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Glass and Rock Dissolution and Zeolitization

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Outline

- Glass composition(s)
- Glass durability tests
- Glass corrosion basics
 - Corrosion mechanisms
 - Corrosion stages/regimes
- Stage III glass corrosion
 - What is stage III
 - Secondary phases
 - Trigger mechanisms what do we know?
 - Zeolitization model
- ASTM C1174 Road Map

SOUTH AFRICA – JANUARY 2017











Glass Composition(s): HLW vs. Basalt

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Oxide	165 Avg	131 HM	131 Purex	Tholeiite	ljolite
				(Barth, Theoretical Petrology)	
Al ₂ O ₃	6.5	13.1	3.8	14.4	20.0
CaO + MgO	3.2	3.7	4.0	17.5	16.3
Fe ₂ O ₃	14.4	14.2	16.8	12.4	4.3
K ₂ O + Na ₂ O + (Li ₂ O)	14.5	15.0	19.6	3.3	13.2
SiO ₂	61.4	54.0	55.9	52.4	46.1

Accelerated Tests Developed from 1980

Waste Form (1980-Pres)					
Chemical Durability	MCC-1, 2, 3, 4, 5 (Soxhlet)				
Aging Effects (thermal and	MCC-6, 7, 12, 13				
radiation)					
Volatility	MCC-8.9,16				
Physical Strength	MCC-10, 11, 15				
Canister Container					
Corrosion Resistance	MCC-101, 102, 103, 104				
Repository Interactions					
Canister/container corrosion	MCC-105 ^a				
Waste Form Durability	MCC-14 ^a				

^a The repository interactions tests are divided into site-specific subcategories, e.g., MCC-105.1 (basalt).





• Three stages:

- Stage I forward rate
- Stage II residual rate
- Stage III resumption
- Different mechanisms control rates in different stages
 - Interdiffusion (ion exchange)
 - Hydrolysis
 - Affinity/Transport
 - Dissolution/Precipitation
 - Crystallization





• Interdiffusion/Ion exchange

 $\equiv Si - OM + H^+ \leftrightarrow Si - OH + M^+$ $\equiv Si - OM + H_2O \leftrightarrow Si - OH + M^+ + OH^-$

- Increasing pH value and OH⁻ concentration in leachate

• Hydrolysis

 $Si - O - Si + OH^{-} \leftrightarrow Si - OH + Si - O^{-}$ $Si - O^{-} + H_2O \leftrightarrow Si - OH + OH^{-}$

- Increasing pH value/OH $^{\rm -}$ and $\rm C_{Si}$
- Diffusion/Affinity
 - Two hypotheses:

Thermodynamic: r = affinity controlled

Ses:

$$r_{0}\left(1-\frac{Q}{K}\right)^{\overline{\sigma}} \stackrel{a_{i}^{n_{i}}\left(1-Q\uparrow^{\sigma}\right)}{\Rightarrow} as r\downarrow_{-}$$

$$r = r_{0}\left(1-\frac{Q}{K}\right) \text{ (simplified)}$$

Alteration

Interdiffusion

Kinetic:

transport limited

Hydrolysis

Basic concept:

$$D_{layer} < D_{bulk\,glass} \Rightarrow r \downarrow_{-}$$

alteration layer

Diffusion/affinity

bulk glass

• Interdiffusion/Ion exchange

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 - Two hypotheses:

Thermodynamic: $r = r_0 \left(1 - \frac{Q}{R}\right)$

$$\left(\frac{Q}{K}\right)^{\sigma} \Rightarrow as \left(\frac{Q}{r}\right)^{\tau+} \downarrow_{-}$$

Kinetic: transport limited



Basic concept:

$$D_{layer} < D_{bulk\,glass} \Rightarrow r \downarrow_{-}$$

alteration layer

bulk glass

Corrosion reactions (solution perspective)

- The residual rate (Stage II)
 - Controlling mechanisms debated
 - Pseudo-equilibrium between glass surface dissolution and leachate
 - ⇒ Slight change in dissolved element concentration in leachate
 - Release rate several orders of magnitude less than forward rate
- Resumption of alteration (Stage III)
 - Sudden increase in release rate of certain elements into solution
 - Marked by the large-scale precipitation of secondary mineral phases (zeolites)
 - Does not occur with all glass compositions!!



Interdiffusion

- Two hypotheses regarding increase in release rate:
 - 1. Precipitation of minerals leads to disruption of diffusion barrier
 - 2. Minerals act as thermodynamic sink for elements in solution causing reduction in affinity



Changes in glass surface

- The preceding slides dealt mostly with what occurs in the leachate solution during corrosion
- What happens to the corroding glass surface during corrosion?
 - Stage I: silica-rich, hydrated layer starts to form



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 - -- Stage II: siepolyicher/zydiratedoaylenstation tonforamorphisis, etc. reactions change gel structure



Reversible reactions as solution and gel form "pseudo-equilibrium" relationship

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Reversible reactions as solution and gel form "pseudo-equilibrium" relationship

– constant pH

- slight increase in

solution concentration

- structural changes in

gel - densification

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 leachate solution is supersatured w.r.t. many phases

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- slight increase in solution concentration

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- gel starts aging during
 Stage II
 - Ostwald ripening
- secondary mineral phases appear
 - clays
 - C-S-H (if Ca present)
 - C-A-S-H (id.)
 - zeolite seeds



 leachate solution is supersatured w.r.t. many phases



Changes in glass surface

- The preceding slides dealt mostly with what occurs in the leachate solution during corrosion
- What happens to the corroding glass surface during corrosion?
 - Stage III: depending on chemistry, nucleation of crystalline secondary phases (zeolites) occurs

- reaction front proceeds into bulk glass until source is depleted or repassivation occurs
- concentration of some glass constituents in solution increases



What leads to zeolitization?

Hydrogel aging

- Systems tend towards lowest energy state → Ostwald ripening
- Glass is thermodynamically metastable
 - \Rightarrow Less stable than crystalline counterpart
- Gel aging decreases the thermodynamic instability of the metastable states
- $\Delta G_{glass} > \Delta G_{gel} > \Delta G_{crystal}$ corrosion reaction progress
- Gels age via step-wise progression through intermediate stages
 - Restructuring, de-watering
- For some glasses/minerals, final gel aging step is zeolitization
- For compositions that don't zeolitize, gel goes to clay



Zeolitization

- Process of conversion from aluminosilicate gels to crystalline zeolites
 - Synthetic methods (lab & industrial)
 - Linde zeolite A industrial
 - Basaltic and HLW glasses lab
 - Geopolymers
 - Natural synthesis (alkaline, geothermal systems)
 - Rhyolitic volcanic glass alteration
- Varying nucleation mechanisms
 - Autocatalytic
 - Heterogeneous
 - Homogeneous





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- [SB] is strong base concentration
- [WA] is weak acid concentration
- Both [SB] and [WA] released as glass/mineral dissolves:

 $M_2O + SiO_2 + B_2O_3 + 6H_2O$ $\rightarrow 2M^+ + 2OH^- + H_4SiO_4 + 2H_3BO_3$ strong base weak acid weak acid

- [SB] from alkali and alkaline earth
 - Li₂O, K₂O, Na₂O, CaO, BaO, etc.
 - 1 mol $M^+ \rightarrow 1$ mol OH^-
 - 1 mol $Me^{2+} \rightarrow 2$ mol OH^{-}



• [SB]-[WA]>0 \Rightarrow Stage III \rightarrow Zeolitization



Excess OH⁻ mineralizing agent ≡

 $(OH^{-})_{ex} = (OH^{-})_{moles} - (H^{+})_{moles}$ or $(OH^{-})_{ex} = (OH^{-})_{moles} - (2AlO_{2}^{-})_{molar}$

• Drives zeolite stoichiometry

 $(Si/Al)_{zeolite} = 1 + b \left(\frac{[SiO_2]}{[OH^-]} \right)_{solution}$



- Controls gel solubility
- Determined by total alkali content and buffering equilibria afforded by silica, aluminate, and boric acid species in solution

$$\Rightarrow [OH^{-}]_{ex} = [SB] - [WA] = [SB]_{ex}$$



- Solutions are typically saturated w.r.t. both clay and zeolite minerals
- AI coordination is important
 - Acidic \rightarrow ^[6]Al (octahedral)
 - Basic \rightarrow ^[4]Al (tetrahedral)

Stage I

pН

glass

Al+3

gel

- [6]Al³⁺ preferentially forms clays
- ^[4]AI(OH)₄ preferentially forms zeolites

 $Si(OH)_4 + AI^{3+}$ exist in solution

Residual

Rate

clay

time

Stage II pH is buffered

- Si is primary zeolite building block
- AlO₂⁻ origin of framework charge
- Alkali ions charge balance and/or guest molecules

Solution is saturated with respect to clay and zeolite Al³⁺ is in octahedral coordination as ^[6]Al and stabilizes clays preferentially

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time

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itime

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DURING ZEOLITIZATION (a textbook tutorial that address this phenomena)

- Alkalinity is one of the most important parameters for the control of zeolite crystallization
- Alkalinity determines the zeolite composition and is responsible for the type of crystallized product produced
- Silicate, aluminate, and aluminosilicate species in the solution are important for the crystallization mechanism but synthesis usually proceeds in the presence of an amorphous gel, i.e. a hydrogel.
- The solubility of the gel phase also depends on the alkalinity.
 - The presence of the gel (in waste glasses the gel + glass) assures the supersaturation of the system which is needed for the nucleation and growth processes
- SiO₂ is considered the primary building unit needed to form the zeolite framework
- AlO₂⁻ is considered the origin of the framework charge
- Alkali cations are considered the counter ions for the framework charge
- Most importantly, the OH⁻ is considered the mineralizer/catalyst

H. Lechert, in "Verified Syntheses of Zeolitic Materials," Elsevier, New York, 2001 266pp. J. C. Jansen, in Introduction to Zeolite Science and Practice, H. van Bekkum, E. M. Flanigen, J. C. Jansen (eds.), Elsevier, Amsterdam, p. 77-136 (1989).



How do we predict waste glass performance?

• HLW \rightarrow need to predict performance for 10³ – 10⁶ years.

-Accelerated testing methods were developed (Slide #3)

• Tests are easy to develop

→Proving that the tests accelerate the correct mechanism is difficult

• Writing models is easy

→ Proving that the models are correct is hard to demonstrate

• ASTM C1174

- Road Map for using tests and models
- Includes: glass, canister, and cement
- Validation w/ natural analogs

Accelerating the Correct Mechanism in Short Term (ST) Testing to Simulate LT is Very Important



* As defined at the August, 1999 NAS/NRC Workshop on Test Methods and Models to Simulate Accelerated Aging of Infrastructure Materials

ASTM C-1174 "The Roadmap to Predicting

Long-term Behavior"

Title: "Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste"

A roadmap for the steps involved in predicting long-term behavior:

- (1) problem definition
- (2) testing
- (3) modeling
- (4) prediction
- (5) model confirmation.

Many iterations between testing and modeling





- Research Agenda for Test Methods and Models to Simulate the Accelerated Aging of Infrastructure Materials: Report of a Workshop, NAS Publication, 1999.
- Jantzen, C.M., Trivelpiece, C.L., Crawford, C.L., Pareizs, J.M., Pickett, J.B., "Accelerated Leach Testing of GLASS (ALTGLASS): I. Informatics Approach to High Level Waste Glass Gel Formation and Aging." IJAGS. 8 [1], 2017, pp 69-83.
- Jantzen, C.M., Trivelpiece, C.L., Crawford, C.L., Pareizs, J.M., Pickett, J.B., "Accelerated Leach Testing of GLASS (ALTGLASS): II. Mineralization of Hydrogels by Leachate Strong Bases." IJAGS. 8 [1], 2017, pp 84-96.
- 4. Trivelpiece, C.L., Rice, J.A., Kabius, B. A., Jantzen, C.M., Pantano, C.G., "Corrosion of Fibers in Alkaline Solutions." JACerS. 100 [10], 2017, pp 4533-4547.



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End of presentation



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