Form 1

Title of Information Submitted:

Highly Selective Sorbents for Radiological Cs^+ and Sr^{2+} Ion Removal from Contaminated Seawaters

Organization Name (or Personal Name)

Sandia National Laboratories

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Form 2

Technology Information	
Area	3 (Select the number from “Areas of Technologies Requested”)
Title	**Highly Selective Sorbents for Radiological Cs^+ and Sr^{2+} Ion Removal from Contaminated Seawaters**
Submitted by	**Tina M. Nenoff**

1. **Overview of Technologies** (*See Appendix for complete list and sorption information.*)

We have over 20 years of success in the development and specific tuning of novel materials to needed selectivity as sorbent and high durability as waste forms. Below is a brief review of the most relevant materials for the needs at Fukushima in the area of **Removal of radioactive materials from the seawater in the harbor (3). See Figure 1 in Appendix.**

- **CSTs:** We discovered and developed the **Crystalline Silicotitanates** (**CSTs**, Sandia ownded and patented # 6,479,427 and # 6,110,378) in the mid 1990s for Cs+ removal from mixed aqueous streams over the entire pH scale. (see Figure 2) UOP licensed and commercialized it (products names IONSIEV IE-910 and IE-911) for use in US waste sites. April 2011, I was contacted by the US Dept of Energy to analyze CSTs for Cs+ removal from seawater. It outperformed all manufactured and mineral zeolites and clays (published 2011). Honeywell UOP LLC relicensed the CSTs from Sandia in 2011 and restarted large-scale production for use in the SARRY process, currently in use at Fukushima. It is a pelletized ceramic molecular sieve and used in aqueous columns or batch systems; can be incorporated into mesh nets.

- **Silicotitanate Sorption Materials**: I co-discovered and developed a number of silicotitanate sorption and in-situ sorption/waste form materials that are highly selective for Cs+ (Sandia owned and patented #6,482,380). They are ceramic based and used in aqueous columns or batch systems; can be incorporated into mesh nets.

- Waste Form: I and my team have proven that CSTs can successfully be incorporated into Glass waste forms (Borosilicate Glass; Sandia low temp sintering Bi-Si glass waste form (Sandia owned and patented #8,262,950)). It can also be heat treated and form a 1-step ceramic pollucite waste form stable to Cs+ -> Ba2+ oxidation state changes with decay.

- **SOMS: I co-discovered and developed the Sandia Octahedral Molecular Sieves** (SOMS, Sandia owned and patented #7,122,164 and # 6,596,254) **for Sr^{2+} removal** over the entire pH scale. It is highly selective for Sr^{2+} over monovalent cations and against competing (eg., Na^+, Cs^+) cations. (See figure 3) It is a molecular sieve easily pelletized and used in aqueous columns or batch systems; can be incorporated into mesh nets. These phases have high selectivity for various metal ions also (see patent). Gamma irradiation testing completed with no detriment to the sorption material or loss of the ion.

- Waste Form: I and my team have proven that Sr-SOMS can be heat treated at 450°C to pervoskites (with no loss of Sr) to form a stable ceramic waste form or be incorporated into our durable Sandia low temp sintering Bi-Si glass waste form (Sandia owned and patented # #8,262,950).

- I co-discovered and developed an **in-situ iodide and iodate immobilization process** from aqueous streams; especially useful in caustic streams (Sandia owned and patented #8,383,021). This low energy, low cost process produces durable, mineral analog, Bi-O-I phases and can be performed in batch or stream processes, and importantly, in-situ to the aqueous stream. Gamma irradiation testing completed with no detriment to the resultant capture material / waste form.

- I co-discovered and developed (Sandia owned and US Patented # 8,262,950) a **low temperature sintering, highly durable, glass based "universal" Waste Form** that is Bi-Si-O based and that successfully incorporates known getter materials for nuclear industrial sorption; it forms a Glass Composite Material waste form (GCM). Durability studies of SPFT, PCT and MCC-1 indicate it has durability greater or equal to nuclear waste glasses. We have successfully included > 20wt % rad-gas or rad-ion loaded zeolites, clays, molecular sieves, metal-organic frameworks (MOFs), etc. The glass sinters at 550°C low enough that volatilization is negligible (eg., AgI-Zeolite has no Iodine loss). Gamma irradiation testing completed with no detriment to the waste form. (See figure 4a,b)

- I co-discovered and developed (Sandia owned and US Patented 13/674,777 filed November 12, 2012, and international PCT patent application PCT/US2012/64698, filed November 12, 2012) a **binder-free pelletization** process that is successfully used on zeolites, molecular sieves and metal-organic frameworks. Surface area, sorption capacity, durability, crystallinity, etc. are all retained post pelletization process. (See figure 5.)

- I co-discovered and developed **metal-organic frameworks (MOFs) for the sorption of radiological fission gases** (eg., Iodine gas, I_2), and the 1-step formation of MOF-I_2 interim waste form via amorphization. (Sandia owned and US and PCT Patent Applications filed October 23, 2012.) This allows for high sorption capacity and non-HIPping easy mechanical pressing to collapse overall MOF framework and destroying pathway for gas escape, thereby rendering material an interim waste form. Our studies show enhanced gas retention with time and temperature. Gamma irradiation testing completed with no detriment to the sorption material or loss of the gas.

1. **Notes**

- **Gamma irradiation** testing of materials (listed above either performed on radwaste (eg., CSTs in Fukushima and Milton Valley) or were irradiated at the Sandia Gamma Irradiation Facility (GIF; both (a) long-term exposure/low dose:□0.1 Rads/sec, with an overall dose of 2.59×10^5 Rads (2218Gy), and (b) short-term exposure/high dose:□800 Rads/sec, 1×10^6 Rads (10,000 Gy)

- **Technology readiness level**

CSTs/IE-910 & IE-911: TRL 9 in use at Fukushima in SARRY process
Other Silicotitanates: TRL 3 (nuclear and metal ion removal)
SOMS: TRL 5 tested at Sandia, US waste sites, Russian sites (nuclear)
Bi-I-O: TRL 4 (nuclear)
Pollucite Cs/Si/Ti waste forms: TRL 5 (tested at SRNL; nuclear)
Low Temp Sintering Bi-Si glass waste forms: TRL 6 (durability testing completed; nuclear)
Pelletization Method: TRL 4 (nuclear and catalysis)

2. **Challenges: Minimal Challenges, generally around scale up production. However ongoing collaborations in the production of CSTs enables a clear pathforward with our materials.**

- The CSTs are commercially available, in production, and in use at Fukushima.
- The SOMS materials are similar in synthesis procedure; it needs scaleup and production.
- The basis of the low temperature Bi-Si Glass is a commercial product from Ferro; The durability studies and tests are completed. Optimization of loading levels of sorption materials and scale up are needed.
- Bi-I-O needs to be tested on large scale.
- Pelletization needs to be tested on large scale.

3. **Others:**

Related Sandia & Nenoff patents:

2. Method of using novel silico-titanates, 6,110,378, August 29, 2000
3. Silico-titanates and their methods of making and using, 6,479,427, November 12, 2002
4. Cesium Silicotitanates for Ion Exchange and Waste Storage, 6,482,380, November 19, 2002.
5. Niobate-based octahedral molecular sieves, 6,596,254, July 22, 2003.

6. Niobate-based octahedral molecular sieves, 7,122,164, October 17, 2006.
7. Low Sintering Temperature Glass Waste Form for Sequestering Radioactive Iodine, 8,262,950, September 11, 2012
8. Mixed-Layered Bismuth-Oxygen-Iodine Materials for Capture and Waste Disposal of Radioactive Iodine, 8,383,021, February 2013
9. Pelletized Molecular Sieves and Method of Making Pelletized Molecular Sieves, US Patented 13/674,777 filed November 12, 2012, and international PCT patent application PCT/US2012/64698, filed November 12, 2012
10. System and Method for the Capture and Storage of Waste, US and PCT Patent Applications filed October 23, 2012

Recent Publications that support the Patents:

1. Hughes, J.T.; Sava, D.F.; Nenoff, T. M.; Navrotsky, A. "Thermochemical Evidence for Strong Iodine Chemisorption by ZIF-8", *J. Amer. Chem. Soc.*, **2013**, Just Accepted: 10.1021/ja406081r.
2. Sava, D.F.; Chapman, K.W.; Rodriguez, M. A.; Greathouse, J. A.; Crozier, P. S.; Zhao, H.; Chupas, P. J.; Nenoff, T.M. "Competitive I_2 Sorption in Cu-BTC from Humid Gas Streams", *Chem. Mater.*, **2013**, *25* (13), 2591.
3. Rodriguez, M., Garino, T.J.; Rademacher, D.X.; Zhang, X.; Nenoff, T.M., "Synthesis of Ba- and Fe- Substituted $CsAlSi_2O_6$ Pollucites", *J. Amer. Ceram. Soc.*, **2013**, *96*(9), 2966.
4. Sava, D.F.; Garino, T.J.; Nenoff, T. M. "Iodine Confinement into Metal-Organic Frameworks (MOFs): Low Temperature Sintering Glasses to form Novel Glass Composite Material (GCM) Alternative Waste Forms", *Ind. Eng. Chem. Res*, **2012**, *51* (2), 614.
5. Nenoff, T.M.; Krumhansl, J.L. "Cs^+ Removal from Seawater by Commercially Available Molecular Sieves", *Solvent Extraction & Ion Exchange*, **2012**, *30*, 33.
6. Chapman, K.W.; Sava, D.F.; Halder, G.J.; Chupas, P.J.; Nenoff, T.M. "Trapping Guests Within a Nanoporous Metal-Organic Framework", *J. Amer. Chem. Soc.*, **2011**, *133* (46), 18583.
7. Sava, D.F.; Rodriguez, M.A.; Chapman, K.W.; Chupas, P.J.; Greathouse, J. A.; Crozier, P.S.; Nenoff, T.M. "Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8", *J. Amer. Chem. Soc.*, **2011**, *133* (32), 12398.
8. Garino, T.J.; Nenoff, T.M.; Krumhansl, J.L.; Rademacher, D. "Low-Temperature Sintering Bi-Si-Zn Oxide Glasses For Use in Either Glass Composite Materials or Core/Shell ^{129}I Waste Forms", *J. Amer. Ceram. Soc.* **2011**, *94*(8), 2412.
9. Park, T-J.; Garino, T.J.; Nenoff, T.M.; Rademacher, D.; Navrotsky, A. "The Effect of

Vacancy and Ba-Substitution on the Stability of the $CsTiSi_2O_{6.5}$ Pollucite”, *J. Amer. Ceram. Soc*. **2011**, *94*(9), 3053.

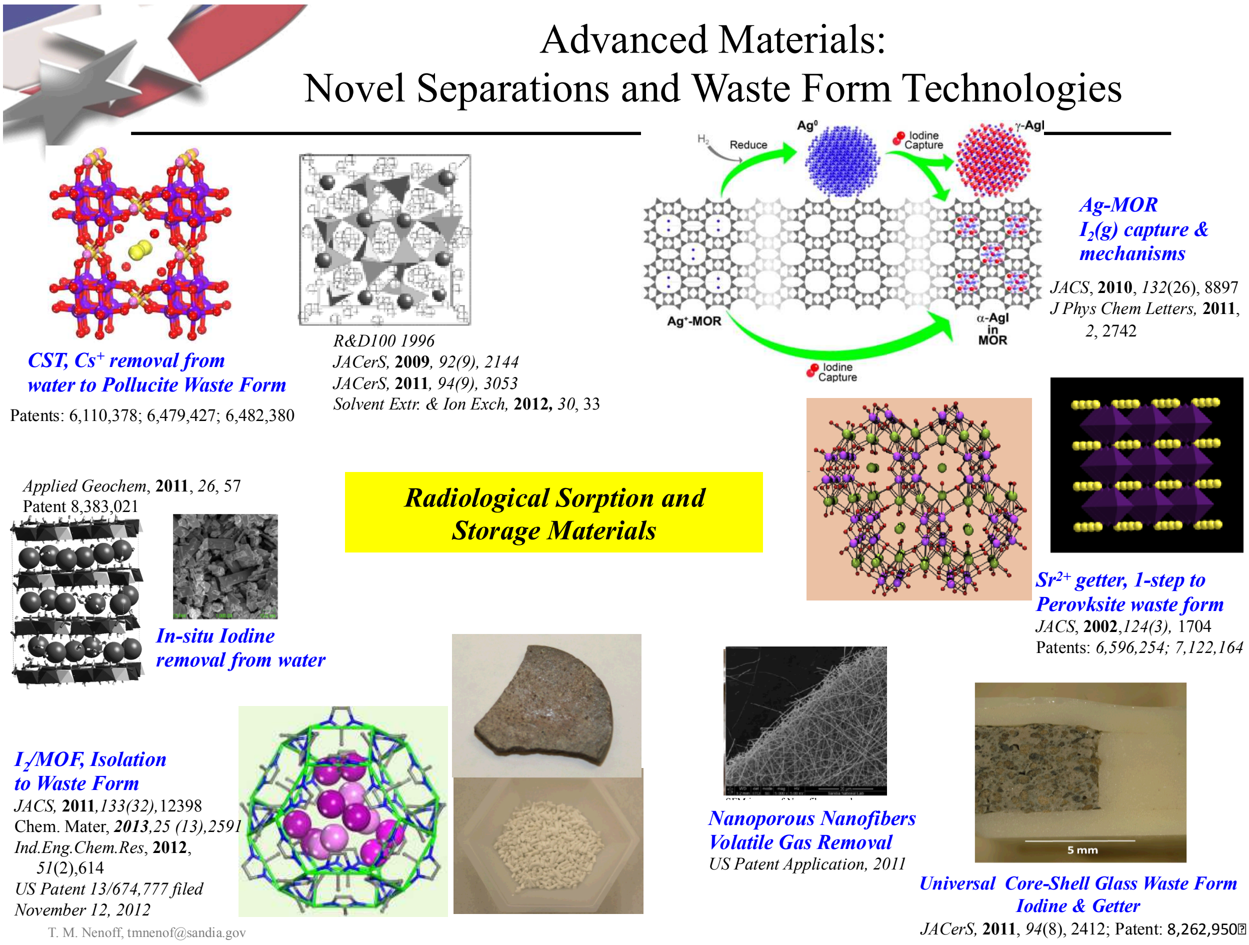
10. Krumhansl, J.L.; Nenoff, T. M. “Hydrotalcite-like Layered Bismuth-Iodine-Oxides as Waste Forms” *Applied Geochemistry*, **2011**, *26(1),* 57.
11. Chapman, K; Chupas, P.; Nenoff, T.M. “Radioactive Iodine Capture in Silver-Loaded Zeolites Through Nanoscale Silver Iodide Formation” *J. Amer. Chem. Soc.*, **2010**, *132* (26), 8897.
12. Nyman, M.; Bonhomme, F.; Maxwell, R. S.; Nenoff; T. M. “First Rb-silicotitanate phase and its K- Structural Analog: New Members of the SNL-A Family (*Cc*-$A_2TiSi_6O_{15}$; A=K, Rb, Cs)”. *Chem. Mater*., **2002**, *13*(12), 4603.
13. Nyman, M.; Tripathi, A; Parise, J. B.; Maxwell, R. S.; Nenoff, T. M. “Sandia Octahedral Molecular Sieves (SOMS): Structural Effects of Charge-Balancing the Heteroatomic-Substituted Framework.” *J. Amer. Chem. Soc*., **2002**, 124(3), 1704.
14. Nyman, M., Gu, B. X., Wang, L. M., Ewing, R. C., Nenoff T. M., "Synthesis and Characterization of a New Microporous Cesium Silicotitanate (SNL-B) Molecular Sieve." *Micro. and Meso. Mater*, **2000**, *40:1-3*, 115.
15. Nenoff, T. M.; Thoma, S. G.; Krumhansl, J.L. “Stability and Selectivity of TAM5: A Silicotitanate Molecular Sieve for Radwaste Cleanup.” Sandia National Laboratories, SAND96-2580, November 1996.

【Areas of Technologies Requested】

(1) Accumulation of contaminated water (Storage Tanks, etc.)
(2) Treatment of contaminated water (Tritium, etc.)
(3) Removal of radioactive materials from the seawater in the harbor
(4) Management of contaminated water inside the buildings
(5) Management measures to block groundwater from flowing into the site
(6) Understanding the groundwater flow

Appendix

Figure 1: Overview of Nenoff, et al., activities on Radiological Sorption Materials & Waste Forms



Advanced Materials:
Novel Separations and Waste Form Technologies

CST, Cs^+ removal from water to Pollucite Waste Form

Patents: 6,110,378; 6,479,427; 6,482,380

R&D100 1996
JACerS, **2009**, *92(9), 2144*
JACerS, **2011**, *94(9), 3053*
Solvent Extr. & Ion Exch, **2012**, *30*, 33

Ag-MOR
$I_2(g)$ capture & mechanisms

JACS, **2010**, *132*(26), 8897
J Phys Chem Letters, **2011**, *2*, 2742

Applied Geochem, **2011**, *26*, 57
Patent 8,383,021

In-situ Iodine removal from water

Radiological Sorption and Storage Materials

Sr^{2+} getter, 1-step to Perovksite waste form

JACS, **2002**,*124(3),* 1704
Patents: *6,596,254; 7,122,164*

I_2/MOF, Isolation to Waste Form

JACS, **2011**,*133(32)*,12398
Chem. Mater, ***2013***,*25 (13)*,*2591*
Ind.Eng.Chem.Res, **2012**, *51*(2),614
US Patent 13/674,777 filed November 12, 2012

Nanoporous Nanofibers Volatile Gas Removal

US Patent Application, 2011

Universal Core-Shell Glass Waste Form Iodine & Getter

JACerS, **2011**, *94*(8), 2412; Patent: 8,262,950

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Figure 2: Cs distribution coefficients of CSTs over pH range

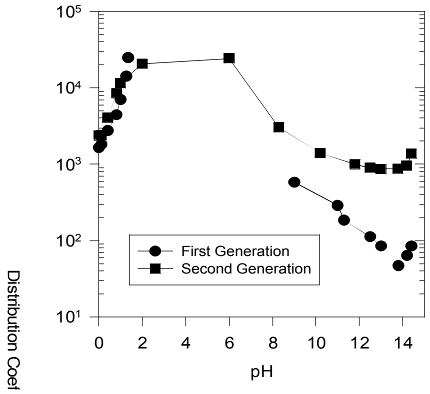


Figure 3: Selectivity (Kd, mL/g) of non-optimized SOMS for Sr as a function of pH and concentration of Na as a competing cation)

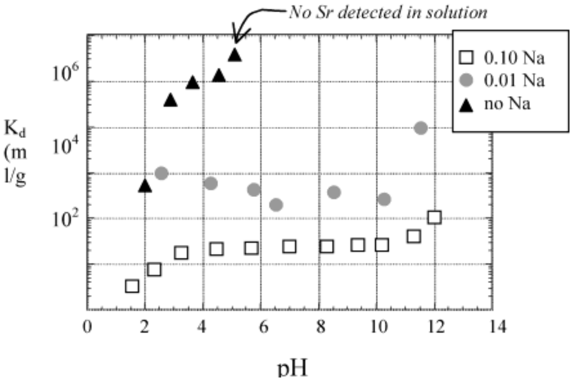
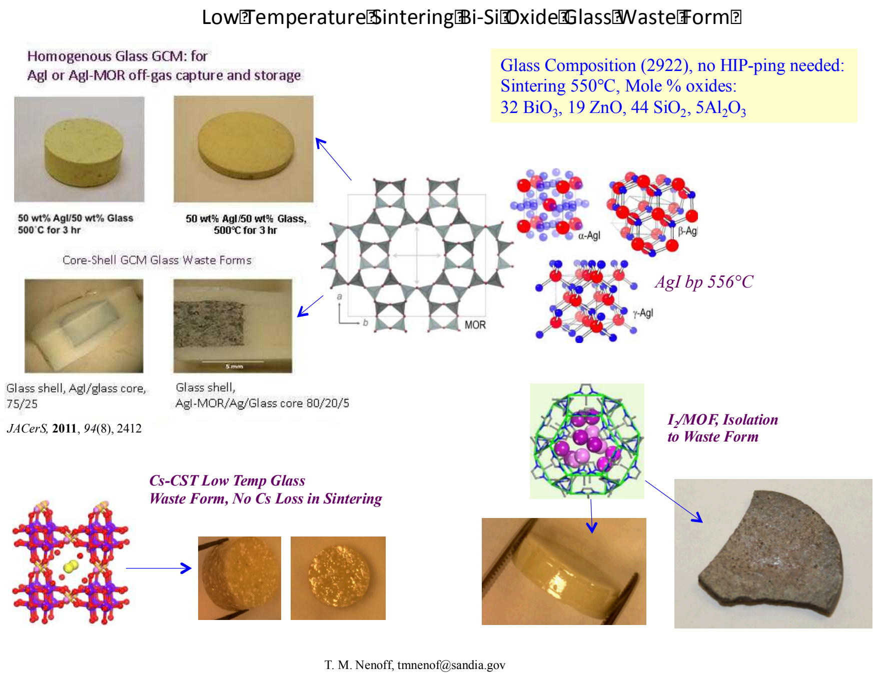


Figure 4: (a) Examples of Successful use of the Low Temperature Sintering Bi-Si oxide glass as a waste form; (b) durability studies showing durability of glass waste form is better or equal to nuclear glasses.

(a)



Low Temperature Sintering Bi-Si Oxide Glass Waste Form

Homogenous Glass GCM: for AgI or AgI-MOR off-gas capture and storage

Glass Composition (2922), no HIP-ping needed: Sintering 550°C, Mole % oxides: 32 BiO_3, 19 ZnO, 44 SiO_2, 5Al_2O_3

50 wt% AgI/50 wt% Glass 500°C for 3 hr

50 wt% AgI/50 wt% Glass, 500°C for 3 hr

Core-Shell GCM Glass Waste Forms

Glass shell, AgI/glass core, 75/25

Glass shell, AgI-MOR/Ag/Glass core 80/20/5

JACerS, **2011**, *94*(8), 2412

AgI bp 556°C

I_2/MOF, Isolation to Waste Form

Cs-CST Low Temp Glass Waste Form, No Cs Loss in Sintering

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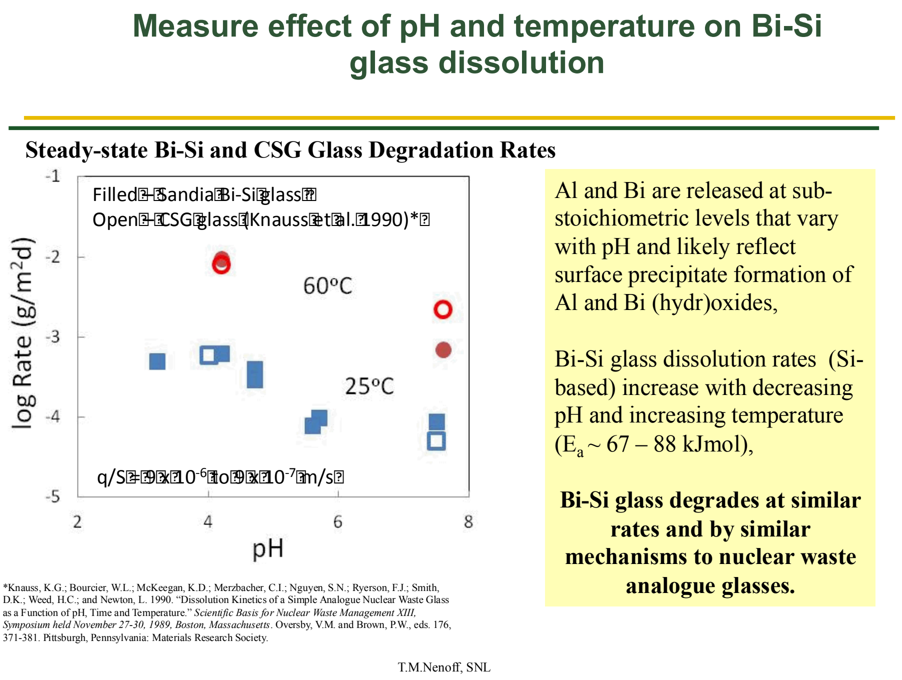
(b)



Measure effect of pH and temperature on Bi-Si glass dissolution

Steady-state Bi-Si and CSG Glass Degradation Rates

Al and Bi are released at sub-stoichiometric levels that vary with pH and likely reflect surface precipitate formation of Al and Bi (hydr)oxides,

Bi-Si glass dissolution rates (Si-based) increase with decreasing pH and increasing temperature (E_a ~ 67 – 88 kJmol),

Bi-Si glass degrades at similar rates and by similar mechanisms to nuclear waste analogue glasses.

*Knauss, K.G.; Bourcier, W.L.; McKeegan, K.D.; Merzbacher, C.I.; Nguyen, S.N.; Ryerson, F.J.; Smith, D.K.; Weed, H.C.; and Newton, L. 1990. "Dissolution Kinetics of a Simple Analogue Nuclear Waste Glass as a Function of pH, Time and Temperature." *Scientific Basis for Nuclear Waste Management XIII, Symposium held November 27-30, 1989, Boston, Massachusetts.* Oversby, V.M. and Brown, P.W., eds. 176, 371-381. Pittsburgh, Pennsylvania: Materials Research Society.

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Figure 5: Sorption data for as synthesized MOF ZIF-8 and after pelletization, with no change in adsorption capacity for Iodine gas.