability limit (r) was calculated to be within 21.8% of the expected value with 95% confidence level**

12.7 The reproducibility limit (*R*) of the test was examined using all 287 data points from the round robin. Because of the differences in dissolution rates due to pH variability and intrinsically for the 12 conditions tested, the reproducibility limits for each condition and overall were calculated from the percent relative residual value for each test, i.e. the percent difference of a value from the value predicted using a best linear pH vs. dissolution rate fit at the same pH value.

12.8 These results were calculated for all 12 glass/condition sets, as shown in Table 2. The overall reproducibility limit was determined from all 287 test datapoints by applying a factor of 2.8 to the reproducibility standard deviation, s_R, per the instructions in the ASTM methods.(ASTM E177-20 2021, ASTM D7778-15(2022)e1 2022, ASTM E691-22 2022)

12.9 Based on the full dataset, **the SRCA test is expected to be precise within 53.3% of the expected value with a 95% confidence level**.

12.10 Considering each glass/condition separately, the *R* values were remarkably consistent. The separate reproducibility limits only ranged from 32 to 75 with an average of 50.

Table 6-2 – Table of statistical analyses for the 12 independent tests done within the round robin, including the repeatability limit (*r*) reproducibility limit (*R*) to a 95% confidence level

Glass	Condition	# of coupons	Average	Median	Min	Max	Standard Deviation	s_r	*r*	s_R	*R*
LAWA44	70-11	25	27.3%	24.9%	0.8%	73.4%	18.0%	7.413	20.76	16.82	**47.09**
LRM	70-11	40	31.3%	30.2%	3.8%	76.7%	21.2%	11.845	33.17	11.85	**33.17**
ISG-2	70-11	25	22.5%	17.6%	1.5%	52.5%	14.2%	6.106	17.10	12.31	**34.48**
LGS19-03	70-11	38	24.1%	21.3%	0.7%	64.5%	18.7%	6.406	17.94	11.42	**31.98**
LAWA44	70-10	18	22.3%	18.0%	1.1%	61.9%	18.8%	4.643	13.00	18.43	**51.62**
LRM	70-10	19	25.7%	17.4%	1.4%	78.5%	22.1%	10.091	28.25	22.46	**62.88**
ISG-2	70-10	18	27.5%	25.9%	4.4%	69.5%	18.3%	5.202	14.57	18.34	**51.36**
LGS19-03	70-10	20	37.5%	32.3%	2.4%	93.7%	27.3%	7.492	20.98	26.93	**75.41**
LAWA44	40-11	22	19.4%	17.2%	0.3%	53.4%	17.2%	6.303	17.65	18.46	**51.69**
LRM	40-11	20	14.7%	15.4%	1.7%	34.2%	9.1%	6.379	17.86	22.05	**61.74**
ISG-2	40-11	20	14.0%	11.5%	0.7%	38.8%	11.2%	9.057	25.36	15.62	**43.74**
LGS19-03	40-11	22	13.3%	11.8%	0.3%	36.6%	10.9%	9.188	25.73	18.62	**52.13**
All	**All**	**287**	**23.8%**	**19.4%**	**0.3%**	**93.7%**	**19.0%**	**7.792**	**21.82**	**19.03**	**53.28**

13. Keywords

13.1 **Glass dissolution rate**
13.2 Glass corrosion
13.3 Nuclear waste glass.

ANNEX

(Mandatory Information)

A1. VESSEL MIXING CALCULATIONS

The SRCA method requires that the solution contacting the glass surface is as free as possible from the influence of ions released from the samples. These conditions are attained in this test by placing a glass sample in a high volume of well-mixed solution.

Regardless of the type of vessel designed, well-mixed conditions (i.e., turbulent flow conditions) must be maintained in the reactor chamber and to avoid the possibility of concentration gradients near the dissolving glass. Figure 4 gives a general dimensional schematic representing a generic reactor system, including the agitator and baffles to achieve consistent turbulent mixing, with the relevant variables. General best practice should be used to design vessels with appropriate mixing near the sample surfaces (Uhl and Gray 1966).

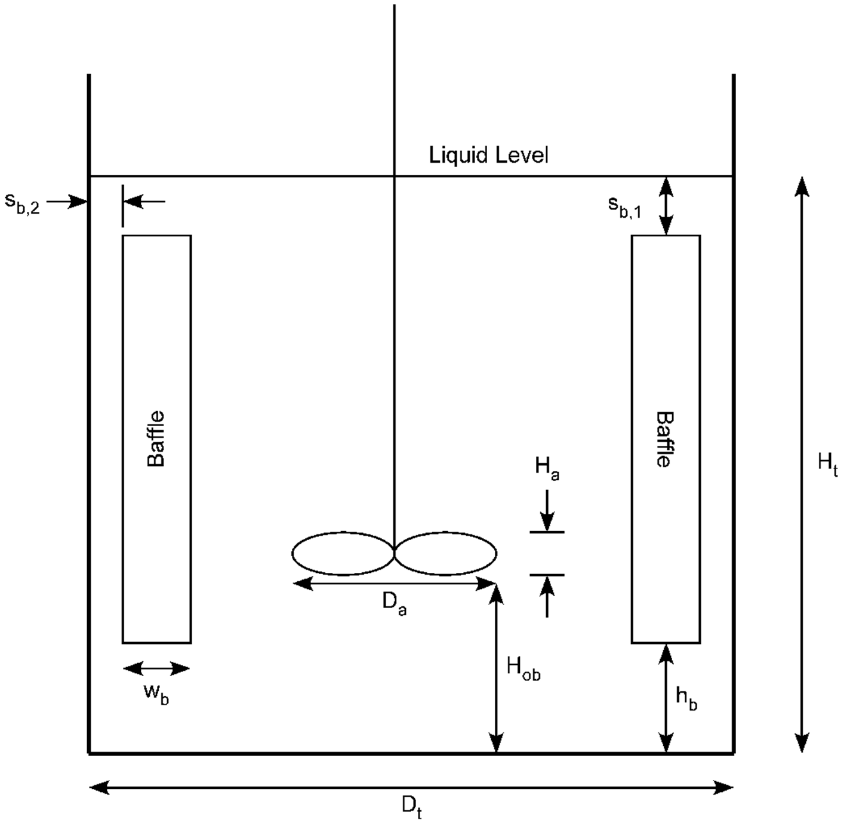

Figure 6-3. General schematic of baffled flat-bottom reactor with important dimensions.

The mixing agitator should be selected with an agitator diameter (D_a) to reactor diameter (D_t) ratio between 0.3 and 0.6 for a baffled reactor. The agitator height (H_a) should be selected such that H_a/D_t is 0.1 to 0.2. While best mixing would suggest an agitator off-bottom installation height (H_{ob}) to be around 1/3 of the reactor diameter, a lower position is still expected to produce acceptable circulation patterns in the reactors, and may be desired to provide more room for samples and less chance for an impact during loading/unloading.

The Reynolds number for stirred-reactor agitation is based on agitator geometry and tip speed and is independent of the baffle configuration. Baffles serve to break up the swirl, encourage top-to-bottom momentum transfer, and reduce vortexing. The stirred-reactor Reynolds number (*Re*) is:

$$Re = \frac{\rho N D_a^2}{\mu} \qquad \text{Eq. A-1}$$

where ρ and μ are the density and viscosity of the fluid (which in dilute aqueous conditions can be assumed to be $\rho = 1000$ kg m^{-3} and $\mu = 0.001$ Pa s) and *N* is the rotation speed of the propeller. Stirred-reactor agitation is considered turbulent when *Re* is above 10,000. An *N* value should be chosen to fulfill this requirement.

Baffles provide additional mixing effectiveness for the same mixing power; the effectiveness increases with the number of baffles up to approximately four. Above four baffles, the impact on mixing effectiveness is negligible and baffle placement primarily impacts flow patterns and eddies that form in the reactor (Uhl and Gray 1966). Baffle placement should be designed to provide as uniform a flow pattern as possible for each sample in the reactor. For a fluid with the viscosity of water, a baffle width of 1/12 D_t is the suggested configuration. It is typical to have baffles set off with respect to the reactor bottom at a height (h_b) of $D_a/2$ and to have 10% of the fluid above baffle tops ($s_{b,1}$), but these recommendations are not critical to the overall mixing quality. Of more importance is to design the baffles with a separation from the reactor wall ($s_{b,2}$) greater than $w_b/6$ to avoid having closed circulation cells.

Due to the turbulent nature of the agitated flow, mixing assessments depend heavily on correlations (or models). The recommended geometry can be assessed using two different metrics, assuming four or more baffles. The first is based on data from Norwood and Metzner (1960). They defined a dimensionless mixing factor f_t:

$$f_t = t_t \frac{\left(ND_a^2\right)^{2/3} g^{1/6} D_a^{1/2}}{H_t^{1/2} D_t^{3/2}} \qquad \text{Eq. A-2}$$

where t_t is the time to complete blending in a reactor of miscible liquids and *g* is the gravitational constant. This was correlated with *Re*, and $f_t \sim 4$ for *Re* in the range from 10000 to 25000**Error! Reference source not found.**. Values for t_t under 10 seconds are recommended.

The second geometry assessment is based on the work of Havas et al. (1978). They measured what they called homogenization time (τ_{95}) which is the time it takes the concentration to achieve 95% homogenization in the reactor. For a baffled reactor with a propeller agitator similar to the schematic above, the data suggested the following correlation

$$\tau_{95} = \left(\frac{4.43}{N}\right)\left(\frac{D_t}{D_a}\right)^{2.24} \qquad \text{Eq. A-3}$$

Using this, a τ_{95} under 45 seconds is recommended. Although these correlations are not expected to be quantitatively predictive due to simplifications and assumptions in geometry and configuration, the recommended values establish a level of confidence that the mixing geometries chosen for a SRCA vessel will keep the reactors well-mixed and avoid impactful concentration gradients near the samples.

APPENDIX

(Nonmandatory Information)

X1.

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