

Degradation of Dome Cutting Minerals in Hanford Waste – 13100

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ABSTRACT

At the Hanford Tank Farms, recent changes in retrieval technology require cutting new risers in several single-shell tanks. The Hanford Tank Farm Operator is using water jet technology with abrasive silicate minerals such as garnet or olivine to cut through the concrete and rebar dome. The abrasiveness of these minerals, which become part of the high-level waste stream, may enhance the erosion of waste processing equipment. However, garnet and olivine are not thermodynamically stable in Hanford waste, slowly degrading over time. How likely these materials are to dissolve completely in the waste before the waste is processed in the Waste Treatment and Immobilization Plant can be evaluated using theoretical analysis for olivine and collected direct experimental evidence for garnet. Based on an extensive literature study, a large number of primary silicates decompose into sodalite and cancrinite when exposed to Hanford waste. Given sufficient time, the sodalite also degrades into cancrinite. Even though cancrinite has not been directly added to any Hanford tanks during process times, it is the most common silicate observed in current Hanford waste. By analogy, olivine and garnet are expected to ultimately also decompose into cancrinite. Garnet used in a concrete cutting demonstration was immersed in a simulated supernate representing the estimated composition of the liquid retrieving waste from Hanford tank 241-C-107 at both ambient and elevated temperatures. This simulant was amended with extra NaOH to determine if adding caustic would help enhance the degradation rate of garnet. The results showed that the garnet degradation rate was highest at the highest NaOH concentration and temperature. At the end of 12 weeks, however, the garnet grains were mostly intact, even when immersed in 2 molar NaOH at 80 °C. Cancrinite was identified as the degradation product on the surface of the garnet grains. In the case of olivine, the rate of degradation in the high-pH regimes of a waste tank is expected to depend on two main parameters: carbonate is expected to slow olivine degradation rates, whereas hydroxide is expected to enhance olivine dissolution rates. Which of these two competing dissolution drivers will have a larger impact on the dissolution rate in the specific environment of a waste tank is currently not identifiable. In general, cancrinite is much smaller and less hard than either olivine or garnet, so would be expected to be less erosive to processing equipment. Complete degradation of either garnet or olivine prior to being processed at the Waste Treatment and Immobilization Plant cannot be confirmed, however.

INTRODUCTION

The Hanford Tank Farm Operations Contractor has used water jet cutting methods to cut holes in the top of tanks so that new risers could be installed [1, 2]. Water jet cutting technology has a number of advantages over other technologies for the purpose, including experience of use and great contamination control. Water jet cutting uses high pressure water with an entrained abrasive mineral to cut through the concrete and steel in the tank surface. Garnet has been used

as the abrasive mineral to date in tank 241-C-107, but olivine is being considered for tank 241-C-105. The small amount of water and abrasive used for dome cutting will mix with the waste when the cutting is complete [2]. The tank temperature depends on the sludge depth, which varies as the waste is retrieved, but the temperature is expected to be near ambient.

Given the abrasive nature of garnet and olivine, these minerals may contribute to the erosion of equipment used to process the waste. Both garnet and olivine slowly degrade in high pH solutions like Hanford waste. The primary scientific question was whether or not garnet and olivine would sufficiently degrade in the caustic waste to prevent the enhanced erosion of downstream equipment; subsequently, the rate of mineral dissolution would determine if these minerals would completely degrade prior to being transferred to the Hanford Waste Treatment and Immobilization Plant (WTP). As a secondary goal, the ultimate reaction products of the silica from these minerals in the waste would be determined.

Olivine and garnet are both families of minerals, so there are different types of olivine and garnet. According to the vendor datasheet [3], the olivine intended for use at Hanford is 94% forsterite (Mg_2SiO_4) and 6% fayalite (Fe_2SiO_4) olivine. Analysis of the sample garnet with energy dispersive X-ray spectroscopy (EDS) as part of a scanning electron microscope (SEM) showed the garnet was an intermediate solid-solution of andradite (Ca-Fe garnet) and pyrope (Mg-Al garnet) (see Figure 1).

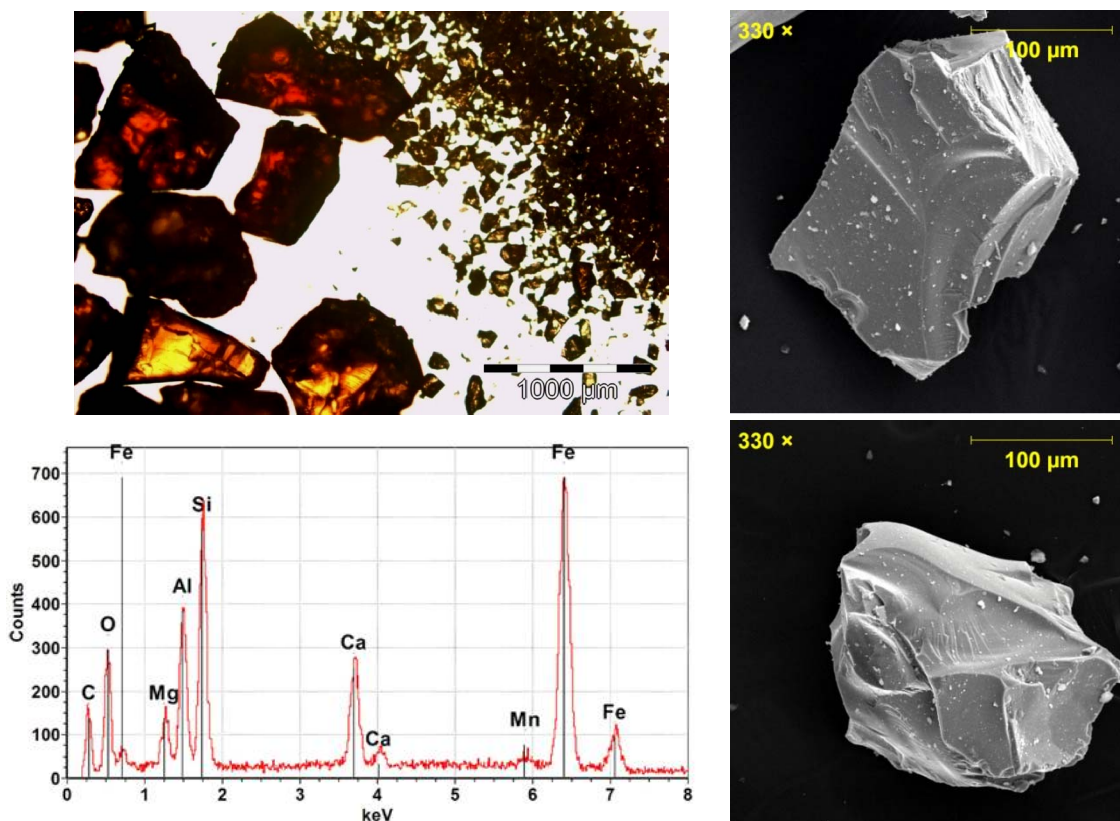


Fig. 1. Microphotograph of garnet before and after use for hydrocutting demonstration (top left); secondary electron images and energy dispersive spectrum of sample material (right and bottom).

There is already a large amount of information on forsterite olivine degradation at high pH reported in the scientific literature [4, 5, 6], but there is essentially no information available on garnet. However, Brady and Walther [4] found that the dissolution rate of essentially all silicate minerals increases with 0.3 power increase in pH in alkaline solutions. Direct experimental data was used to evaluate the degradation of garnet. The degradation rate of olivine was investigated theoretically, taking advantage of reaction mechanisms and data from the literature.

GARNET DEGRADATION

Materials and Methods

The garnet evaluated came from a simulated dome cut experiment. This experiment used commercially available garnet to cut a riser in simulated 241-C Tank Farm single-shell tank surface using water jet technology. While the garnet was in the meantime used in the cutting of a riser in the actual tank 241-C-107, the material for the experiments was provided by the vendor, Barton International, from a simulated cutting demonstration in 2010. Figure 1 shows the garnet before and after the test cut, demonstrating the large decrease in particle size upon cutting. The secondary electron image shows the fractures within the garnet due to the hydrocutting activity.

Garnet was used to cut the new 55-inch-diameter riser into single-shell tank 241-C-107 and the waste from tank 241-C-107 was ultimately transferred into tank 241-AN-101. The estimated composition of the tank 241-AN-101 supernatant liquid at that time is shown in Table I. The simulant was then amended with additional NaOH to raise the pH, because silicate minerals are known to degrade faster as the pH increases [4]. Thus, the NaOH amended simulants are expected to represent the upper bounding rate of garnet degradation. Aliquots were treated at both 25 and 80 °C. The waste was expected to be near 25 °C in the tanks, and 80 °C was used as high temperature that is expected to truly bound the degradation rate.

After preparing 3 liters of the supernatant liquid (1 liter of each caustic concentration), the garnet samples were weighed into 250-milliliters Erlenmeyer flasks made of Teflon. Then 250 milliliters of supernatant liquid were added to each of the flasks and either placed in the hood (25 °C) or into the drying oven set to 80 °C. After three weeks, the first samples were taken. Four samples were taken from the 2-Molar NaOH solutions for SEM analysis, since the 2-Molar solution should have had the highest impact on the integrity of the garnets.

After agitating and allowing several minutes for solids to resettle, a very small amount (about 250 microliters of slurry from the bottom of each flask) was sampled. Using vacuum filtration, this material was filtered onto 0.4-micrometer pore-size polycarbonate filters. After the filters had dried, the section with the most particulate was cut and affixed to a graphite planchet on an aluminum SEM stub, then coated with a thin conductive carbon coating with a graphite rod arc

sputter. The samples were examined on the ASPEX¹ SEM at the 222-S Laboratory on the Hanford Site.

TABLE I. Composition of Tank 241-AN-101 Supernatant Simulant

	Mass added [g]	Mol weight [g/mol]	Target molarity [mol/L]
NaAlO ₂ × H ₂ O ⁱ	70.80	100	0.708
Na ₂ CO ₃	45.80	106	0.432
Na ₂ C ₂ O ₄	8.20	134	0.061
KNO ₃	10.40	101	0.103
NaNO ₃	213.30	85	2.510
NaNO ₂	165.00	69	2.391
Na ₂ SO ₄	8.70	142	0.061
Na ₃ PO ₄ × 12H ₂ O × 0.25 NaOH ⁱⁱ	15.60	390	0.040
NaCl	12.70	58	0.217
Na ₂ Cr ₂ O ₇ × 2H ₂ O	2.00	298	0.007
NaOH add. 1	80.0	40	2
NaOH add. 2	4.0	40	0.1
NaOH add. 3	-- ⁱⁱⁱ	40	0.01

ⁱ In general, sodium aluminate contains 2 H₂O per formula unit – however, the material used in the lab contains the empirically determined amount of 1 H₂O (thus a molecular weight of 100 in Table I).

ⁱⁱ The ¼ mol NaOH is included by the manufacturer in the ACS grade sodium phosphate for stabilization purposes.

ⁱⁱⁱ The contribution from the Na-phosphate makes up 0.01 M caustic.

A 2-milliliter sample was taken from all tests for chemical analyses. The sample was diluted to 20 milliliters using de-ionized water and submitted to Advanced Technologies and Laboratories International for inductively coupled plasma atomic emission spectroscopy analysis for aluminum as well as for free hydroxide-determination by titration.

After 12 weeks, a garnet and liquid sub-sample was taken from each flask in addition for chemical analysis. The remainder of the solids was filtered and washed with de-ionized water until all water-soluble white precipitate was removed. The dried solids were weighed and optically inspected for signs of corrosion.

All samples had formed a white precipitate during the course of the treatment, which was intermingled with the garnet at the bottom of the flasks. Flexing the filter liberated most of the particulate from the filter surface. The loose particulate was allowed to collect in the center of the filter. This particulate was transferred to a small SEM stub that had been covered with a carbon adhesive tab. The stub was tapped lightly to remove loose particulate and then the top of a Petri dish was used to press the particulate in place. These were affixed to the SEM stub with a separate piece of conductive adhesive tape and carbon coated as above. The fine-grained powder

¹ ASPEX is a registered trademark of ASPEX Corporation, Delmont, Pennsylvania, USA.

on the filter cakes of each sample were analyzed with SEM-EDS. Samples of the filtered and washed precipitates were taken for X-ray diffraction and SEM-EDS analysis.

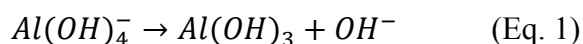
Experimental Results

Table II reports solution phase sample results for the garnet degradation tests at both 25 and 80 °C. The degradation of silicate minerals consumes hydroxide, but the hydroxide concentration of the waste actually increased with time. This increase in free hydroxide concentration is concomitant with a decrease in aluminum concentration.

TABLE II. Results of Chemical Analysis of Supernate for Al and OH (in microgram/milliliter)

Supernate Sample		Original	3 weeks dissolution	6 weeks dissolution	9 weeks dissolution	12 weeks dissolution	
25 °C	NaOH add. 1	Al	23,200	20,200	18,900	19,400	21,485
		OH	39,700	33,700	32,000	32,700	36,567
	NaOH add. 2	Al	23,100	15,800	12,000	17,900	11,244
		OH	3,460	5,990	8,080	3,830	9,405
	NaOH add. 3	Al	23,900	13,100	19,900	9,800	18,161
		OH	1,630	6,390	3,990	8,290	5,455
80 °C	NaOH add. 1	Al	23,200	20,800	20,000	20,600	19,856
		OH	39,700	34,100	33,300	35,700	33,740
	NaOH add. 2	Al	23,100	20,700	20,300	16,200	9,593
		OH	3,460	3,080	3,060	6,590	10,140
	NaOH add. 3	Al	23,900	20,700	20,900	13,800	7,414
		OH	1,630	1,510	1,320	8,660	10,091

The X-ray diffraction pattern of the particles separated from the garnet in Figure 2 shows that gibbsite was the dominant mineral present after a mild water wash of the loose precipitate in the flasks. Gibbsite is known to precipitate via the reaction



where one mole of free hydroxide is produced per aluminum precipitated. Thus, this reaction can account for the increase in hydroxide concentration and decrease in aluminum concentration. Gibbsite did not appear to precipitate in the samples amended with 2 molar (M) NaOH at either 25 or 80 °C. The supernatant simulant used was modeled after the supernate in tank 241-AN-101. Hanford waste is known to have elevated concentrations of aluminum for a given hydroxide concentration [7].

A complicating factor of the aluminum precipitation is that it means that the aluminum and free hydroxide concentration could not be used to monitor garnet dissolution in tank waste. The liquid phase concentrations of other garnet constituents could not be used to monitor dissolution rate because of their low solubility in waste; they simply re-precipitate in another form as soon as

they dissolve. Thus, going forward the focus will be on the monitoring of the garnet surface using SEM.

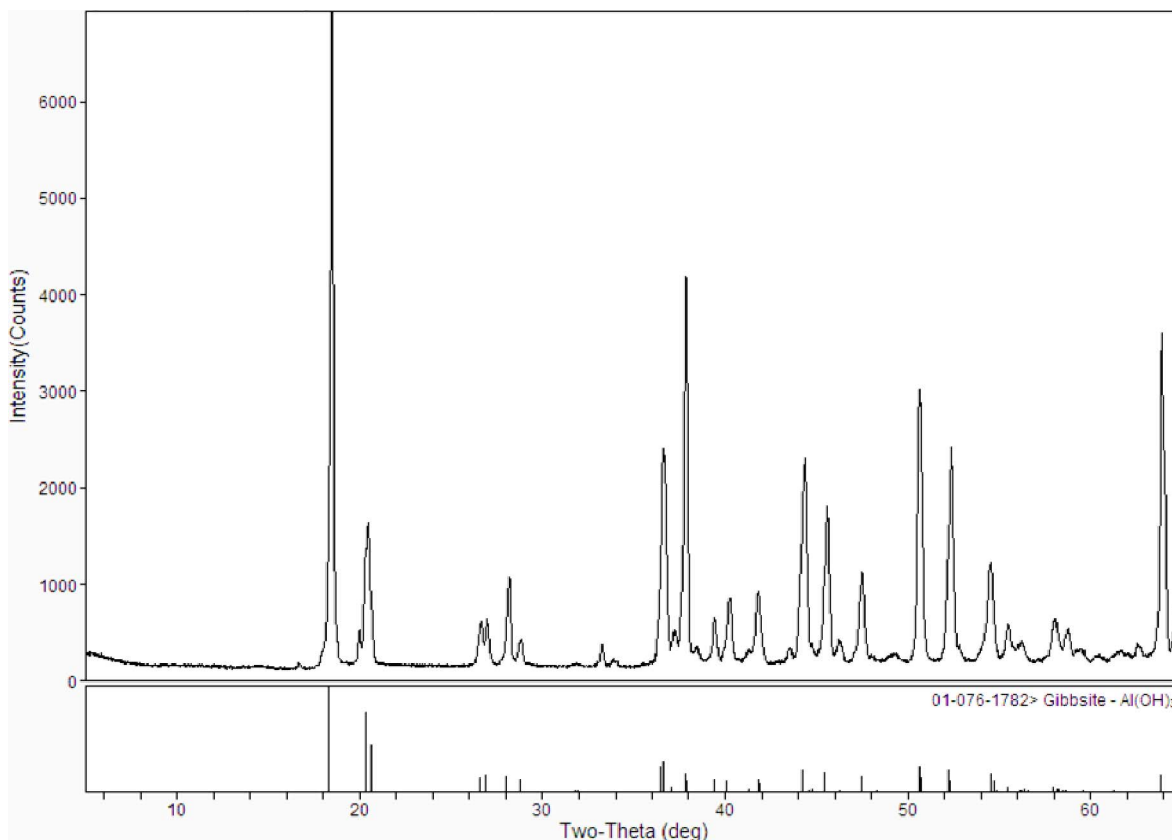


Fig. 2. X-ray diffraction pattern of precipitate after 12 weeks.

The presence of gibbsite in the samples made it difficult to identify damage to the garnet with the SEM. Consequently, the following discussion focuses on the 2 M NaOH samples that had no gibbsite precipitation. As noted earlier, the 2 M NaOH samples are expected to have the most rapid degradation rate because silicate dissolution is promoted by high hydroxide concentrations [4]. What can be qualitatively said, however, is that the samples with less free hydroxide showed less damage to garnet than the 2 M NaOH samples.

Essentially no damage was seen to the garnet after three weeks at 25 °C. SEM analysis, however, identified a mixture of sodium carbonate hydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, Thermonatrite) and sodium fluoride phosphate hydrate ($\text{Na}_7\text{F}[\text{PO}_4]_2 \cdot 19\text{H}_2\text{O}$, Natrophosphate) in the 25 °C samples (Figure 3). These salts likely precipitated because of the added sodium when the tank 241-AN-101 simulant sample was amended with NaOH.

The 80 °C samples also had a white precipitate, but in this case the precipitate was a single phase with a morphology and a sodium aluminosilicate composition that is consistent with the mineral cancrinite ($\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}[\text{NO}_3]_2$).

The small crystallite size (see Figure 4) suggests that the phase may be poorly crystalline. The garnet is the only source of silica in these experiments. Figure 5 shows an aggregate of the white precipitate, a close-up of the area within the box, and an EDS spectrum from the spot marked with the “+.”

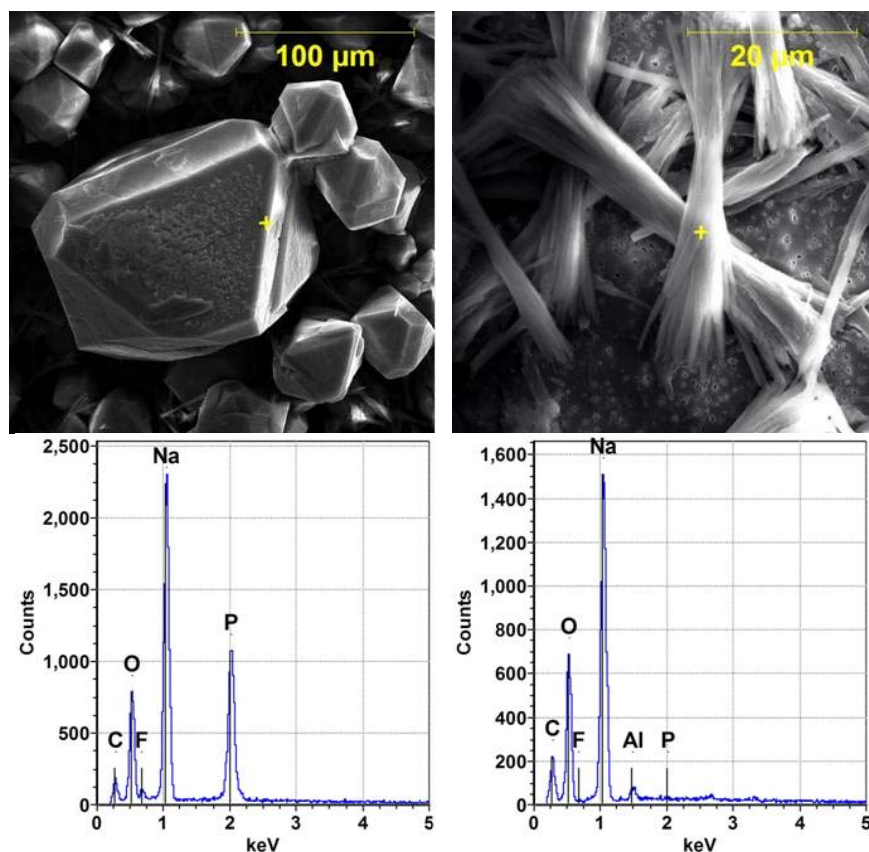


Fig. 3. Secondary electron image and energy dispersive X-ray spectrum of natrophosphate (left) and thermonatrite (right) after three weeks at 25 °C.

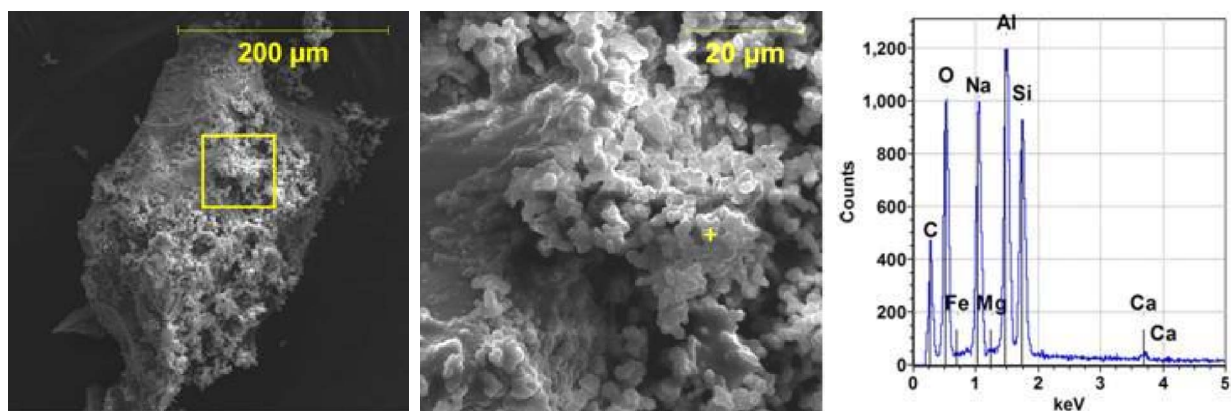


Fig. 4. Secondary electron image and energy dispersive X-ray spectrum of heavily coated garnet grain after three weeks at 80 °C.

The SEM cannot conclusively identify cancrinite because there are many silicates that have both Na, Al, and Si as the dominant SEM-EDS observable elements. Nonetheless, the similarity with electron micrographs from other cancrinites identified in Hanford waste [8] is compelling.

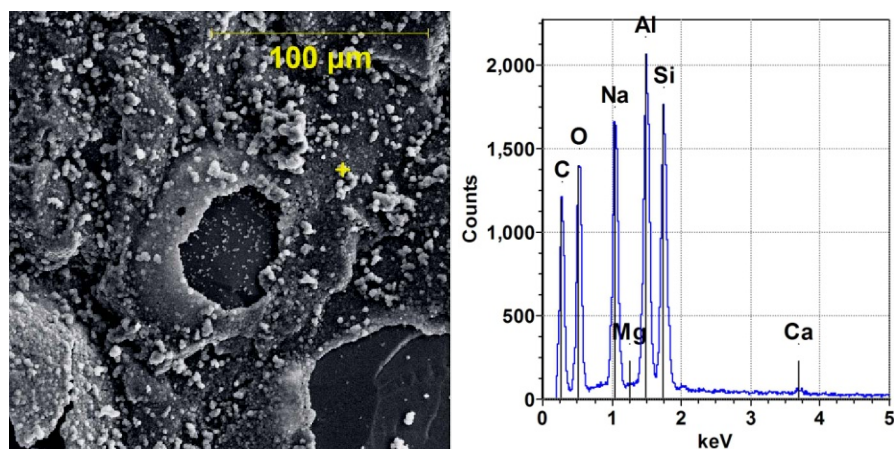


Fig. 5. Secondary electron image and energy dispersive X-ray spectrum of a garnet partially coated with sodium aluminosilicate precipitate after 12 weeks at 80 °C.

In addition to the loose aggregates of the sodium aluminosilicate, the garnets treated at 80 °C are lightly to heavily coated with this phase. There is little evidence of etching or corrosion on the uncovered garnet surfaces. It is easy to see how these sodium aluminosilicate spherules could coalesce and form the continuous coatings and particle aggregates in Figure 4. These coatings, unless disturbed, would serve as a barrier to slow the reaction converting garnet to sodium aluminosilicate. Coatings from almandine garnet reaction products have been observed to retard corrosion in nature [9, 10].

There was minimal damage observed to the garnet in the simulant in the six- and nine-weeks samples at 25 °C (to save space, the SEM figures are not shown here). After 12 weeks, the 25° C samples show slight but obvious evidence of a corrosive reaction. Still, after 12 weeks there are numerous surfaces that appear to be fresh and relatively unaffected by the caustic. Figure 6 is a typical surface with etch pits along the edges and sharp conchoidal fractures. Figure 7 shows the white sodium aluminosilicate suspected to be cancrinite that precipitated from this sample.

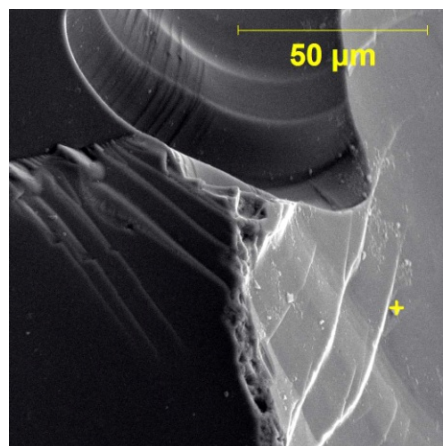


Fig. 6. Secondary electron image showing small etch pits and fresh surfaces of garnet after 12 weeks at 25 °C.

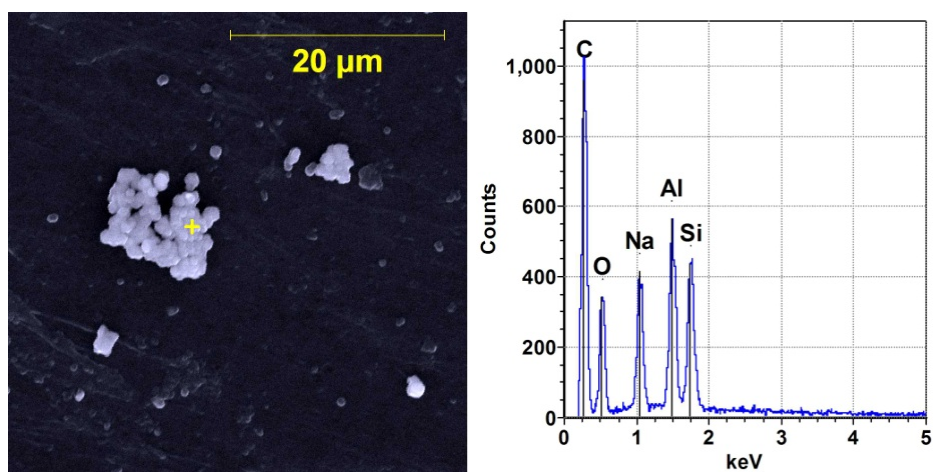


Fig. 7. Secondary electron image and energy dispersive X-ray spectrum of the sodium aluminosilicate precipitate after 12 weeks at 25 °C.

At 80° C and six and nine weeks, the garnet shows increasing amounts of damage as observed as cracks on the surface in the SEM (data not shown). At 12 weeks, the 80 °C, 2-M hydroxide samples continue to show obvious evidence for garnet dissolution and sodium aluminosilicate precipitation. The dissolution and deposition is shown on the garnet surface in Figure 5. A thicker coating of sodium aluminosilicate is evident than at three weeks. Figure 8 demonstrates substantial corrosion of the garnet surface. While these figures show increasing degradation of the garnet, the garnet is still largely intact, even when held at 80 °C for 12 weeks. The coating of (suspected) cancrinite on the surface may slow the rate of degradation.

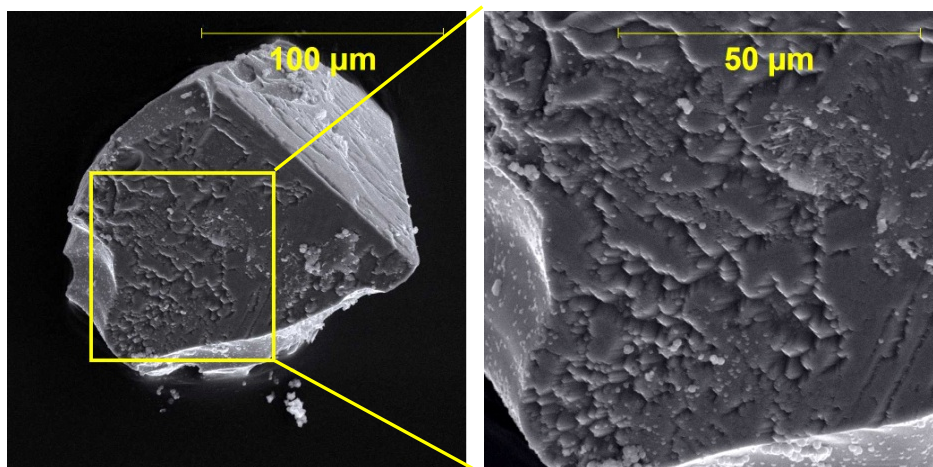


Fig. 8. Secondary electron images of overview (left) and close-up (right) of the corroded garnet surface after 12 weeks at 80 °C.

OLIVINE DEGRADATION

General

Wogelius and Walther [6] determined that the rate of forsterite olivine dissolution at pH values greater than 8 was given by the following equation:

$$R = 2.33 \times 10^{-17} a_{H^+}^{-0.31} \quad (\text{Eq. 2})$$

where R is the rate in moles per cubic centimeter of surface area per second, and a_{H^+} is the activity of H^+ in solution, which is a function of pH. The pH of Hanford waste ranges from about 10.3 to free hydroxides greater than 2 M. Thus, the term in Equation 2 is small, and raised to -0.3 power, results in a large number. Solving Equation 2 for pH 10.3 and pH 14 results in a number of moles of olivine dissolved per centimeters squared of surface area between 1.15×10^{-06} and 1.61×10^{-05} . Using the molecular weight of Mg_2SiO_4 , this comes out to be between 1.61×10^{-04} and 2.26×10^{-03} grams of olivine per year per cubic centimeter of surface area.

Unfortunately, this number cannot simply be used in Hanford waste applications, because Hanford waste is not identical to these solutions. It is not clear how solution ionic strength would affect the results, for instance. Hanford waste is typically more than 5 molar in sodium, whereas the experiments of Wogelius and Walther [6] were performed at 0.01 M Na concentration. Thus, it is not clear how two orders of magnitude difference in ionic strength would affect the rate. Likewise, other anions in the waste may impact the rate. These differences limit our ability to quantitatively extrapolate the literature results to tank waste conditions.

Earlier studies showed that silica selectively dissolves from the forsterite surface at high pH, leaving a surface of magnesium oxide linkages [5, 11]. They found that anything that adsorbed onto this surface can influence the rate of forsterite dissolution. For instance, they found that

carbonate adsorbs onto the surface at high pH [5, 11] inhibiting the forsterite dissolution rate [5, 6]. Hanford waste has considerably higher concentrations of carbonate than the solutions used by the earlier studies [5, 6, 11], and it is not clear how this much higher concentration of carbonate will impact olivine dissolution rates in Hanford waste. Though carbonate was shown to inhibit dissolution, it is conceivable that other anions would disrupt the Mg-O bonds and enhance forsterite dissolution. There have been no studies of the effect of most of the common anions in Hanford waste on forsterite olivine dissolution. Thus, these results indicate that some, and maybe even lots, of olivine will degrade in Hanford waste, but the percentage cannot be quantitatively determined.

Silicate Degradation in High-pH Solutions

The transformation of olivine or garnet in Hanford waste has not been studied experimentally previously. The degradation of many other silicates has been studied, however, and they all have essentially the same silicate reaction products. Table III lists all of the studies available that show the transformation of silicates in Hanford waste, or other high pH systems of similar composition to Hanford waste. In all cases, the transformation product was either the mineral cancrinite or mixtures of cancrinite and sodalite. Over time, sodalite transforms into cancrinite [12]. Based on these results for many silicates reported in the literature, we can conclude that cancrinite is the most common stable silicate in Hanford waste.

TABLE III. Examples of Studied Mineral Species Transforming into Cancrinite in Hanford Waste

Original Silicate Mineral or Species	Reference
Dissolved Silica	[14, 15, 16]
Whole Hanford Soil	[17, 18]
Biotite	[19]
Kaolinite	[20, 21]
Illite, Vermiculite, Montmorillonite	[22]
Quartz	[8, 23]
Sodalite	[12]
Garnet	This study

While the transformation of olivine into cancrinite in Hanford waste has not been specifically identified, forsterite olivine is well known to dissolve at high pH (in simple solutions) to form dissolved silica [4, 5, 6, 11]. Of note in Table III is that dissolved silica re-precipitates as cancrinite in Hanford waste. Thus, it is reasonable to assume that olivine will slowly transform into cancrinite, just as do all other primary silicates tested to date. This is consistent with a Hanford waste mineralogical compilation, where cancrinite was by far the most common silicate mineral identified in Hanford waste [13], even though cancrinite has never been added to the tanks.

The reaction product for the magnesium during olivine dissolution is more speculative. While the amount of magnesium in the waste is much higher than the amount of magnesium being

added by olivine and garnet during dome cutting, magnesium is nonetheless a minor component in Hanford waste. Consequently, there is no mineralogical precedence available on Hanford waste to predict magnesium mineral products [13]. Magnesium could conceivably precipitate with any of the major anions in the waste, including hydroxide, carbonate, and sulfate.

Deng et al. [15] studied the precipitation of cancrinite from Hanford waste in the presence of small amounts (0.25 M) Mg^{2+} . They found that amesite $[(Mg_2Al)(Si, Al)O_5]OH_4$ of less than one micro-meter in size formed from these solutions at 1 M NaOH whereas brucite $(Mg[OH]_2)$ formed at 16 M NaOH. Magnesium did not interfere with cancrinite precipitation in their study. It is not clear if either amesite or brucite will form in the tank waste when olivine is reacted with the waste, but they certainly should be considered candidates. Of note, however, is that Deng et al.'s [15] waste simulant did not have any carbonate or sulfate, both anions with which magnesium might precipitate.

DISCUSSION

Rate equations for olivine dissolution are available in the literature, but they are only available at low ionic strength, and it is not clear how relevant to Hanford waste they are. Spectroscopic data from the literature indicates that forsterite forms a MgO-rich surface phase, and adsorption of solutes on this surface can influence the rate of olivine degradation. Most notably, carbonate decreases the olivine dissolution rate. Hanford waste has lots of carbonate, and it is not clear how other solutes will influence the dissolution rates, but many Hanford solutes likely interact with the MgO rich surface.

Even at elevated temperature (80 °C) and elevated NaOH concentrations (2 M), garnet did not substantially degrade in 12 weeks. There were signs of damage at 12 weeks (even at 25 °C), but the garnet was still essentially intact. While the experiment only covered 12 weeks, the garnet will sit for years in the waste before being treated at the WTP. With the minimal damage seen after 12 weeks at 80 °C and 2 M NaOH, however, it is unreasonable to assume that the garnet will degrade at 25 °C and low levels of hydroxide even after many years.

With a number of issues about the degradation rate still raised, it is not possible to ensure complete degradation of olivine and garnet prior to treatment in the WTP. Nonetheless, the results here indicate that they will likely partially degrade into the mineral cancrinite, and the cancrinite will likely have a fine particle size. Thus, these results indicate that mineral degradation will at least partially mitigate downstream erosion. Given that the absolute rate of degradation cannot be determined from the present study or data available, we cannot assume that the degradation that does occur before waste treatment will meaningfully prevent excessive erosion of equipment. Therefore, waste treatment equipment needs to be sufficiently robust to deal with a small amount of erosive material mixed in with a large amount of waste.

CONCLUSION

Experimental results have shown that both garnet and olivine will at least partially degrade in Hanford waste. The silicate reaction product is cancrinite or a similar mineral of small particle size. This is good because cancrinite is both smaller and less hard than either olivine or garnet, which will result in less erosion of downstream equipment. Unfortunately, the rate of

degradation is relatively slow. Therefore, we cannot be assured that either olivine or garnet will be completely degraded by the time they are processed in the WTP.

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