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Supporting Information

ABSTRACT: Understanding the long-term release of radionuclides from nuclear waste to the environment is critical for public acceptance and sustainability of nuclear energy. Iodoapatite, a synthetic material similar to mineral vanadinite proposed for radioactive iodine-129 immobilization, is employed in this study as a model system for iodine waste forms and ceramic waste forms in general to understand its long-term chemical durability. Semidynamic leaching experiments were performed in cap-sealed Teflon vessels to evaluate the chemical durability at temperatures from 20 to 90 °C and pH values from 4 to 9 using deionized water and pH buffer solutions. The leachates were analyzed using inductively coupled plasma-mass spectrometry. The leached surfaces were examined by X-ray diffraction, scanning electron microscopy, and Raman spectroscopy. Effects of test variables including surface-to-volume ratio, leachant replacement interval, and environmental variables including temperature and pH on the dissolution rate were systematically investigated. The activation energy of the dissolution was 16.9 ± 1.5 kJ/mol for the matrix elements and 34.4 ± 3.9 kJ/mol for the diffusive iodine release. The order of the pH effect on the dissolution rate as a power law exponent was 0.87 ± 0.08 . The effect of the surface-to-volume ratio and replacement interval was approximated by a single exponential function rise to maximum. Fully parametrized models were then combined to predict iodine release rate under various conditions. The result suggests that the long-term iodine release is controlled by iodide diffusion when the matrix dissolution rate is very low in near neutral pH solutions and by matrix dissolution when the dissolution rate is high at low pH. The present study demonstrates a mechanistic approach to parametrize models that can be used to evaluate the performance of nuclear waste forms under various disposal environments.

KEYWORDS: apatite, iodine, radionuclides, fission product, waste form, activation energy, saturation effect, waste disposal

INTRODUCTION

Sustained development of nuclear energy requires safe disposal of radionuclides produced from nuclear fission. Many of these fission products are short-lived, and those with great concerns include technetium-99, cesium-135, and iodine-129.^{1–6} There are 37 known iodine isotopes, all of which are radioactive except iodine-127. Nuclear fission produces at least three radioactive isotopes: iodine-129, 131, and 132. The latter two are short-lived with a half-life of about 8 days and 2 h, respectively. Iodine-129 (~15.7 million years half-life, ~0.8% yield) is particularly important because of its long half-life and weak interactions with the engineering barriers and near field rocks of geological formations in disposal environment; as a result, iodine-129 is a primary dose contributor to the environment considered in disposal safety analyses.⁷ Once released from the waste form, the iodine is expected to remain stable in the form of iodide (I^-), which occupies a large area of

the Eh-pH stability field in the aqueous environment.^{8,9} Its low ionic potential (charge to radius ratio) makes iodide less likely to form insoluble compounds by interactions with the rocks and dissolved species in the environment. In addition, surfaces of silicate minerals, common in disposal environments, are often negatively charged because their point of zero charge is usually lower than the pH values of ground waters expected to occur in the near field and geological formations, leading to negligible iodide adsorption on those materials. Under oxidizing conditions, iodide may get oxidized to I_2 at acidic and iodate (IO_3^-) at neutral to basic conditions. Both these species are expected to be mobile. Therefore, the immobiliza-

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tion of iodine (including I-129) has remained a topic of ongoing research and development interest.^{10–20} Iodine waste forms can be classified into two categories based on immobilization mechanism: incorporation and encapsulation. In incorporation, iodine (e.g., iodide, iodate) is immobilized in a chemical coordination environment, which can be a crystalline phase where iodine occupies the crystallographic sites (e.g., iodoapatite, iodosodalite) or a glass where iodine is dissolved. The incorporation can be stoichiometric if iodine is the sole species fully occupying a crystallographic site or nonstoichiometric if a variable fraction of the crystallographic site is occupied. The amount incorporated often depends on iodine solubility in the material. For borosilicate glass used for high level nuclear waste, the solubility of iodine is very low largely because of the volatility of iodine at vitrification temperatures and structural incompatibility in borosilicate glass.²¹ Small to trace amount of iodine can always be incorporated in a variety of materials mostly due to the entropic contribution to the free energy of the incorporation. However, iodine loading in a material needs to be sufficiently large to be cost-effective for an acceptable waste form. In encapsulation, iodine is retained in a phase (e.g., AgI) different from its host matrix such as low-temperature glass.¹⁵ The matrix provides a mechanical and chemical barrier to contain the iodine phase. A number of waste forms have been considered for iodine-129 with varying amount of iodine loading capacities,²⁰ including borosilicate glass for high-level waste, low-temperature glasses,^{15,22–25} and crystalline phases^{17,26–30} such as iodosodalite^{26,27} and apatites.^{13,19,31–38} Many of the iodine waste forms developed in the literature provide promising properties for iodine immobilization by either incorporation or encapsulation.²⁰ However, the level of difficulty in evaluation of their long-term durability in the environment varies significantly, which is a great challenge for those encapsulated multiphase waste forms due to their phase and microstructure complexities. In comparison, the durability of single phase crystalline iodine waste forms can be more easily evaluated because of their well-defined crystal structure and crystallographic sites of the interested elements, simpler microstructure, and relative ease of test results interpretation. Among the single phase crystalline waste forms, apatite has a number of advantageous properties including long-term durability,^{39,40} structural and chemical flexibility,^{41–43} and tolerance against the aging effect of radionuclides due to radioparasitism.^{44–46} A number of iodoapatite compositions have been synthesized, and their physical properties have been characterized for immobilization of iodine-129.^{13,19,31–38,47–49} Pb–V iodoapatite ($\text{Pb}_5(\text{VO}_4)_3\text{I}$), inspired by mineral vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$), can be readily synthesized to dense monolith pellets, which are suitable for durability test.^{38,40} Static, semidynamic, and flow-through leaching experiments have been carried out to quantify the chemical durability of iodoapatite in deionized water in order to evaluate its performance in the aqueous environment.^{40,47,48,50–52} The results from these experiments consistently point to a chemical durability that is comparable to or better than nuclear glass,⁴⁸ using different leaching methods and samples with different compositions. For instance, a rate of 2.5×10^{-3} g/m²/d was reported after 2 weeks using a flow-through method at 90 °C for an iodoapatite ($\text{Pb}_{10}(\text{VO}_4)_{4.8}(\text{PO}_4)_{1.2}\text{I}_2$).⁵⁰ In a recent leaching experiment of iodoapatite $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$, a rate of 2.3×10^{-3} g/m²/d was reached after 21 days of experiment using a

semidynamic leaching method at 90 °C.⁴⁰ In a static leaching experiment at 50 °C, an initial release rate of iodine 2×10^{-2} g/m²/d and a residual rate of 7×10^{-5} g/m²/d with a S/V ratio of 800 and 8000 m⁻¹, respectively, were reported for iodoapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{IO}_3)_{0.92}(\text{OH})_{1.08}$.^{19,48} Although these reported rates vary largely due to differences in sample compositions, test methods, test parameters, sample synthesis methods, and how the rate was reported, iodoapatite was found to be chemically durable, comparable to or better than nuclear glass residual rate (1.1×10^{-2} to 1×10^{-4} g/m²/d).^{48,53} Due to the large difference in terms of iodine loading (~8–20 wt % iodine in iodoapatites and ~1 wt % in borosilicate glass^{21,54}), the ceramic waste form incorporates about ten times more iodine than nuclear glass with at least a comparable release rate. In order to understand the iodine release mechanism from iodoapatite, a semidynamic test method was used to distinguish between dissolution-controlled and diffusion-controlled release processes.⁴⁰ Elemental analysis, X-ray diffraction, and IR spectroscopic results suggest that the iodide release is initially dominated by ion exchange of iodide (I^-) with hydroxide (OH^-) in solution, while lead and vanadium are released via constant dissolution.⁴⁰ Such a release mechanism has also been considered previously to explain incongruent dissolution, time-dependent release rate of iodine, and the pH evolution using flow-through and static leaching experiments.^{48,50,52}

In order to predict the long-term release behavior of iodine from iodoapatite, experiments designed to probe a range of environmental conditions are needed to fully understand the dissolution behavior. In addition to pH and temperature, the dissolution rate is also affected by the saturation condition of the aqueous solution. For instance, in a scenario where water is limited, the concentration of the dissolved species is high, and the chemical affinity and dissolution rate decrease quickly and become diminished when the solution is at equilibrium. However, when water is abundant, similar to experiments at far-from-equilibrium conditions, the concentration of relevant species in the solution is low, the free energy driving force for the dissolution is large, and the dissolution rate is high and approximately a constant. The saturation conditions can be mimicked using a semidynamic leaching experiment by changing surface to volume ratio and leachant replacement interval.⁵⁵

The present study uses iodoapatite, a synthetic material as a model system for iodine waste forms and ceramic waste forms in general, to understand its long-term chemical durability. The experiments were designed to extend the previous leaching tests⁴⁰ to longer time scales when the short-term dissolution rate components diminish, and to systematically evaluate the effects of test and environmental variables on the dissolution including saturation state (i.e., S/V, interval), temperature, and pH. The goal is to understand the kinetics of leaching behavior under certain sets of conditions to contribute toward establishing iodoapatite as a feasible iodine waste form, by parametrizing mechanistic models that consider all critical processes and a range of test and environmental conditions for the prediction of iodine release. Such a mechanistic approach, generally applicable to other nuclear waste forms, could be used to predict the dissolution rate under various environmental conditions and to evaluate the durability of the iodoapatite at longer time scales than examined.

EXPERIMENTAL METHODS

Sample and Materials Characterization. Three pellets of iodoapatite samples up to 14 mm in diameter and 3 mm in thickness with a composition of $\text{Pb}_{9.85}(\text{VO}_4)_6\text{I}_{1.7}$ and ~96% theoretical density were used in the leaching experiments (Figure 1a).³⁸ Details regarding synthesis and characterization

Figure 1. Optical and SEM images of the pellets and surfaces of the iodoapatite samples from leaching experiments. (a) Fresh polished surface of an iodoapatite pellet. Inset: pellets of apatite synthesized using high energy ball milling and sparking plasma sintering. (b) Surface of a leached pellet of apatite after 3 weeks of test with DI water at 90 °C. (c) Surface of a leached pellet using a pH 6 buffering solution for 2 weeks. (d) Surface of a leached pellet using pH 4 buffering solution for 2 weeks. Majority of the surface is covered by the secondary phase chervetite precipitates.

an uncertainty of less than 10%. Based on measurements from different batches of experiments, the overall error of the measured concentration is estimated to be ~20%, which is propagated from ICP–MS analysis, dilution of the leachate before analysis, geometric surface area estimation, leachant weight loss during experiment, and oven temperature control homogeneity, among others.

Leaching Protocol. The leaching experiments employed an accelerated leaching method,⁵⁵ which provides a procedure for measuring the leaching rate of elements from a solid material. The method is based on a semidynamic dissolution procedure in which the sample is immersed in a leachant for a given time interval. The leachate is periodically replaced with new leachant after each interval (replacement interval). The experiments were conducted in cap-sealed Teflon vessels in a digitally controlled oven at 90 ± 0.5 °C using deionized (DI) water and pH buffer solutions. Temperature-dependent tests were conducted at 20, 40, 70, and 90 °C. The effect of pH on dissolution was performed using organic buffer solutions at pH = 4 (potassium hydrogen phthalate with formaldehyde), 6 (citric acid with sodium hydroxide), and 9 (borax with HCl). Three different sizes of Teflon vessels (30, 60, and 120 mL) were used. The pellet geometric surface area was in the range of 4 to 0.56 cm^2 , and surface to volume (S/V) ratio was in the range of 2 to 50 m^{-1} , which remained constant during each experiment as the leached fraction of the sample was negligible ($\sim 10^{-5}$) with respect to the sample. Leachant replacement intervals were 1, 3.5, and 7 days. Each experiment lasted 1–3 weeks. Initially, sample surfaces were deeply polished after leaching and reused for the following test. However, samples reused with and without polishing did not show statistically significant difference in the leaching rate except the first day. Thus, the rest of the reused samples were not polished during subsequent tests. The vessels were weighed before and after each interval to monitor the solution weight loss caused by the cap sealing of the Teflon vessel, which has a loss within 1% of the solution mass. Acid strip was performed, and the result confirmed that any deposits or sorption of leached elements on the vessel were negligible.

Rate Calculation and Côté Model. The cumulative mass released was calculated using eq 1:

$$m_i(n) = \sum_{j=1}^n m_{i,j}/S \quad (1)$$

where $m_i(n)$ is the cumulative mass released of species i (mg/m^2) at the n^{th} interval, $m_{i,j}$ is leached amount of element i in milligrams of the j^{th} leachate, and S is the geometric surface area of the sample in square meters. $m_{i,j}$ and $m_i(n)$ can be converted to millimoles (mmol) and millimoles per square meter (mmol/m^2), respectively. Due to the additive nature of eq 1, the error of $m_i(n)$ accumulates as n increases:

$$\text{error}[m_i(n)] \approx \left(\sum_{j=1}^n (\text{error}[m_{i,j}])^2 \right)^{1/2} \approx \sqrt{n} \cdot \text{error}[m_{i,j}] \quad (2)$$

To avoid working with cumulative mass, leaching rate was used for modeling using eq 3:

$$r_i(j) = m_{i,j}/(St_j) \quad (3)$$

where $r_i(j)$ is the leaching rate of species i at time j , and t_j is the time interval at j .

of the samples are summarized here and were reported in separate publications.^{38,40} Iodoapatite was synthesized using high energy ball milling (HEBM) and spark plasma sintering (SPS) techniques. The slightly under-stoichiometry of the composition with respect to $\text{Pb}_{10}(\text{VO}_4)_6\text{I}_2$ is a result of loss of some of the iodine during the synthesis. Impurities such as PbI_2 and $\text{Pb}_3(\text{VO}_4)_2$ from incomplete reaction are negligible as determined by X-ray diffraction. Graphite peaks sometimes may appear in X-ray diffraction as a result of a residual from the sample chamber material during SPS synthesis, which is inert to dissolution reactions in this study. Samples were mechanically polished with ethanol lubrication and were thoroughly rinsed using ethanol and air-dried before leaching experiments. Samples were reused after each leaching test. Due to the time dependence of iodine release, for the experiments at different pH values and temperatures, a pellet was cut to a number of pieces with approximately the same size to provide consistent pH- and temperature-dependent results. Before and after a leaching experiment, sample surfaces were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman spectroscopy on the surfaces of the pellets (Figure 1). The leachate was analyzed with an inductively coupled plasma–mass spectrometry (ICP–MS) system with

Côté model is a semiempirical mathematical model based on leaching rate limiting mechanisms.⁵⁶ The model was developed to understand leaching mechanisms including terms attributed to diffusion, dissolution, and surface effect of a solid matrix material. The model has been instrumental in understanding the leaching behavior of materials such as cement and ceramics in aqueous solutions.^{57,58} The model is defined by eq 4:

$$m(t) = k_1 t^{1/2} + k_2 t + k_3(1 - e^{-k_4 t}) \quad (4)$$

where the cumulative amount of the element of interest $m(t)$ is described by the coefficient of diffusive character k_1 , the coefficient of constant dissolution character k_2 , and coefficients of surface effect k_3 and k_4 . Côté and others originally proposed to use regression analysis on the cumulative amount of materials leached from the solid.^{56,59} Error propagation from the individual measurements to the cumulative value was not considered in the regression analysis. However, the accumulated error could become large as the number of data points increases (i.e., $\propto \sqrt{n}$), which makes an unambiguous interpretation of the data challenging. Therefore, we use the rate instead of the cumulative mass when applying the regression analysis of the Côté model in this study. The release rate can be expressed as eq 5 by taking a derivative of eq 4 as

$$r(t) = \frac{1}{2} k_1 t^{-1/2} + k_2 + k_3 k_4 e^{-k_4 t} \quad (5)$$

The diffusion contribution to the rate has a $1/\sqrt{t}$ time dependence. The constant dissolution is determined by k_2 , and the third term, surface effect, is defined by the first-order rate equation to account for rapid release of surface species into the aqueous solution.⁵⁶

RESULTS AND DISCUSSION

Effect of Solution Saturation. As shown in Supporting Information Figures S1 and S2, S/V ratio and leachant replacement interval have a significant effect on the test response. For all three elements, an increase of S/V ratio (Supporting Information Figure S1) causes a rate decrease as a result of the solution feedback of the dissolved species, i.e., reverse reaction of the dissolution reaction. For instance, as the S/V ratio increased from 5 to 50 m^{-1} , iodine release rate decreased from 5.5 to 1.1 $\text{mg}/\text{m}^2/\text{d}$ (Supporting Information Figure S1a). Similarly, as shown in Supporting Information Figure S2, an increase of the replacement interval leads to a rate decrease. As the interval increases from 1 to 7 days, the average release rate per day of iodine decreases from 2.5 to 0.5 $\text{mg}/\text{m}^2/\text{d}$ because of the increased solution feedback of longer intervals as a result of longer duration in the leachate solution (Supporting Information Figure S2a). Lead and vanadium release rates follow a similar trend as a result of the change of S/V and replacement interval.

In general, an increase of S/V or interval generates a solution with more dissolved species, which causes the chemical potentials of dissolved species and the solution saturation state to increase, resulting in an increase of the free energy of dissolution (less negative), a decrease of free energy driving force (chemical affinity), and a reduced dissolution rate. Such a solubility-controlled kinetics of dissolution is well-documented in the literature for ceramics and minerals.^{60–63} With assumptions of transition state theory^{64,65} and principle of

detailed balance,^{66,67} the dependence of dissolution rate on free energy driving force follows eq 6:

$$r = k_f(1 - e^{(\Delta G/RT)}) = k_f(1 - (Q/K)) \quad (6)$$

where k_f is forward rate constant, ΔG is the free energy of the dissolution reaction, R is gas constant, T the temperature, Q the activity product, K the equilibrium constant, and Q/K the saturation index. To account for the overall reaction related to the activated surface complex, Temkins average stoichiometric number n was introduced:^{61,62,68}

$$r = k_f(1 - e^{(n\Delta G/RT)}) = k_f(1 - (Q/K)^n) \quad (7)$$

To account for the effect of crystal defects on dissolution, an exponent m was introduced:^{61,62,68}

$$r = k_f(1 - e^{(\Delta G/RT)})^m = k_f(1 - (Q/K))^m \quad (8)$$

To accommodate both reaction stoichiometry and defects, the constants n and m can be applied at the same time.^{61,62,68} The defects here, in general, refer to the surface defects that lead to complex surface dissolution phenomena,^{62,68} for instance, etch pit formation from a screw dislocation. These equations that relate a dissolution rate to the free energy driving force (saturation index) are well established. Furthermore, a mechanistic-based analytical form that can relate dissolution rate to experimental control parameters such as S/V ratio and leachant replacement interval in a semi-dynamic leaching experiment should exist and be well-defined. Such a relation can be instrumental for normalization of the test results carried out at different S/V and interval values. In addition, when parametrized, such a relation can then be used to predict the release rate under various S/V and leachant replacement intervals that mimic different disposal conditions.

As shown in Figure 2, the effects of the inverse of S/V ratio and interval are not linear. As V/S ratio or 1/interval becomes

Figure 2. Effect of the reciprocal of the test parameters (V/S and 1/interval) on the release rates of lead, vanadium, and iodine. The lines are the fitted result of eq 9 of leaching rate data with interval = 1 day (solid lines and symbols) and the data with S/V = 10 m^{-1} (dashed lines and filled symbols). The rates were normalized to the stoichiometry of iodoapatite.

zero, the rate is expected to tend to zero. As V/S ratio or 1/interval approaches to infinity, the rate is expected to reach the maximum value established by the dissolution reaction kinetics without attenuation by solution feedback. Such boundary conditions can be approximated by a single exponential

function with a three parameter rise to maximum in the form of

$$r(p_s) = k_s(1 - e^{-\phi p_s})^m \quad (9)$$

where $r(p_s)$ is rate, p_s is saturation control parameter (1/interval or V/S), k_s is the maximum rate (or forward rate constant), and ϕ is constant for a given saturation control parameter. Note that V/S ratio and 1/interval are used because of the construction of eq 9. For iodoapatite, m is close to 1.0 after fitting experimental data with eq 9 without constraints. Similarity of the mathematical form between eqs 7 and 9 suggests an underlying assumption: saturation control parameter (p_s) is linearly proportional to the free energy of the dissolution reaction. Although such an assumption is simplistic, in the absence of an analytical form to describe their relationship, the equation models the boundary conditions correctly: as p_s approaches zero, the rate of dissolution approaches zero, and as p_s increases, the rate gradually reaches a plateau and approximately becomes a constant. Such behavior has been observed for a number of dissolution experiments using flow-through method.^{69–71} Therefore, eq 9 was used to fit the 1/interval and V/S test data simultaneously with the plateau values for the 1/interval and V/S constrained to be the same. Regression equations with a R^2 of 0.96 were attained by using $k_s = 31.5 \pm 4.1 \times 10^{-6}$ mol/m²/d and $\phi = 1.7 \pm 0.3$ m⁻¹ for V/S , and 0.20 ± 0.03 day for 1/interval. As shown in Figure 2, these equations can be used to normalize the rates measured in leaching experiments conducted at different intervals and S/V ratios to account for differences in solution saturation.

Time Dependence of Iodine Release. Molar ratio I/Pb in leachate solutions as a function of time is plotted in Figure 3a. The ratio decreases with time and gradually approaches the stoichiometric ratio of iodoapatite (0.17). There is a ~10-fold decrease of the ratio measured in the test solution from the initial value of 1.7. In contrast, the V/Pb ratio (Supporting Information Figure S3) remains constant in the test solutions with a stoichiometric ratio of V/Pb (0.61) within the error (~28%), which is estimated using an error propagation equation similar to eq 2. In order to check if there was any precipitations or adsorptions during leaching tests that might have altered the molar ratios of the dissolved species, SEM was performed on the sample surfaces (Figures 1b–d) and acid strip tests were carried out on the Teflon vessels, respectively. The results showed there were no precipitates on the sample surfaces and no detectable amounts of Pb, V, or I present in the strip solutions. Thermodynamic calculations using MINTEQA⁷² confirmed that the leachate solutions were undersaturated with respect to all relevant low solubility solid phases including $Pb_2V_2O_7$ and $Pb_3(VO_4)_2$. The difference between the measured and the stoichiometric I/Pb molar ratios indicates the release of iodine is incongruent with respect to Pb and V, which is consistent with our previous study based on 3-week-long experiments.⁴⁰ Similar iodine release behaviors were also observed in other studies of iodoapatite dissolution reported in the literature.^{47,48} The incongruent release behavior of iodine originated from the chemistry of iodoapatite where iodide is more ionic bonded at the channel in the apatite structure site, while lead and vanadium are more covalently bonded.⁷³ Such bonding difference leads to different leaching behavior.

Figure 3. (a) I/Pb molar ratio in leached solutions as a function of time. The data points are from the experiments with different S/V ratios and intervals using DI water at 90 °C. The solid line is the fitted result using eq 5. The horizontal dashed-line is the stoichiometric I/Pb ratio of iodoapatite. (b) Iodine leaching rate normalized to $S/V = 1$ m⁻¹ and interval = 1 day using DI water at 90 °C. The dashed-line is iodine long-term release rate. Insets in (a) and (b) include S/V and interval values. (c) Côté fitting result of the iodine release rate data normalized to interval = 1 day and $S/V = 1$ m⁻¹ as a function of time using DI water at 90 °C based on eq 5. Symbols are experiment data. The solid line (red) is the total release rate, the short-dashed line (orange) is the contribution from the diffusion term, the long-dashed line (green) is from the surface effect term, and the dot-dashed line (blue) is from the constant dissolution.

In order to directly compare the release rates based on experiments using different test parameters (i.e., S/V ratio and interval), the rates were normalized by S/V and replacement interval. For Pb and V, the normalization is straightforward using eq 9 since releases of these two elements are constant over time. However, I release rate is time dependent (Figure 3a), which needs to be normalized first. The Côté equation (eq 5) was used to normalize the time dependence. To eliminate the effect of test conditions, I/Pb ratio (i.e., iodine release rate normalized to Pb) was used for this normalization. As shown in Figure 3a, I/Pb ratio was fitted well with eq 5. This fitted equation was then used to normalize the iodine rate measured

at a given time to its long time rate when iodine release rate would be congruent with respect to Pb and V. And then, the release rates of all three elements were normalized to $S/V = 1 \text{ m}^{-1}$ and interval = 1 day, and plotted for I (Figure 3b), V (Supporting Information Figure S4a), and Pb (Supporting Information Figure S4b). Based on the normalized rate, iodine release rate was fitted with eq 5 of Côté model. As shown in Figure 3c, both diffusion and surface effects have significant initial contributions to the total release of iodine, but the surface effect becomes negligible after about 2 weeks and constant dissolution becomes the dominant process after approximately 100 days. This analysis predicts the long-term iodine release rate will eventually become controlled by the constant matrix dissolution rate, which is $\sim 6.0 \text{ mg/m}^2/\text{d}$ at conditions of pH 7, $S/V = 1 \text{ m}^{-1}$ and interval = 1 day using DI water and 90°C . Note that the long-term I release rate is significantly lower than the rate measured in short-term laboratory tests, which is controlled by a transient diffusion process (surface effect). The parametrized eq 5 can thus be used to predict the time dependent release of iodine from the iodoapatite.

Effect of Temperature. Temperature effect on the iodoapatite dissolution rate is plotted in Supporting Information Figure S5. Same experimental protocol was employed using DI water as leachant with 1 day interval and S/V of 5.0 m^{-1} . The temperatures were 20.0, 40.0, 70.0, and 90.0°C . The release rates of all three elements increase with temperature. The temperature effect is better understood by plotting the logarithm of the rate as a function of inverse temperature based on the Arrhenius eq (Figure 4a):

$$r(T) = A e^{-E_a/RT} \quad (10)$$

where A is the pre-exponential factor, R the gas constant, T the temperature in K, and E_a the activation energy. The activation energy was extracted from a linear fit (Figure 4a) to be $22.2 \pm 0.9 \text{ kJ/mol}$ for iodine and $16.9 \pm 2.5 \text{ kJ/mol}$ for Pb and V. The leachant change interval and S/V ratio were kept constant to minimize the saturation effect on the rates, which is neglected in this study. If all three elements were released stoichiometrically in the same chemical process, the activation energy derived using each element should be the same. Since lead and vanadium are dissolved congruently, their activation energy represents the dissolution rate of iodoapatite matrix. For iodine, both diffusion and dissolution contribute the iodine release (Figure 3c). The activation energy from fitting the iodine curve in Figure 4a accounts for both processes. The diffusion portion of iodine release can be approximately extracted by subtracting the constant dissolution contribution given by the Pb or V rate from the iodine release rate. By attributing the difference in the data to diffusion, an activation energy of $34.4 \pm 3.9 \text{ kJ/mol}$ was then obtained for the diffusion process, which is similar to the previously reported value of $37 \pm 4 \text{ kJ/mol}$ based on the initial release rate in pure water at 25, 50, and 90°C when at the initial stage the diffusion is the dominant contribution to the release.⁴⁷ Note that the estimated activation energy for dissolution of iodoapatite matrix is lower than for the iodide diffusion, which is counterintuitive. However, the activation energies are consistent with a reported dissolution experiment of iodoapatite conducted at pH values 5.5–6 and 4.1 at different temperatures.⁵⁰ Based on those experimental results, the activation energy at pH 5.5–6 is higher than at 4.1.⁵⁰ Since iodide diffusion is pH independent, the activation energy

Figure 4. (a) Arrhenius plot of logarithm rates as a function of inverse temperature. The dashed lines are fitted lines. The rates were normalized to the stoichiometry of iodoapatite. (b) Dissolution rates as a function of solution pH for iodoapatite and natural apatite. The experimental data of natural apatite were obtained at far-from-equilibrium conditions at 25°C . The data for iodoapatite were scaled to far-from-equilibrium conditions and 25°C based on S/V ratio and interval, and the activation energy. All rates are normalized by the stoichiometry of the apatite. The dashed lines are the results of linear fitting.

derived from the lower pH data has more contribution from dissolution because of the higher dissolution rate of iodoapatite at the lower pH. At higher pH values such as pH 9, the activation energy becomes increasingly influenced by the diffusion process as the dissolution rate decreases.

In an effort to cross-check the activation energy of iodide diffusion in apatite structure, first-principles calculations were carried out to estimate the migration energy of iodide along channels in iodoapatite structure. The calculations were based on density functional theory and plane wave basis sets as implemented in VASP.⁷⁴ Projector-augmented wave method⁷⁵ and exchange-correlation as parametrized by Perdew–Wang functional^{76,77} were applied in the generalized gradient approximation.⁷⁸ The computations employed a $2 \times 2 \times 2$ supercell and the k-meshes were generated in the Brillouin zone with a $1 \times 1 \times 2$ Monkhorst–Pack grid. The energy cutoff was set as 520 eV. A vacancy-based migration mechanism was assumed. Nudged elastic band method was used for the calculations.⁷⁹ The calculated migration energy is 0.33 eV or 31.9 kJ/mol, which is consistent with the activation energy $34.4 \pm 3.9 \text{ kJ/mol}$ from this study and $37 \pm 4 \text{ kJ/mol}$ reported in the literature.⁴⁷

The activation energy for iodoapatite matrix dissolution at pH 7 using DI water (16.9 kJ/mol) is low and less than half of the reported values of natural apatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), which are in the range of 34.7 to 46.0 kJ/mol.^{70,80} For natural fluorapatite, an activation energy of 46.0 kJ/mol was extracted from experiments at temperatures of 5, 25, and 50°C , and pH from 1 to 6 using closed-system reactors.⁸⁰ For a similar natural apatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, an activation energy 34.7 ± 1.6

kJ/mol was reported from experiments at 25, 35, and 55 °C and pH of 3.0 using a flow-through method.⁷⁰ Although natural fluorapatite and iodoapatite have the same crystal structure, they have different chemical compositions. The difference in the activation energies of the two apatite compositions is related to difference in the chemical bonding and crystal chemistries of the materials. Ionic radius of Pb^{2+} is 1.19 Å, 0.36 Å for V^{5+} , and 2.20 Å for I^- of iodoapatite, corresponding to 1.00 Å for Ca^{2+} , 0.17 Å for P^{5+} , and 1.33 for F^- of natural apatite, or 13%, 53%, and 40% decreases, respectively, from iodoapatite to natural apatite. The decrease causes an increase in the ionic potential at each crystallographic site, increase in the chemical bonding strength, and decrease in bond distances, as reflected in the unit cell volume, which is 702.39 Å³ for iodoapatite,⁸¹ and 527.91 Å³ for fluorapatite⁸² or 25% decrease. The stronger bonding and shorter bond distance lead to a higher activation energy for fluorapatite dissolution than for iodoapatite.

Effect of pH. The cumulative mass released in solution as a function of time is plotted in Supporting Information Figure S6 for tests conducted at different pHs. The rates for all elements are significantly higher at low pH values over the pH range 4–9, which is consistent with previous leaching test results.⁴⁷ Dissolution rates are low in DI water and at pH 9. Lead was not detected in the leachates of the experiment at pH 9. In both cases, individual grains of the leached surface became exposed as a result of grain boundary dissolution, as shown by the SEM image (Figure 1b). At pH 6, the dissolution rate increased by more than 2 orders of magnitude from that at pH 9. The surfaces were dramatically corroded with severe roughness and grain boundaries deeply exposed (Figure 1c). No secondary phases were observed on the surfaces. At pH 4, a large fraction of the surface became covered by precipitates, a secondary phase (Figure 1d). Severe corrosion is visible where the surface is not blocked by the precipitates (top right and bottom left corners of Figure 1d). Using Raman spectroscopy, the precipitated phase was identified to be chervetite ($\text{Pb}_2\text{V}_2\text{O}_7$) as shown in Supporting Information Figure S7. Although it is expected that the dissolution rate at pH 4 should be much higher than at pH 6, the measured rates of all three elements in the solution are actually lower at pH 4 than those at pH 6 because of the precipitation of chervetite and reduced surface area accessible to the solution (Supporting Information Figure S6, Figure 1d). The I release rate is slightly lower at pH 4 than at pH 6, but the solution-based rates for Pb and V at pH 4 are less than half of those at pH 6 because a significant amount was precipitated in chervetite. It needs to be emphasized that the calculated rate based on solution concentrations and initial surface area does not represent the dissolution rate for elements sequestered in secondary phases. A thermodynamic calculation based on measured concentrations of the leachate solutions using MINTEQA confirmed that chervetite was supersaturated with respect to the dissolved species at pH 4. No other secondary phases were observed on the leached surfaces at pH 4 based on SEM images and Raman spectra.

The effect of pH on natural apatite dissolution is well documented in the literature.^{70,80,83} In general, dissolution rate decreases as pH increases from acidic to near neutral conditions, which is often modeled by eq 11:

$$r(\text{pH}) = k_{\text{pH}}^0 [\text{H}^+]^\eta = k_{\text{pH}}^0 10^{-\eta \text{pH}} \quad (11)$$

where k_{pH}^0 is a constant and η is the exponent. As shown in Figure 4b, the logarithm of the rate is a linear function of pH. By fitting of the data, k_{pH}^0 and η were determined to be $10^{2.8 \pm 0.5}$ and 0.87 ± 0.08 , respectively, for iodoapatite. For natural apatite, the k_{pH}^0 and η values were determined to be $10^{-0.9 \pm 0.2}$ and 0.75 ± 0.05 based on the literature data.^{70,80,84} Similar η values have been reported for natural apatite, 0.8 for apatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{F}_{1.4}\text{OH}_{0.6})_2$,⁸³ 0.6 for apatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$,⁸⁰ and 0.81 for apatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$.⁷⁰ Since the empirical η value is interpreted as the order of the dissolution reaction with respect to pH, it is reasonable to expect that both natural apatite and iodoapatite have a similar dissolution reaction mechanism. However, the k_{pH}^0 value is near 3 orders of magnitude higher for iodoapatite than natural apatite. Similar to the difference in the activation energy of dissolution between natural apatite and iodoapatite, the higher dissolution rate of iodoapatite as reflected in the k_{pH}^0 value at a given pH is a result of the weaker chemical bonding in iodoapatite.

Results presented above suggest iodoapatite is much less durable than natural apatite, given that iodine release rates from iodoapatite are about 3 orders of magnitude higher than natural fluorapatite, and with an activation energy about half of the natural fluorapatite. In addition, the Pb–V iodoapatite has a low melting point and relatively low iodine weight loading capacity (~8 wt %). However, the fact that the compositional space of iodoapatite has not been fully explored means new apatite compositions that incorporate more iodine and have better chemical durability and physical properties are possible. Based on an artificial neural network simulation, a number of iodoapatite compositions may be able to incorporate iodine.⁴³ Since an increased chemical bonding strength enhances chemical durability and increases the activation energy of the dissolution, apatites with elements having a smaller ionic radii than Pb and V, such as Sr, Ca, Cd, and Zn for Pb, and Cr, As, Si, and P for V, are expected to have higher activation energies for dissolution and increased chemical durability.

Prediction of Iodoapatite Dissolution. Dissolution rate of iodoapatite can be described by combining equations 5, 9, 10, and 11, resulting in eq 12 below:

$$r(t, p_s, T, \text{pH}) = r(t) A k_s k_{\text{pH}}^0 \times 10^{-\eta \text{pH}} [e^{-E_a/RT}] [1 - e^{-\phi p_s}] \quad (12)$$

where t , p_s , T , pH are time, the experimental test parameter that controls the solution saturation, solution temperature, and solution pH. The empirical parameter A , k_s , and k_{pH}^0 are the pre-exponential factor of Arrhenius equation, dissolution rate constant, and rate constant at pH = 0, respectively. The terms η , R , E_a , and ϕ are the order of dissolution reaction with respect to pH, the gas constant, the activation energy for dissolution, and a constant related to saturation, respectively.

The $r(t)$ term in eq 12 is described in eq 5, which addresses the time dependence for elemental release. For lead and vanadium, $r(t) = k_2$, a constant, in eq 5. For iodine, $r(t)$ is initially dominated by the diffusion term ($\frac{1}{2} k_1 t^{-1/2}$) and a significant contribution from the surface effect ($k_3 k_4 e^{-k_4 t}$), then becomes dominated by the constant dissolution term (k_2) at longer times. As a result of different release mechanisms, the terms in eq 5 have different pH, T , and saturation dependences for different elements. Since these processes occurred simultaneously, accurately estimating the parameters for the

individual mechanisms is challenging. However, it is understood that iodine diffusion in bulk iodoapatite is independent of both pH and the saturation state of the leachant solution. The temperature dependence of iodine diffusive release is controlled by the activation energy of the diffusion in the channel. For iodide release contributed by matrix dissolution, its pH and T dependences should be the same as those for lead and vanadium. The pH and T dependences of the short-term surface effect is expected to be similar to all three elements for the dissolution. The final parametrized empirical values at 90 °C, 1 day interval, $S/V = 1 \text{ m}^{-1}$, and pH = 7 are listed in Supporting Information Table S1. Examples of predictions at two given sets of conditions are illustrated in Figure 5.

Figure 5. (a) Prediction of iodine release rate as a function of time at different pHs and temperatures under the conditions of $S/V = 1 \text{ l/m}$ and interval = 1 day. The lines are predictions using eq 12. The symbols are experiment data. Open circles are the measured rates using DI water at 90 °C and normalized to $S/V = 1 \text{ l/m}$ and interval = 1 day. The triangles are data at 90 °C and pH 9 (blue), pH 7 (green), and pH 6 (red). The brown diamonds are data at pH 7 and temperatures from 20 °C (thick edge), 50 °C (medium thick edge), 70 °C (thin edge), and 90 °C (thin edge with a cross). (b) Prediction of iodine release rate as a function of time at different S/V ratios and intervals under the condition of pH = 7 and temperature of 25 °C. The S/V ratio and interval are indicated. The lines are predictions using eq 12. The high release rate line marks the far-from-equilibrium limit (thick red line), and the low release rate line is diffusion limit (thick blue line).

Figure 5a shows a prediction of parametrized eq 12, which highlights the effects of temperature and pH on the iodine release rate under test conditions of $S/V = 1 \text{ m}^{-1}$ and interval = 1 day. pH has a significant effect on iodine release rate. The initial rate increases about 3 orders of magnitude from pH 9 (blue curves) to 5 (pink curves). At low pHs, the release rate is quite high, with contributions from dissolution, diffusion, and surface effects, and exceeds 3000 mg/m²/d at 90 °C and pH 5 after 1 day. The initial release rates are very low at pH 8 (green curves) and pH 9 (blue curves), as low as $\sim 3 \text{ mg/m}^2/\text{d}$ at 25 °C and pH 9 after 1 day (solid blue curve), at which point the iodine release rate is dominated by diffusion (Figure 5a). The

iodine release becomes controlled by constant dissolution at pH 7 (brown curves), pH 6 (red curves), pH 5 (pink curves), and pH 8 (green curves at low temperatures) after ~ 100 days, but remains controlled by diffusion at pH 9 (blue curves) beyond 1000 days. Figure 5b shows a prediction of solution saturation effect (i.e., S/V ratio and leachant replacement interval) based on the parametrized eq 12 at pH of 7 and temperature of 25 °C. As S/V ratio and interval become smaller, the iodine release rate increases, approaching the far-from-equilibrium limit where dissolution is dominated, represented by the thick red line (Figure 5b). While as the S/V and interval become larger, the iodine release rate decreases and approaches the diffusion limit when the diffusion is dominated, represented by the thick blue line (Figure 5b). In the short term, the effect of S/V ratio and interval on the iodine release rate can reach as high as 2 orders of magnitude for the difference between a diffusion limit line at high S/V ratios and large intervals (e.g., $S/V > 100 \text{ m}^{-1}$ and interval > 1 day) and far-from-equilibrium line (e.g., $S/V < 0.1 \text{ m}^{-1}$ and interval < 0.1 day). In the long term, iodine release under far-from-equilibrium condition is controlled by dissolution, with a release rate of up to about 10 mg/m²/d (long-term maximum rate). Under the conditions near the diffusion limit line, the release rate diminishes quickly to below 0.1 mg/m²/d (long-term minimum rate).

SUMMARY AND CONCLUDING REMARKS

A systematic chemical durability study of iodoapatite was carried out under semidynamic conditions using DI water and pH buffering solutions at various surface-to-volume ratios, leachant replacement intervals, and temperatures. The results were utilized to parametrize a combined dissolution rate equation (master equation) that takes into account the critical dissolution processes of diffusion, dissolution, and surface artifacts. The time-dependent process was estimated using a semiempirical model based on rate limiting mechanisms. The effect of solution saturation state on the dissolution rate was modeled with a function that relates the saturation state with the surface-to-volume ratio and leachant replacement interval. By placing the experimental leaching test results in the mechanistically based models, the parametrized general equation was then used to predict the release rate for each of the constituent elements under various environmental conditions. The result suggests that the long-term iodine release rate is significantly lower than the rate measured in short-term laboratory tests, which is controlled by a transient diffusion process and surface effect. The result demonstrates that it is possible to parametrize a model by considering all critical processes and environmental variables and to predict the performance of a ceramic waste form such as iodoapatite and other nuclear waste forms under various environmental conditions. Applying the methodology employed in this study to other viable iodine waste forms would provide a consistent data set on their chemical durability and dissolution kinetics. Such a data set can be used to establish practical iodine waste forms among those proposed in the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.8b00162.

Parameters used in eq 12 for prediction of iodine release; cumulative dissolved mass as a function of time with different S/V ratios, and leachant change intervals for Pb, V, and I; V/Pb ratio as a function of time, and normalized rate for V and Pb; cumulative dissolved mass released as a function of time at different temperatures and pHs; Raman spectra of leached surface and chervetite precipitate (PDF)

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