Investigating Geochemical Processes of Fluid-Rock Interactions on Materials Related to Energy and Environment

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INVESTIGATING GEOCHEMICAL PROCESSES OF FLUID – ROCK INTERACTIONS ON MATERIALS RELATED TO ENERGY AND ENVIRONMENT

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College
in partial fulfillment of the requirements of the degree of Doctor of Philosophy

in

The Department of Geology and Geophysics

by

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August 2020
PREFACE

Research on geochemical processes bridges the realms of materials science and earth science. Once a material is exposed to an environmental fluid, geochemical processes commence at solution–solid interfaces.\textsuperscript{1} Understanding fluid–rock interactions is essential to subsurface energy applications, such as fossil fuel development, nuclear waste disposal, CO\textsubscript{2} sequestration, and geothermal energy extraction.\textsuperscript{2} Geochemical reactions, such as adsorption and desorption, dissolution and precipitation, reduction and oxidation, ion exchange, hydration, hydrolysis are fundamental factors for evaluating the performance as well as the properties of materials in natural environments.\textsuperscript{3,4} This dissertation addresses how geochemical processes at fluid–rock interfaces affect (1) the safe disposal of nuclear waste and (2) the oil recovery from an unconventional reservoir such as shale. The main body of this dissertation collects two recently published articles. The first one appears in *Journal of Nuclear Materials* and the second one was published in *Energy & Fuels*. 
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ABSTRACT

Understanding the potential processes of radionuclides released from nuclear waste forms is essential to the safe disposal and containment of nuclear waste. Iodoapatite, a potential waste form for radioiodine, was chosen as a model system to examine the impact by common aqueous anions on iodine release processes. Four semi-dynamic leaching tests were performed using 0.1 mol/L NaCl, Na₂CO₃, Na₃PO₄, and Na₂SO₄ solutions respectively under 90 °C, 1 bar, fixed S/V ratio 5/m (sample surface area to solution volume), and with 24-hour replacement of the leaching solutions. Solution analysis and surface characterization show that these ion-rich solutions accelerated the iodine release processes due to the increased ionic strength, reduced concentration coefficients of dissolved species, and elevated solution pH. Secondary phases produced by the experiments were observed at the leached surfaces. These produces were induced by ion-exchange, dissolution, and re-precipitation. This research suggests that maintaining neutral pH and low ion content in aqueous environments is imperative to ensure the safe disposal of radioactive iodine when contained by this apatite waste form.

Characterizing the behavior of petroleum-bearing fluids in natural reservoirs is challenging due to the heterogeneous composition of hydrocarbon systems. However, the fluid–rock interactions are important for recovering oil from the natural reservoirs. Molecular dynamics simulations were used to investigate the interactions of octane and octanethiol with kerogen and with calcite, respectively. To quantify their interactions, free energy surfaces were computed by umbrella sampling to obtain the minimum energy required to recover oil molecules from kerogen and from calcite surfaces. The effects of surface composition, oil molecular polarity, surface water, and size of the oil molecular cluster were examined through the calculations. The results suggest that (1) polar oil compounds require more energy to be
recovered from the reservoir rocks than non-polar molecules, (2) isolated oil molecules or oil clusters of a smaller size are more difficult to be displaced than a larger size of molecular clusters, and (3) the presence of surface water reduces the energy required for oil recovery. This study provides an energetic perspective on the interfacial interactions for oil recovery in natural reservoirs.
CHAPTER 1. INTRODUCTION

1.1. Effect of Solution Chemistry on The Iodine Release from Iodoapatite in Aqueous Environments

The deployment of nuclear energy is motivated by the pressing demand to mitigate climate change.\textsuperscript{5} Sustainable development of the nuclear energy requires concrete plans to safely dispose radionuclides waste generated by nuclear fission.\textsuperscript{6} Among those radionuclides, iodine-129 is particularly challenging to handle due to its long half-life (15.7 million years), high yield (0.7% yield per fission of uranium-235),\textsuperscript{7} and weak interactions with common materials in repository environments such as engineering barrier and rock in geology formation.\textsuperscript{8,9} Iodide (I\textsuperscript{-}) is the most stable form of iodine in an environment with pH and redox potential typically found in nature.\textsuperscript{10–12} Under highly oxidizing conditions, iodide can be oxidized to iodine (I\textsubscript{2}) and/or iodate (IO\textsubscript{3}\textsuperscript{-}). All these iodine species are highly mobile in nature given their high volatility and or high solubility.\textsuperscript{13,14} Iodine, as an essential element for human health, can accumulate in human bodies.\textsuperscript{15} For a healthy adult, 30% of the total iodine, approximately 15-20 mg, is concentrated in the thyroid gland.\textsuperscript{16} Chronical radiation from iodine-129 beta decay can induce cancer to the thyroid follicular cells.\textsuperscript{15} Therefore, iodine-129 is a primary contributor of the radiation dosage when analyzing the safety of disposal environments.\textsuperscript{8} The immobilization of iodine-129 is one of the critical research subjects for nuclear waste management.\textsuperscript{8,17–22}

The most probable scenarios that compromise nuclear waste forms in a repository environment are the contact with aqueous solutions.\textsuperscript{1,23} In a typical repository, nuclear waste forms are packed into corrosion resistant metallic canisters underground.\textsuperscript{24} Canister corrosion and degradation are anticipated to be the result of corrodents carried by groundwater.\textsuperscript{25} Through infiltration and percolation of precipitation and groundwater aquifer, water can reach the
canisters and supply corrodenents to react with the canister material. Upon the breaching of the canister, the waste forms are exposed to an aqueous environment. Owing to the long half-life of iodine-129, it is crucial to predict the long-term chemical durability of iodine waste forms. To enable such prediction, it is necessary to obtain a fundamental understanding of corrosion mechanisms of waste forms and how iodine in the host material is released in various solutions that may occur under repository conditions.

Several waste form materials including glass, ceramics, glass-ceramics, cement, and composite have been proposed to immobilize iodine. These waste forms immobilize iodine via two major mechanisms: encapsulation and incorporation. To encapsulate iodine, the host matrices need to contain iodine in a designated phase different from the host material. One example is zeolite structure, in which iodine-bearing phases can be adsorbed on zeolite’s framework. Iodine can also be incorporated as a compositional element into the host matrix structure through chemical bonding, such as iodoapatite Pb₅(VO₄)₃I and sodalite Na₄(AlSiO₄)₃I.

The difficulty to study the durability of different waste forms varies on a case-by-case basis. It is particularly challenging to evaluate the encapsulation waste forms due to the complexity of multi-phase and microstructures. On the other hand, characterizing the corrosion mechanism can be relatively straightforward for single-phase crystal waste forms which have well-defined crystal structures and simple microstructures. Based on the simplicity of its crystal structure and microstructure, iodoapatite is chosen in this study as the model system of ceramic waste forms that can incorporate radionuclides. In addition, apatite ceramics is a promising material due to its thermal, mechanical, and chemical stability. These advantages are also
demonstrated in nature as apatite has been found as a retention matrix for actinides and fission products in natural fission reactors at Franceville basin in Africa.\textsuperscript{25,33}

Several chemical durability tests have been performed on single-phase crystal waste forms. Uno et al. in 2001 conducted soxhlet leach method on apatite Pb\textsubscript{10}(VO\textsubscript{4})\textsubscript{6}I\textsubscript{2}.\textsuperscript{34} Soxhlet leach method is designed to maximize the number of leachable constituents in leachant by allowing a continuous contact between the waste and recycling leachant in a closed system.\textsuperscript{35} The iodine release rate, 3.98×10\textsuperscript{-5} g cm\textsuperscript{-2} d\textsuperscript{-1}, was reported.\textsuperscript{34} Guy et al. in 2002 studied apatite Pb\textsubscript{10}(VO\textsubscript{4})\textsubscript{4.8}(PO\textsubscript{4})\textsubscript{1.2}I\textsubscript{2} dissolution in aqueous solutions.\textsuperscript{36} The resulting data shows that iodine release was incongruent and exhibited dependency on temperature and pH. They also discovered a secondary phase, lead vanado-phosphate, precipitated at the sample surface. Zhang et al. in 2007 performed static leaching test on Pb\textsubscript{5}(VO\textsubscript{4})\textsubscript{3}I powder in a basic KOH/KHCO\textsubscript{3} buffer solution.\textsuperscript{37} Spectroscopic evidences show that OH\textsuperscript{-} and CO\textsubscript{3}\textsuperscript{2-} can substitute I\textsuperscript{-} and VO\textsubscript{4}\textsuperscript{3-} in apatite. Maddrell et al. in 2014 conducted static leach tests on crushed powder iodide sodalite Na\textsubscript{4}(AlSiO\textsubscript{4})\textsubscript{3}I in KOH/KHCO\textsubscript{3} buffer solutions.\textsuperscript{29} The result suggests a congruent dissolution.\textsuperscript{29} Three leaching static experiments with durations of 3, 7, and 14 days exhibited a logarithmic increase of iodine release. More recently, in 2017 Coulon et al. applied static leaching technique to study the iodate-substituted hydroxyapatite in deionized water and groundwater.\textsuperscript{38} They reported that the iodine release is controlled by congruent dissolution under unsaturated conditions and controlled by diffusion through ion exchange under saturated condition. Interestingly, when groundwater was used as leachant, secondary phase hydroxyapatite precipitated on the sample surface. Based on these studies, static leach test is a preferable method to study the waste form durability due to the following reasons: 1) its simple procedure can accommodate a wide range of test conditions; 2) the resultant data can be used to interpret the
release mechanism.\textsuperscript{39} Static leaching method assumes that the solution feedback is negligible, which is valid under conditions of sufficiently low surface to volume ratio.\textsuperscript{39} However, the solution feedback can gradually increase over time in a static leaching experiment. In cases where the solution is oversaturated for phases of low solubility, secondary phases can precipitate at the leached surface. Therefore, it can be problematic to use data from static leaching tests to predict waste form behavior in a repository environment.\textsuperscript{40} To address the issues of solution feedback, a semi-dynamic leaching method was implemented by Zhang et al. in 2018 to quantify the processes involved in the iodine release of an iodine-bearing apatite.\textsuperscript{32} In their experiment, deionized water solutions, as the leachant, were replaced periodically to minimize the solution feedback. They demonstrated that iodine released from apatite is driven by short-term diffusion and long-term matrix dissolution. This semi-dynamic approach was employed to produce essential datasets to parameterize a mechanistic model suitable for predicting the kinetics of iodine release under different conditions.\textsuperscript{40}

Since the aqueous systems in natural environment contain a variety of dissolved species, it is necessary to understand how these aqueous species affect the iodine release from iodine waste forms in an aqueous environment. For instance, the iodine release from apatite structured materials can be enhanced by rapid substitution of halogen element\textsuperscript{41–44} or inhibited by precipitation of secondary phase.\textsuperscript{36,38,40} In this study, we conducted semi-dynamic leach tests on single phase crystal ceramics of iodoapatite in 0.1 mol/L NaCl, Na\textsubscript{2}CO\textsubscript{3}, Na\textsubscript{3}PO\textsubscript{4} and Na\textsubscript{2}SO\textsubscript{4} solutions. The goal is to examine the impact of the solution chemistry on the kinetics of iodoapatite dissolution. We hypothesized that dissolved aqueous species, via ion exchange and precipitation, can substantially impact the dissolution kinetics; this effect should highly depend on the chemistry of the aqueous species and the surface reactions of specific phases. The finding
of this study is expected to provide important insight into the long-term performance of iodine waste forms and guidance to improve the disposal safety of nuclear waste.

1.2. Energetics of Interfacial Interactions of Hydrocarbon Fluids with Kerogen and Calcite Using Molecular Modeling

Oil is the main energy source for our modern civilization and will remain as a major contributor of global energy in the foreseeable future. However, only a portion of oil preserved in a reservoir can be recovered. Thus, it is imperative to improve the recovery efficiency of petroleum reservoirs. Current methods to improve oil production including primary, secondary, and tertiary oil recovery techniques can yield 30%–60% of the original oil in place, leaving up to 70% of the original oil in a reservoir.

The pressing demand of energy for modern civilization has spurred technical innovations to improve oil recovery, especially through tertiary oil recovery or enhanced oil recovery. However, there is a limited understanding of how hydrocarbon-bearing fluids interact with the materials in reservoir formations. This knowledge gap impairs the assessment of the economic potential of a hydrocarbon reservoir. For example, relative permeability, an essential parameter of fluid flow characteristics for formation evaluation, is measured by special core analysis (SCAL) through conducting flow experiments on core plugs taken from a reservoir. However, SCAL results are often contradictory or cannot be properly implemented in the reservoir modeling and petrophysical evaluation. A myriad of factors may complicate the results, including the hydrofracture geometries, networks of preexisting fractures, adsorption and desorption processes, non-Darcy multiphase flow, chemically and structurally heterogeneous formations, etc.

The interfacial interactions between the fluid and rock play a key role in all these complications. As shown in Figure 1.1., if a pore has a less than 100 nm radius and the
intermolecular interaction has an effective distance of 3 nm, a significant portion (12% – 100% volume) of confined fluid can be directly affected by the interfacial interactions. Therefore, to further improve recovery efficiency, a fundamental understanding of the fluid–rock interactions is indispensable.

To probe the interfacial interactions at the nanoscale, molecular-level characterization is necessary. Both experimental and computational approaches have been applied to study the hydrocarbon fluid behavior in the rock at the nanoscale. Extensive experimental studies have been conducted on the reservoir formations to characterize the organic content, pore structure, and petrophysical properties. These studies aimed to calibrate the empirical models in reservoir engineering to describe the fluid flow and to provide a basis for reservoir assessment and production optimization. However, due to the compositional and structural heterogeneity of reservoir formations, it is challenging to interpret the dynamics and kinetics of interface interactions without knowing the molecular scale details. Current understanding of the hydrocarbon systems heavily relies on the characterization technologies to conduct experiments.

Figure 1.1. Effect of intermolecular interaction on the fluid confined in nanostructures.
on surfaces and interfaces\textsuperscript{63–65} such as focus ion beam scanning electron microscopy (FIB-SEM),\textsuperscript{59,66,67} transmission electron microscopy (TEM),\textsuperscript{67,68} atomic force microscopy (AFM),\textsuperscript{60,69,70} X-ray Diffraction (XRD),\textsuperscript{71,72} X-ray microtomography (Micro-CT),\textsuperscript{73,74} nuclear magnetic resonance (NMR),\textsuperscript{75,76} etc. Implementing these methodologies to characterize microscopic phenomena becomes challenging at the molecular level. Unlike experiments, computational simulations can study physical phenomena over a range of scales,\textsuperscript{77} directly connecting the microscopic details of a system to macroscopic properties of experimental interest.\textsuperscript{78} Due to the intensive computation, quantum mechanics (QM) simulations have strict limits on the size, time, and complexity of the systems.\textsuperscript{77–79} Molecular simulations, built on classical molecular mechanics (MM) such as Monte Carlo (MC) and molecular dynamics (MD), are more appropriate than QM methods to address the issues of size and complexity of the hydrocarbon systems. MC methods are a stochastic approach, suitable for system equilibrium, while MD techniques are deterministic, suitable for both equilibrium and transport properties of a given system.\textsuperscript{78,79} Thus, this study used MD to investigate the energetics of fluid–rock interactions. Currently, there are several studies using MD to investigate hydrocarbon fluid interactions with kerogen and minerals, such as (1) the adsorption, diffusion, and permeation of hydrocarbon fluid in shale kerogen and kerogen analogue;\textsuperscript{80–87} (2) slippage, displacement, and adsorption of hydrocarbon flow on quartz, calcite slits, and montmorillonite slits;\textsuperscript{88–91} (3) detachment of oil cluster from silicate surfaces in surfactant solution.\textsuperscript{92} These studies evaluated the effect of nanopores on the properties of hydrocarbon fluid, such as bulk viscosity, contact angle, and slippage with focuses on the phenomena of the interactions. For instance, Liu et al. in 2012 stated that water can penetrate the oil–water interface and form a surface water layer on a hydrophilic silica surface, enhancing the oil detachment from the hydrophilic surface.\textsuperscript{92}
However, there is a lack of direct approaches to assess the energetics of these interactions, leaving the energetic aspect largely underexplored. Knowledge on energetics, such as the interaction thermodynamics, can improve the understanding of the fundamental mechanism in hydrocarbon fluids interactions with reservoir formations.

The present study intends to examine the feasibility of the computational approach to evaluate the free energy profile of the interactions between oil compounds and the surfaces of reservoir rock materials. Umbrella sampling, widely used in computational biology and biochemistry, was adopted to compute the free energy profiles of the oil interactions with the rock materials. We studied the surfaces of kerogen and calcite to evaluate the effect of four different variables including oil polarity (polar vs non-polar oil), oil cluster size (a single molecule oil vs 30 molecules oil cluster), surface composition (inorganic calcite mineral vs organic kerogen), and surface water (the presence vs the absence of surface water). Probing the free energy changes in oil–rock interactions can provide insight into the thermodynamics of the surface wettability and hydrocarbon behaviors in reservoir formations.
CHAPTER 2. EFFECT OF SOLUTION CHEMISTRY ON THE IODINE RELEASE FROM IODOAPATITE IN AQUEOUS ENVIRONMENTS

2.1. Experimental

2.1.1. Materials and methods

The material of interest in this study is lead vanado-iodoapatite Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$, a ceramic crystalline with apatite structure. Apatite is a promising waste form structure to immobilize iodine because i. apatite structure is chemical and structural flexible which can accommodate a wide range of radionuclides and ii. the over two-billion-year presence of apatite minerals in natural nuclear reactors has proven that apatite structure is resistant to radiation over geological time. Our samples, obtained from previous studies, were dense ceramic chips in quadrilateral shape: 4.7 – 10.3 millimeter long by 1.1 – 1.8 millimeter thick with a chemical composition of Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$ according to the EDS and X-ray diffraction.

![Figure 2.1. A single crystal cell of lead vanado-iodoapatite Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$ visualized by CrystalMaker (colorblind-friendly).](image)

refinement, as shown in Figure 2.4., 2.5. and 2.6. The iodoapatite samples were synthesized by using high energy ball milling (HEBM) and spark plasma sintering (SPS) techniques. As shown in the Figure 2.1., the crystal structure of this sample belongs to the apatite family $M_{10}(XO_4)_6Y_2$ with a deficiency of lead and iodine. Sample surfaces were polished by 4000-grit sandpaper on a mechanical polishing wheel lubricated with ethanol. Details of the synthesis and characterization of these samples were reported previously in separate publications.\textsuperscript{28,32,40}

Leaching test can reveal the degradation behavior of the waste form materials and enable interpretations of the release mechanism of immobilized radionuclide. Several standardized protocols of leaching test have been developed to evaluate the performance of waste form materials designed to immobilize HLW, which can be categorized into three classes: (1) dynamic, to determine the maximum of a forward rate of dissolution; (2) static, to emulate static aqueous solution in a flooded repository (a closed thermodynamic system); and (3) semi-dynamic, to determine if mass diffusion is involved in the release of radionuclides and the corresponding diffusion factor.\textsuperscript{97}

\begin{figure}[h]
    \centering
    \includegraphics[width=0.5\textwidth]{leaching_experiment.png}
    \caption{Schematic diagram of a leaching experiment}
\end{figure}
Iodine release from apatite structure can be controlled by either dissolution or diffusion. Therefore, semi-dynamic leaching test protocol was performed to assess the contribution from dissolution and diffusion towards the long-term iodine release from iodoapatite (Figure 2.2.). This experiment protocol is adapted from the Standard Test Method for Accelerated Leach Test, ASTM C1308-08. A typical experiment is conducted in cap-sealed Teflon vessels (Savillex) in a digital oven at a constant temperature of 90 ± 0.5 °C. In the Teflon vessel, a sample was placed on a Teflon mesh stand and exposed to fresh leachant periodically. The leached solution was completely replaced every 24 hours. The replaced solutions were collected for solution elemental analysis. And the leached samples were retrieved, rinsed by deionized water and ethanol, and air-dried for surface characterization. The leaching method was adopted from ASTM C1308 standard test, as described in the previous study. Four parallel experiments were conducted simultaneously for 14 days in four different leaching solutions: 0.1 mol/L NaCl, 0.1 mol/L Na₂CO₃, 0.1 mol/L Na₃PO₄, and 0.1 mol/L Na₂SO₄. Sample surface area (m²) to solution volume (m³) ratios (S/V) of all four tests were fixed and maintained at 5/m. The leached solutions were replaced every 24 hours. All reactor vessels were weighed before and after each interval to monitor the solution losses which were within 0.5 % of the initial solution mass. In addition, a control test was conducted in deionized water under identical conditions for 7 days using the same protocol. All samples after leaching experiments were collected, rinsed by deionized water and ethanol, and air-dried.
2.1.2. Characterization

The elements of interest in the leachate solutions are I, Pb, and V. The leached solutions, depending on the solution chemistry, were analyzed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, PerkinElmer Elan 9000) in the lab of Dr. Kalliat T. Valsaraj at LSU Chemical Engineering and Inductively-Coupled Plasma-Optical Emission Spectrometry (ICP-OES, SPECTRO Ametek Spectro ARCOS) in the Soil Testing & Plant Analysis Lab of LSU AgCenter. ICP-MS can measure element concentration from ppb (part per billion, $10^{-9}$) and up to ppm (part per million, $10^{-6}$) levels, depending on the elements of interest. ICP-OES is usually for detection of ppm levels and above. ICP-MS and ICP-OES use inductively coupled plasma (ICP) to introduce sample as aerosols into the center of plasma, e.g., ionized argon. Inside the ICP, sample aliquots together with the carrier solution were introduced into the plasma through nebulizer which can convert liquid into aerosol. The aerosol was broken down into charged ions by the intense collision with the plasma.\textsuperscript{99–101}

For ICP-MS, solution aliquots were prepared by mixing sample solution and internal standard. The internal standard was introduced to improve the accuracy and precision by minimizing non-spectral interferences.\textsuperscript{100–102} The ions created by the plasma were channeled into a mass spectrometer (MS), in which the ions were separated by the different ratios of mass to charge (m/z). The concentrations of elements of interest were calculated based on the signal proportion to internal standards and calibration standards. Cesium (Cs), manganese (Mn), and bismuth (Bi) were selected as the internal standards of iodine (I), vanadium (V), and lead (Pb), respectively. The standard solutions of these elements listed above were obtained from Inorganic Ventures.
For ICP-OES, internal standards were not implemented due to the relatively low sensitivity of this technique.\textsuperscript{100,101} In the optical spectrometer, emitted light from the plasma was separated into different wavelengths.\textsuperscript{100,101} The intensity of each wavelength was measured and compared with the calibration curve to calculate the concentrations of elements of interest. ICP-OES simultaneously measure all analyte wavelength (nm) including 178.276, 179.909, and 183.038 for iodine, 168.215, 220.353, 167.153, 172.680, and 261.418 for lead, and 292.402, 292.464, 309.311, and 311.071 for vanadium. This study used wavelength (nm) 179.909 and or 183.038 for iodine, 167.153 for lead, and 292.402, 292.464, 309.311, and 311.071 for vanadium.

Both ICP-MS and ICP-OES in this study used calibration curve method to calibrate instrument measurement. Calibration curve technique uses a series of standard solutions, analyte solutions with known concentration, to evaluate the instrument response as a function of analyte concentration.\textsuperscript{103} Therefore, the response to the unknown solution can be interpreted accordingly. Moreover, both ICP-MS and ICP-OES are sensitive to the residue effect, the residue of high concentration solution can substantially deviate the measurement of low concentration solution.\textsuperscript{104} To minimize the residue effect, solution analysis started from low concentration to high. Reagent blank, an analyte-free sample, was applied during the ICP-MS calibration to offset the matrix effects caused by dissolved concomitant salt ion.\textsuperscript{100,101}

Two standard solutions from Inorganic Ventures were used in the solution analysis: 1) 1.001 ± 0.007 μg/ mL iodide in H₂O solution and 2) 1.000 ± 0.007 μg/ mL lead and 1.000 ± 0.006 μg/ mL vanadium in 1% HNO₃ solution. Chemical properties of solution at equilibrium state such as pH, ionic strength, speciation, and activity were calculated by Visual MINTEQ package.\textsuperscript{105}

Chemical and structural alterations of the sample surfaces were examined by
Scanning Electron Microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS, FEI Quanta 3D FEG Dual Beam with integrated EDAX Pegasus EDS & EBSD system, operated in Shared Instrumentation Facility at LSU), X-ray Diffraction (XRD, PANalytical Empyrean X-Ray Diffractometer, operated in Shared Instrumentation Facility at LSU), and Infrared spectroscopy (IR, Thermo Nicolet Continuum Infrared Microscope, operated in Center for Advanced Microstructures and Devices of LSU).

In SEM, an electron beam is scanning the material surface that leads to the emission of photons and electrons from or near the sample surface.\textsuperscript{106} SEM has different detection modes, such as secondary electron imaging, energy-dispersive X-ray spectroscopy (EDS), backscattered electron imaging, electron channeling, Auger electron microscopy, etc.\textsuperscript{107} One of the most common mode is secondary electron imaging. To form a secondary electron image, inelastic interactions between the primary electron beam and the sample produce secondary electrons from the surface or the near-surface regions of the sample. Secondary electrons have low energy and limited mean free paths on solid surface, leading to highly localized signals at the point of impact on sample surface. Therefore, secondary electron imaging can achieve a resolution of 1 nm approximately, making SEM suitable to characterize the topography of sample surfaces.\textsuperscript{106} For this study, typical settings of SEM secondary electron mode are listed as follows: high vacuum, acceleration voltage of 10 kV or 20 kV, and magnification from 100X (submillimeter) to 100,000X (submicrometer).

EDS takes advantage of the electron beam of SEM to conduct element analysis of the surface chemistry.\textsuperscript{108} During EDS, the electron beam excites electrons in inner shells (low energy), promoting electrons in outer shells (high energy) to fill the vacancies.\textsuperscript{109}
The electron transition from higher energy shells to lower energy shells releases energy in the form of X-ray.\textsuperscript{109} The EDS detector measures the number of emitted X-rays versus their energy level. Because energy differences between outer and inner shells are unique for each element, the emitted X-rays can indicate the elemental composition of sample surface. EDS data can be obtained at a point, along with a line, or over an area of sample surface. The penetration depth of EDS analysis is approximately several to tens of micrometers.\textsuperscript{110,111} In this study, typical EDS experiments were conducted using high vacuum, acceleration voltage of 10 kV, and magnification from 2500 to 10000 X. The elements of interest in the EDS analysis include carbon at 0.277 keV, oxygen at 0.523 keV, phosphorus at 2.013 keV, sulfur at 2.307 keV, lead at 2.342 keV, iodine at 3.937 keV, and vanadium at 4.952 keV.

X-ray diffraction techniques can determine the structure of a crystalline material.\textsuperscript{112} A beam of incident X-rays generated by the X-ray diffractometer is diffracted by the crystalline structure into certain directions. The resulting X-ray diffraction pattern is presented as the angles of the diffracted beams with respect to their corresponding intensity. To obtain quantitative analysis of lattice parameters and site occupancy, it is necessary to fit the XRD pattern by refinements such as Rietveld method and Le Bail method.\textsuperscript{113} The Rietveld method uses theoretical calculations to produce the calculated diffraction pattern of a crystal structure model, while the Le Bail method use unit cell models to fit peak intensity of each reflections empirically.\textsuperscript{113,114} For this study, XRD analysis was performed by a PANalytical Empyrean X-ray Diffractometer in Shared Instrumentation Facility (SIF) at LSU using monochromated Cu-K\textalpha radiation (λ = 1.5406 Å), 45 kV, 40 mA, a step size of 0.026°2θ, a scanning range from 5 to 100°2θ, scan step
time of 87.4650 s, continuous scanning, a length of position sensitive detector 2.00 °2θ, automatic divergence slit, generator 40 mA and 45 kV, and sample spinning. The Le Bail refinement was applied to analyze the XRD data using Jana2006 program. Crystallographic parameters of standard Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$ ICSD No. 280065 were used as the initial input of refinement. These parameters are listed in Chapter 2 Section 3.3. All parameters were refined by the least-squares method. The pseudo-Voigt function was used as the peak profile function.

Infrared spectroscopy (IR) relies on the photon interactions with molecules that induce vibrational excitation of covalently bonded atoms and groups. Different functional groups absorb different frequency of radiation. The adsorbed energy of radiation can induce the molecular vibration due to the change in the dipole moment. IR detects the adsorbed frequencies of radiation, which can identify the corresponding functional groups of molecules. IR band positions are expressed in wavenumber (cm$^{-1}$), which is the inverse of wavelength $\lambda$. Wavenumber is proportional to the frequency $\nu$, given $\nu = c / \lambda$ ($c$ is the speed of light). IR uses infrared spectrometer to produce an infrared spectrum in infrared region from 4000 to 400 cm$^{-1}$. In this study, IR experiments were performed by a Thermo Nicolet Continuum Infrared Microscope in specular reflection mode and transmission mode with a fixed incident angle and an aperture area of 10 µm by 10 µm covering 4000 to 650 cm$^{-1}$ at a spectral resolution of 2 cm$^{-1}$. The crystal structures were refined by Le Bail algorithm using Jana2006 program. All parameters were refined by the least-squares method. The pseudo-Voigt function was used as the peak profile function. Structural parameters of Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$ measured by Audubert et al. were used as initial input (hexagonal, space group P63/m, $a = b = 10.422$ Å, $c = 7.467$
Å, α = β = 90°; γ = 120°).\textsuperscript{116}

2.2. Results

2.2.1. Leached surface characterization by SEM/EDS

In Figure 2.3. (a-c), no changes observable by naked eyes occurred on the surfaces of samples leached by NaCl and NaSO\textsubscript{4} solutions for 14 days, whereas white layers were gradually formed on the sample surfaces leached by Na\textsubscript{2}CO\textsubscript{3} and Na\textsubscript{3}PO\textsubscript{4} solutions within the first week of the experiments. The SEM images in Figure 2.3. (d-i) show that the surface alterations on samples leached by NaCl and Na\textsubscript{2}SO\textsubscript{4} solutions were moderate, similar to the water leached surface. However, samples leached by Na\textsubscript{2}CO\textsubscript{3} and Na\textsubscript{3}PO\textsubscript{4}
solutions demonstrated significant surface corrosion and possible formation of new phases. The surface leached by Na₂CO₃ exhibited large grains, while congregated structures of similar size appeared on the surface leached by Na₃PO₄.

According to EDS analysis, the surface chemical compositions in Figure 2.4. indicate considerable changes between the leached samples and the pristine one. The key features of EDS spectrum of pristine iodoapatite are: a carbon peak at 0.3 keV from background (carbon tape), an oxygen peak at 0.5 keV, a broad Pb band from 2.34 to 2.45 keV shouldered with two small Pb peaks at 1.8 and 2.6 keV, three iodine peaks at 3.9, 4.2, and 4.5 keV, and vanadium peaks at 4.9 and 5.4 keV. Overall, the iodine peaks at 3.94 keV are nearly diminished in the EDS spectra of all four leached surfaces. The samples leached by NaCl and Na₃PO₄ exhibited a substantial amount of chloride and phosphorus signals at 2.62 and 2.01 keV, respectively. On the sample leached by NaCl, the Pb peak at 2.62 keV is comparable to the Pb peak at 1.8 keV, while the 2.62 keV peaks of the rest samples are much weaker than their corresponding 1.8 keV peaks.

![Figure 2.4. EDS spectra of a pristine iodoapatite and the samples leached by deionized water, 0.1 mol/L NaCl, 0.1 mol/L Na₂CO₃, 0.1 mol/L Na₃PO₄, and 0.1 mol/L Na₂SO₄ solutions.](image-url)
Carbon signal at 0.27 keV from Na$_2$CO$_3$ leached sample cannot be properly quantified due to the background interference from carbon tape and the graphite impurity introduced during sample synthesis. Sulfur EDS peak at 2.31 keV overlaps with the broad central peak of Pb at 2.34 keV. Na$_2$SO$_4$ leached surface exhibited no sulfur peak near 2.3 keV given the resemblance of the band shape between the sample leached by Na$_2$SO$_4$ and the rest. We noticed variations of carbon and oxygen EDS signals among these samples which were induced by the instrument settings such as sample orientation and beam parameters. Therefore, carbon and oxygen were not considered in the EDS analysis.

### 2.2.2. Leached surface characterization by IR analysis

The IR spectroscopy results are listed in Figure 2.5. All these four samples yielded two main peaks near 750 and 890 cm$^{-1}$, which are attributed to V-O bond.$^{37}$ Pristine iodoapatite and samples leached by water, Na$_2$SO$_4$, and NaCl showed nearly identical spectra. Surfaces leached by Na$_2$CO$_3$ and Na$_3$PO$_4$ exhibited position shifts of these two

![Infrared spectroscopy](image)

Figure 2.5. Infrared spectroscopy of pristine iodoapatite and leached samples by deionized water, NaCl, Na$_2$SO$_4$, Na$_2$CO$_3$, and Na$_3$PO$_4$ solutions.
V-O peaks to the region of 700 to 900 cm\(^{-1}\) and multiple new bands. Sample leached by Na\(_2\)CO\(_3\) yielded sharp bands near 785, 890, 960, 1200, and 1450 cm\(^{-1}\), in which the broad band at 1450 cm\(^{-1}\) is attributed to the stretching vibration of CO\(_3^{2-}\). The Na\(_3\)PO\(_4\) leached surface generated IR peaks near 785, 870, 950, 1110, 1420, 1800, and 2200 cm\(^{-1}\), in which some can be assigned to the PO\(_4^{3-}\) (e.g., \(v_1 - 950\) cm\(^{-1}\), \(v_3 - 1100\) cm\(^{-1}\)).

Interestingly, both CO\(_3^{2-}\) and PO\(_4^{3-}\) leached surfaces showed visible OH\(^-\) stretching vibration near 3500 cm\(^{-1}\), which also occurred on water leached surface under IR transmission mode.

### 2.2.3. Leached surface characterization by XRD

The XRD data are shown in Figure 2.6. All these leached samples demonstrated substantial differences compared to the pristine sample. Based on the XRD pattern, these

![X-ray Diffraction](image)

Figure 2.6. XRD patterns of a pristine iodoapatite and the samples leached by deionized water, 0.1 mol/L Na\(_2\)SO\(_4\), 0.1 mol/L NaCl, 0.1 mol/L Na\(_2\)CO\(_3\), and 0.1 mol/L Na\(_3\)PO\(_4\). In addition, standard XRD spectra of iodoapatite, vanadinite, and hydroxylvanadinite are listed for comparison. * denotes the graphite impurity introduced during sample synthesis.
leached samples can be categorized into two groups: I) surfaces leached by NaCl and Na₂SO₄ solutions, the pristine, and water leached sample; II) surfaces leached by Na₂CO₃ and Na₃PO₄ solutions, which were similar to the standard hydroxylvanadinite. The XRD patterns of Group I are alike, which indicates no substantial structural changes compared to the pristine. The XRD patterns of Group II display enhanced peak splitting between 25° and 28°. The original peak splitting of the pristine sample reflects the apatite structure deformation which accommodates the relatively large iodide incorporated in the apatite framework. The peak splitting of Na₂SO₄ leached surface is slightly enhanced, compared to the pristine, but is weaker than the water leached sample. Interestingly, NaCl leached surface yielded a diminished splitting at 26° and a new peak occurred at 29°, later identified as (131) shown in Figure 2.7. The Full Width at Half Maximum (FWHM) of XRD from NaCl leached surface was considerably broadened to ~0.4° compared to ~0.2° from other samples, which may be attributed to the peak overlapping resulting from the

![XRD of iodoapatite leached by 0.1 mol/L NaCl](image)

**Figure 2.7.** XRD phase analysis of the iodoapatite sample surface leached by 0.1 mol/L NaCl solution. Two phases were identified: iodoapatite and vanadinite.
presence of a secondary phase. Both Na$_2$CO$_3$ and Na$_3$PO$_4$ leached samples exhibited nearly identical XRD pattern, resembling the pattern of standard hydroxylvanadinite Pb$_{10}$(VO$_4$)$_6$(OH)$_2$. The two highest bands on Pb$_{10}$(VO$_4$)$_6$(OH)$_2$ standard are (112) and (1$ar{3}$1) with an order of intensity $I_{112} < I_{131}$. Same bands (112) and (1$ar{3}$1) also have the highest intensity on Na$_2$CO$_3$ and Na$_3$PO$_4$ leached samples, however, the intensity of

<table>
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<th>Leach test condition</th>
<th>Refined parameters</th>
<th>GoF</th>
<th>$R_p$ (%)</th>
<th>$R_{wp}$ (%)</th>
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<td>$a$, $b$ (a=b, Å)</td>
<td>$c$ (Å)</td>
<td>GoF</td>
<td>$R_p$ (%)</td>
</tr>
<tr>
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<td>7.4756 (3)</td>
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<tr>
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<td>7.4656 (2)</td>
<td>1.65</td>
<td>4.85</td>
</tr>
<tr>
<td>0.1 mol/L Na$_3$PO$_4$</td>
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<td>7.4449 (2)</td>
<td>1.43</td>
<td>4.74</td>
</tr>
<tr>
<td>0.1 mol/L NaCl (2 phases)</td>
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<td>7.4796 (5)</td>
<td>1.17</td>
<td>4.12</td>
</tr>
<tr>
<td></td>
<td>10.3536 (8)</td>
<td>7.3735(8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Pb$_{4.925}$(VO$_4$)$_3$I$_{0.85}$ [ICDD#04-011-4267] | 10.422 | 7.467 | Crystal system: hexagonal |
| Pb$_5$(VO$_4$)$_3$(OH) [ICDD#01-075-7576] | 10.2242 | 7.4537 | Space group: P63/m #176; $\alpha$=90°; $\beta$=90°; $\gamma$=120° |
| Pb$_5$(VO$_4$)$_3$Cl [ICDD#01-073-1732] | 10.31 | 7.34 |
is higher than that of (131), $I_{(112)} > I_{(131)}$.

The Le Bail method was applied to obtain structural information from the XRD data. Table 2.1 compares the refined lattice parameters between sample surfaces of different conditions and standards. No noticeable changes occurred in the crystal structures of samples leached by deionized water and Na$_2$SO$_4$ when compared to that of pristine sample (their length of $a$-, $b$-, and $c$-axes are approximately ~10.4, ~10.4, and ~7.5 Å, respectively). On the other hand, a ~0.2 Å contraction along both the $a$- and $b$-axes were observed for the samples leached by Na$_2$CO$_3$ and Na$_3$PO$_4$ solutions while the $c$-axis remains the same and is consistent with other samples at ~7.45 Å. The observed and calculated diffraction patterns, the residual and the indices of the main reflections of NaCl leached sample are shown in Figure 2.7. We identified a secondary phase vanadinite Pb$_5$(VO$_4$)$_3$Cl, indicating the substitution of iodine by chlorine during NaCl leaching.

2.2.4. Solution composition analysis by ICP-MS and ICP-OES

The results of the solution analysis on the leachates collected from the leach tests are shown in Figure 2.8. The release rates of iodine, lead, and vanadium are depicted as green circles, blue squares, and red triangles, respectively. In Figure 2.8a., iodine release in NaCl solution gradually increased over time, reaching a maximum rate near 0.8 mmol/m$^2$/d at day 11, and then slightly decreased near the end of the 14-day test. The Pb and V release exhibited similar patterns with a relatively high initial rate around 0.075 mmol/m$^2$/d, then gradually decreased, and eventually approached a plateau near 0.05 mmol/m$^2$/d. In Figure 2.8b., the release patterns of iodine and vanadium in Na$_2$CO$_3$ are similar: release rates rapidly reached maximum near day 2 and then gradually decreased over time approaching a plateau. However, the long-term rate of Pb in Na$_2$CO$_3$ appears to
be constant. In Figure 2.8c., the iodine release in Na$_2$SO$_4$ exhibited a high initial rate approximately 0.32 mmol/m$^2$/d and then its rate gradually decreased, eventually approaching a plateau around 0.15 mmol/m$^2$/d. Despite no high initial release, the Pb and V release patterns follow the trend of iodine release: gradually decreased over time and then rebounded near day 10. The Figure 2.8d. describes the element release of iodoapatite in Na$_3$PO$_4$, which shows constant rates of ~4.5, ~3.5, and ~13 mmol/m$^2$/d for the release for iodine, Pb, and V, respectively. Due to the instrumentation limitation and sample consumption, only four leachates from the Na$_3$PO$_4$ experiment was analyzed for their Pb content.

![Graphs showing element release rates](image)

Figure 2.8. Solution analysis of collected leachates from 14 days semi-dynamic leach tests on iodoapatite samples in (a) 0.1 mol/L NaCl, (b) 0.1 mol/L Na$_2$CO$_3$, (c) 0.1 mol/L Na$_2$SO$_4$, and (d) 0.1 mol/L Na$_3$PO$_4$. 

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Leaching rate of I, Pb, and V based on the solutions analysis are compared in Figure 2.9a-c., respectively. In general, leaching tests conducted in the ionic solutions present significantly higher element release rates than those of deionized water in the order of \( \text{Na}_3\text{PO}_4 > \text{Na}_2\text{CO}_3 > \text{Na}_2\text{SO}_4 > \) water, except in the NaCl solution. In Figure 2.9a., iodine release from \( \text{Na}_3\text{PO}_4, \text{Na}_2\text{CO}_3, \) and \( \text{Na}_2\text{SO}_4 \) solutions exhibited a long-term leach pattern similar to that of water leaching: started with a high initial release, then gradually decreased, and eventually stabilized and reached a plateau. The iodine release in NaCl solution, however, presents a different pattern: iodine rate increased from the beginning of leach test to day 11, when the rate reached maximum and then stabilized.

![Graphs showing leaching rates and molar ratios](image)

Figure 2.9. Comparison of element release rate of iodine (a), vanadium (b), and lead (c) in the leachate solutions from different leach tests. Molar ratios of Pb/V (d) and I/V (e) in leachate solutions from leach tests in NaCl, \( \text{Na}_2\text{SO}_4, \text{Na}_2\text{CO}_3, \text{Na}_3\text{PO}_4 \), and deionized water.
The release rates of Pb and V from NaCl test are relatively constant but not higher than those of water leached as shown in Figure 2.9b,c.

The molar ratios in leachate solutions are illustrated in Figures 2.9d,e. Except for the anomalous NaCl data, the long-term I/V ratios in Figure 2.9d. fluctuate around the ratio of water-leached sample within the range of [0.34, 1.02], which are higher than the stoichiometric value 0.28. In Figure 2.9e., the long-term Pb/V ratios of NaCl and Na₂SO₄ tests are 1.36 and 1.65, approximate to the stoichiometric value 1.64, whereas the long-term ratios from Na₂CO₃ and Na₃PO₄ tests are 0.95 and 0.27, significantly lower than 1.64.

2.2.5. Overview of leaching rates in solutions

The phases of interest in this study are the aqueous solutions and the solid surfaces. The leachate solution chemistry in Figure 2.9. shows that iodine release from the sample leached by the NaCl solution has a distinctive pattern. For the other leach tests, the long-term iodine rates (plateau region in Figure 2.8.–2.9.) are at least one magnitude higher than that from water leaching. And the order of iodine leach rate, based on solution analysis in Figure 2.9a., is consistent with the orders of Pb and V rates in Figure 2.9b,c.: $R_{Pb/V/I}(Na_3PO_4) > R_{Pb/V/I}(Na_2CO_3) > R_{Pb/V/I}(Na_2SO_4) > R_{Pb/V/I}$ (deionized water). In the following section, we will analyze the anomalous result of NaCl leach test and then explain how element release behaviors differentiate due to the different solution chemistry, such as pH and ionic species.
2.3. Discussion

2.3.1. Anomaly of the sample leached by NaCl solution

Iodoapatite sample leached by 0.1 mol/L NaCl solution exhibited unique surface phase composition and iodine release pattern. The XRD data in Figure 2.6. and 2.7. show leached surface has no apparent splitting in the region from 25° to 28° (2θ) and a new peak (131), attributed by a vanadinite phase. This anomaly suggests a reduced structural distortion, which can be contributed by substituting iodide with smaller chloride. The refinement in Figure 2.7. confirmed new phase vanadinite was formed on the surface, which resembles the XRD pattern of iodoapatite Pb9.85(VO4)6I1.7. The XRD data is consistent with the EDS result and solution analysis. The Pb EDS band at 2.6 keV, in Figure 2.4., is comparatively enhanced due to the overlap by chlorine signal at 2.6 keV. The release rates of iodine from the NaCl test in Figure 2.8a. suggest the new phase was growing until the equilibrium state was reached. A similar iodine release pattern was observed in a pH 4 semi-dynamic leaching experiment, of which the rate anomaly was caused by the formation of a secondary phase.40 The molar ratios of Pb/V in Figure 2.9e. approximate to the stoichiometric value 1.6, indicating a congruent dissolution of Pb and V. The variation of I/V molar ratios in Figure 2.9d. is consistent with that of iodine rates in Figure 2.8a. Both the I/V ratios and iodine rates suggest an incongruent release for iodine, unlike the congruent Pb and V. The SEM images in Figures 2.3b,e. show that both surfaces leached by NaCl and deionized water share similar morphology. The new phase vanadinite Pb5(VO4)3Cl, confirmed by the XRD refinement, suggests ion-exchange process between iodide and chloride. This postulation is supported by the solution and surface analysis that 1) a significant amount of iodine was released into NaCl solution.
while the Pb and V rates are comparable to the data of water leach test as shown in Figures 2.8–2.9.; 2) the surface alteration revealed by SEM in Figure 2.3. and the surface chemistry by EDS in Figure 2.4. resemble those of deionized water. Interestingly, the structural deformation of the original iodine-bearing apatite Pb$_{9.85}$(VO$_4$)$_6$I$_{1.7}$ appeared to be restored in the chlorine-substituted structure vanadinite Pb$_5$(VO$_4$)$_3$Cl. Given that the ionic radius of chloride (Cl$^-$, 1.68 ± 0.19 Å) is considerably smaller than that of iodide (I$^-$, 2.11 ± 0.19 Å),$^{119}$ exchanging the iodide with smaller chloride seems to have repaired the structural deformation.

2.3.2. Effect of pH on iodine release and secondary phase formation

The solution pH has a strong effect on the iodine release of the iodoapatite. Chemical properties of the leaching solutions calculated by VMINTEQ are listed in Table 2.2. According to our previous studies, iodoapatite dissolution in deionized water can be represented by the congruent release of Pb and V.$^{32}$ In Figure 2.9b,c., the Pb and V rates from different solutions are generally constant, indicating a constant-dissolution controlled process. The overall dissolution rates from low to high appears to be: $R_{(\text{deionized water})} < R_{(\text{Na}_2\text{SO}_4)} < R_{(\text{Na}_2\text{CO}_3)} < R_{(\text{Na}_3\text{PO}_4)}$, which corresponds to the solution pH values ~6.1, ~6.2, ~10.3, and ~10.9 under 90 °C as listed in Table 2.2. Therefore, increasing pH from neutral to basic can increase the iodine release by enhancing the overall dissolution of the iodoapatite, which is consistent with previous experimental results on synthetic iodoapatite and natural apatites.$^{36,120}$ However, due to the secondary phase formed in Na$_2$CO$_3$ solutions, the dissolution process was being continuously hindered by the accumulating precipitates. Interestingly, the trend of iodine released in Na$_2$CO$_3$ solution of pH 10.3 resembles that of leaching iodoapatite under pH
Despite the rate difference, both surfaces leached by pH 4 and pH 10.3 formed secondary phases (chervetite and hydroxyvanadinite, respectively). Our previous study showed that the equivalent long-term rate of iodine release under pH 6 is 8.1 mmol/m²/d, over two magnitudes higher than that of the deionized water 0.036 mmol/m²/d. Nevertheless, the release rates of iodine leached by the solutions of non-neutral pH are at least one magnitude higher than that of the neutral pH solutions due to the enhanced dissolution process.

Surface characterizations indicate the presence of new phases under the basic conditions. The XRD analysis in Figure 2.6. and Table 2.1. shows the surfaces leached by the Na₂CO₃ and Na₃PO₄ solutions were dominated by secondary phases resembling hydroxyvanadinite Pb₁₀(VO₄)₆(OH)₂. The SEM in Figure 2.3. reveals different grain shapes and sizes from the water leached, while the EDS in Figure 2.4. demonstrates that iodine was depleted on the surface. The solution analysis also supports the formation of new phase given the similar element release pattern to that of pH 4 and incongruent Pb/V ratios far away from the stoichiometric value. As shown in Figure 2.9., the leaching rates of all elements are at least one magnitude higher than the water leach rates of corresponding elements. The results from this study and those from relevant literature suggest that the solution pH exerts significant effects on the dissolution rate and the secondary phase formation in aqueous environments such as chervetite and hydroxyvanadinite precipitated under acidic and basic conditions, respectively.⁴⁰,¹²¹,¹²²
2.3.3. Effect of ionic species on the dissolution rate

In this study, dissolved species affected the sample dissolution process by increasing the ionic strength in solution, which consequently reduced the activity coefficient of dissolved species. As a result, saturation state and solution feedback were reduced, which in return increased the dissolution rate.\textsuperscript{120} Although the 0.1 mol/L Na\textsubscript{2}SO\textsubscript{4} and 0.1 mol/L NaCl solutions have approximately the same solution pH as deionized water, the dissolution rates in these ionic solutions are significantly higher than that of the deionized water. As shown in Table 2.2, 0.1 mol/L Na\textsubscript{2}SO\textsubscript{4} solution gives total ionic

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<th>mol/L 90 °C</th>
<th>Deionized water</th>
<th>0.1 mol/L NaCl</th>
<th>0.1 mol/L Na\textsubscript{2}SO\textsubscript{4}</th>
<th>0.1 mol/L Na\textsubscript{2}CO\textsubscript{3}</th>
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<td>Na\textsuperscript{+}</td>
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</table>
strength of 0.26 mol/L, 0.1 mol/L NaCl solution 0.098 mol/L, and deionized water 2.04×10^{-6} \text{ mol/L} close to zero. The vast difference in ionic strength leads to different degrees of saturation state. The activity coefficient of the major ions Na^+ , Cl^−, and SO_4^{2−} in these ionic solutions are ranging from 0.25 to 0.76, considerably lower than the major ions H^+ and OH^− with a respective activity coefficient 1.00 in the deionized water. The dissolution rate in 0.1 mol/L Na_2SO_4 solution is higher than the rate in the 0.1 mol/L NaCl solution and deionized water under the same pH and reaction mechanism, as shown in Figure 2.9. Moreover, the average release rate of iodine in Na_3PO_4 (pH 10.9) is about one magnitude higher that of Na_2CO_3 (pH 10.3) despite their similar pHs. The difference in rates can be inferred from the difference in ionic strength: 0.29 mol/L for 0.1 mol/L Na_3PO_4 and 0.25 mol/L for Na_2CO_3 solution.

In addition, no substantial structure change happened to the sample leached by 0.1 mol/L Na_2SO_4 solution. It is unlikely that anion SO_4^{2−} can be incorporated into apatite structure as there is no evidence from surface characterization and solution analysis to support that. No structural change was detected by the XRD characterization. The SEM images and EDS analysis in Figures 2.3 and 2.4 show that the Na_2SO_4 and water leached surfaces have a similar grain size, surface morphology, and chemical composition. The element release rates and ratios in Figure 2.7 and 2.8 demonstrate a similar leach behavior between samples leached by Na_2SO_4 and deionized water. The similarities in surface alteration and leaching behavior between samples leached by Na_2SO_4 and water suggest that the iodine release in Na_2SO_4 solution was controlled by short-term diffusion and long-term dissolution and the release of Pb and V is controlled by congruent dissolution. No
precipitated was observed on Na2SO4 leached surface, which is also similar to the surface leached by water.

In terms of the surface precipitation, the SEM images in Figure 2.3c,f. reflect intense surface alterations in the solutions of Na3PO4 and Na2CO3. The leached surfaces yielded XRD patterns similar to the standard hydroxyvanadinite Pb5(VO4)3OH. However, significant contractions of a- and b-axes as shown in Table 2.2 indicate the size of VO4 site was reduced, which could be caused by a substitution of smaller groups.123 The IR spectroscopy of the sample leached by Na3PO4 confirms the existence of P-O bond and OH−. Furthermore, the EDS detected phosphorus signal, which also supports that PO4 group was in VO4 site. The molar ratios of Pb/V in Figure 2.9. show a deficiency of Pb relative to V in Na3PO4 leaching test. These evidences suggest the precipitates are a product of hydroxyvanadinite with mixed site: Pb10(VO4)6−n(PO4)6−x(OH)2. The site mixing is possible since Pb10(VO4)6−x(PO4)6−x(OH)2 can occur during wet chemistry reactions under similar conditions.121 Carbonate is known to be incorporated into apatite structure by substitution.123–126 Given that phosphate (PO43−, ionic radius 2.30 ± 0.42 Å)119 can replace vanadate in iodoapatite,121 it is reasonable to presume that carbonate of a smaller ionic radius (CO32−, 1.89 ± 0.19 Å)119 can substitute vanadate in a similar crystal structure. Therefore, the secondary phase formed on in the Na2CO3 solution is Pb10(VO4)6−m(CO3)1.5m(OH)2.

2.3.4. Mechanism of iodoapatite dissolution and surface reactions in aqueous environments

Figure 2.10. generalizes the mechanism of iodoapatite dissolutions with multiple processes contributing to the iodine release. Our previous study on iodine release in deionized water suggests that the iodine release is driven by short-term diffusion and
long-term dissolution.\textsuperscript{32} Diffusion and dissolution are affected by various factors of the solution chemistry, such as solution ionic strength, pH, and secondary phase formation resulted from a supersaturation of the solution with respect to low solubility species. In neutral pH solutions, the iodine release is subjected to the substitution of iodine by anionic species in solution such as OH\textsuperscript{-} and Cl\textsuperscript{-}. When dealing with solutions of comparable pH, a higher ionic strength, due to the ionic content, can enhance the dissolution by changing saturation conditions. Solution pH other than near neutral can increase the dissolution by exponentially accelerating the dissolution process. The resulting rapid dissolution can often lead to the precipitation of secondary phases when the solution approaches the supersaturation state of low solubility phases. Possible secondary phases include chervetite Pb\textsubscript{2}V\textsubscript{2}O\textsubscript{7} under acidic condition\textsuperscript{40} and hydroxylvanadinite Pb\textsubscript{5}(VO\textsubscript{4})\textsubscript{3}OH under basic condition.

Figure 2.10. Schematic diagram illustrates major processes that control the iodine release from iodoapatite in aqueous environments.
CHAPTER 3. ENERGETICS OF INTERFACIAL INTERACTIONS OF HYDROCARBON FLUIDS WITH KEROGEN AND CALCITE USING MOLECULAR MODELING

3.1. Method

3.1.1. Molecular models for oil, kerogen, and calcite

Crude oil is a mixture of a wide range of polar and non-polar compounds with varying proportions, compositions, and molecular weights. Typically, crude oil contains over 45% non-polar (e.g., alkanes and cycloalkanes) and less than 15% polar species (e.g., N-, S-, O-, and metal-containing compounds).127,128 Polar components can significantly affect properties of hydrocarbon fluid in reservoir such as viscosity, contact angle, interfacial activity, emulsion, and chemical stability.129–131 The oil–rock interactions are largely attributed by the polar species,132 particularly in organic phases that usually retain more polar components than minerals.129 Thioalkanes are common sulfur compounds found in crude oils.133 Crude oil, especially from shale, can have a high content of light oil (C₁–C₉).134,135 Therefore, we selected 1-octanethiol (C₈H₁₈S) with a dipole moment of 2.9 D136 and its non-polar counterpart n-octane (C₈H₁₈) as the

Figure 3.1. Molecular structure of type II kerogen fragment (left), non-polar oil n-octane (right top), and polar oil 1-octanethiol (right bottom).

This chapter was modified from a peer-reviewed article published as Zhang, Zelong, et al. "Energetics of Interfacial Interactions of Hydrocarbon Fluids with Kerogen and Calcite Using Molecular Modeling". Energy & Fuels. 2020 34 (4), 4251-4259. Used by permission of American Chemical Society.
models for polar and nonpolar oil, respectively, in our simulations as shown in Figure 3.1. In addition, to model a small oil drop, we prepared two oil clusters consisting of 30 molecules of octanethiol and octane for polar and non-polar oil droplets respectively as shown in Figure 3.2c.

Reservoir rocks have complex microstructures and mineralogy and contain various amount of inorganic and organic constituents. Major mineral phases include clays, quartz, and carbonates (calcite and dolomite). Due to its simple structure and ubiquitous presence in formation rocks, the calcite (104) face was chosen as a model for hydrophilic surface of reservoir rocks. The calcite (104) is a flat stoichiometric surface. It is one of the most common mineral faces occurring in both geological and biological systems and has been well studied both computationally and experimentally. The key organic phase in shale involved in the interactions with hydrocarbon fluid is kerogen. Despite the complexity of kerogen in reservoir formations, many studies used graphene to represent kerogen. The

![Figure 3.2. Kerogen slab (a), calcite (104) slab (b), 30-molecule non-polar oil cluster (c), and 30-molecule polar oil cluster (d). “x.1” and “x.2” denote different orientations.](image)
differences between graphene and kerogen, such as bonding environment of functional groups\textsuperscript{146,147} and surface morphology,\textsuperscript{141} give rise to different chemical and mechanical properties and interfacial interactions. These deviations can lead to inaccurate modeling with respect to experimental measurements.\textsuperscript{147,148} To capture fundamental properties of kerogen, we employed a molecular fragment $\text{C}_{22}\text{H}_{13}\text{ON}$ directly derived from type II kerogen to build kerogen surfaces,\textsuperscript{81} which is the most common kerogen in hydrocarbon-bearing shale formations.\textsuperscript{141} The kerogen molecule has five benzene rings, a secondary amine, and a phenol group, making this kerogen molecule a polar compound. To create kerogen surfaces, a computational supercell containing a layer of frozen dummy atoms and 511 randomly-added kerogen molecules (18907 atoms in total) was quenched from 3000 to 300 K using an NPT ensemble. The surface was then created by removing the dummy atoms sandwiched by the kerogen aggregate, followed by a stabilization and a relaxation of the surface at 300 K using an NVT ensemble.

The calcite (104) surface in Figure 3.2b. was built with 1620 $\text{CaCO}_3$ molecule units with a dimension of approximately 7 nm $\times$ 7 nm $\times$ 2 nm with 8,100 atoms. The kerogen surface in Figure 3.2a. was built with 511 $\text{C}_{22}\text{H}_{13}\text{ON}$ molecule units with a dimension of approximately 8 $\times$ 8 $\times$ 3 nm with 18,907 atoms. Because of the ubiquitous presence of water in the reservoir formations, water molecules were added to the fluid. To ensure the oil molecules were surrounded by water, 7250 and 10000 water molecules were added to the calcite surface of single oil molecule or oil cluster, respectively, while 7500 and 10000 water molecules were placed on kerogen surfaces of single oil molecule or oil cluster, respectively.

A previous experimental study indicates that the calcite (104) surface exhibits a neutral charge due to the stoichiometry and alternating of $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$.\textsuperscript{149,150} Kerogen surfaces can be
negatively charged due to the deprotonation of functional groups, such as OH and NH. However, classical MD models only simulate interatomic interactions by empirical potentials for bond length, angle, and dihedral, whereas formation and breaking of covalent bonds are not considered unless specified by force field. Both calcite and kerogen surfaces maintain electrical neutrality, owing to the charge balance of each model molecule. Layers of alternating Ca$^{2+}$ and CO$_3^{2-}$ on the calcite (104) create a flat surface, while the benzene rings and polar functional groups of kerogen molecule yield highly heterogenous surfaces of kerogen.

3.1.2. Molecular dynamics (MD) simulation and Gibbs free energy profiles

MD simulations use Newton’s equation of motion to describe the motion of each individual atom based on integration of discrete time steps. The force ($F$) acting on each atom can be derived from the energy expression $E(r)$. The $E(r)$ defines intramolecular bonding interactions and intermolecular interactions. Intramolecular interactions are described by three bonding potentials: i. bonding between adjacent pairs of particles within the same molecule $\sum_{i,j} 0.5 \cdot K_b (b - b_0)^2$, ii. bending of an angle $\sum_{\text{angles}} 0.5 \cdot K_\theta (\theta - \theta_0)^2$, and iii. torsion angle $\sum_{\text{dihedrals}} K_\phi (1 + \cos (n\phi - \delta))$, (Figure 3.3.) The intermolecular interactions, also called non-bonded interactions, are represented by Lenard-Jones potential $\sum_{i,j} \{4\varepsilon_{ij} [\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6]\}$ and Coulomb potentials $\sum_{i,j} \frac{q_i q_j}{4\pi \varepsilon_0 r_{ij}}$ to account for electrostatic interactions, in which $\varepsilon_{ij}$ is depth of the potential well, $\sigma_{ij}$ the distance at which the potential between particle $i$ and $j$ is zero, $r_{ij}$ distance between particle $i$ and $j$, $q$ the partial charge of particles, and $\varepsilon_0$ the permittivity of free space.

Therefore,

$$E(r) = \sum_{i,j} 0.5 \cdot K_b (b - b_0)^2 \hspace{1cm} \text{bond length}$$

$$+ \sum_{\text{angles}} 0.5 \cdot K_\theta (\theta - \theta_0)^2 \hspace{1cm} \text{bending}$$
\[ + \sum_{dihedrals} K_\theta (1 + \cos (n\theta - \delta)) \quad \text{torsion angle} \]
\[ + \sum_{i,j} \left\{ 4 \varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi \varepsilon r_{ij}} \right\} \quad \text{intermolecular interaction} \]

MD simulation describes individual atom and molecule explicitly to calculates the force (\(F\)) acting on each atom. Thus, the position (\(X_{i+1}\)) and velocity (\(V_{i+1}\)) of each atom at the next time step (\(t+\Delta t\)) can be computed via Newton’s equation of motion.

\[ F = m \cdot a = -\nabla E \]
\[ V_{i+1} = V_i + \Delta t \cdot a = V_i + \Delta t \cdot F(x_i)/m \]
\[ X_{i+1} = X_i + V_i \cdot \Delta t \]

To initialize a MD simulation, the initial position and velocity of each atoms need to be set properly. In this study, the initial position of each model is either based on i) default lattice, ii) experiments /theoretical modeling, or ii)trajectory from a previous simulation, while the initial velocity is assigned either i) according to Maxwell-Boltzmann distribution of a given temperature or ii) based on the trajectories from previous simulations.

Figure 3.3. Illustration of intramolecular potentials among particles 1, 2, 3, and 4. \(r_{23}\) bonding between two adjacent atom 2 and 3, \(\theta_{234}\) bend angle, and \(\Phi_{1234}\) torsion angle.
MD simulation calculates the motion of atoms and molecules by integrating the Newton’s equation of motion based on discrete time step ($\Delta t$). To capture the molecular motion properly, the time step should be 1/10 of the period of the highest frequency of molecular vibration in the system.\textsuperscript{151} Typical time step is set as 1 femtosecond (1 fs = 10\textsuperscript{-15} sec) in order to be comparable to one-tenth of the highest vibrational frequencies of 10\textsuperscript{14} Hz approximately, corresponding to a period of 10 fs.\textsuperscript{151} For example, O–H stretch bond has relatively high vibrational frequency ranging from 3300 to 2500 cm\textsuperscript{-1}, equivalent to 10.1 to 13.3 fs. To maximize the computation efficiency, it is desirable to set the time step as large as possible without destabilizing the simulation. If the time step is too large, the system can be unstable by the occurrence of large error during the integration. On the other hand, the simulation length can be inefficient for certain processes if the time step is too small.

A few algorithms such as Verlet, leapfrog, velocity Verlet, Beeman, etc. can integrate the Newton’s equations and produce the trajectory in coordinate space. Verlet algorithm, proposed by Verlet, can be expressed as\textsuperscript{152}

$$x_{i+1} = 2x_i - x_{i-1} + a_i \cdot h^2$$

where $x_i$ is the coordinate, $a_i$ is the acceleration, $i$ is the number of time step, and $h$ is the step size. The leapfrog algorithm is introduced by Hockney and Eastwood, which is\textsuperscript{153}

$$v_{i+1/2} = v_{i-1/2} + a_i \cdot h$$
$$x_{i+1} = x_i + v_{i+1/2} \cdot h$$

where $v_{n+1/2}$ is the half-step velocity.

The velocity Verlet algorithm can be written as\textsuperscript{154}

$$x_{i+1} = x_i + (v_i + a_i \cdot h/2) \cdot h$$
$$v_{i+1} = v_i + (a_i + a_{i+1}) \cdot h/2$$

39
The Beeman algorithm is expressed as

$$x_{i+1} = x_i + v_i \cdot h + (a_i \cdot 2/3 - a_{i-1} /6) \cdot h^2$$

$$v_{i+1} = v_i + (a_{i+1} /3 + a_i \cdot 5/6 - a_{i+1} /6) \cdot h$$

MD simulations in this study were deployed using the software package GROningen MAchine for Chemical Simulations (GROMACS). All simulations employed three-dimensional periodic boundary conditions. The OPLS-AA force field was used to describe oil molecules and kerogen. The SPC potential is used to describe the water molecule. A previously developed force field was used for calcite. All these potentials have been tested and are capable of producing satisfactory results on bulk and interfacial properties, which are consistent with experimental data. Newton’s equations of motion were integrated using the leapfrog scheme with a time step of 1 fs, fast smooth particle-mesh Ewald (SPME) electrostatics, Verlet cutoff-scheme, and temperature coupling using a Nosé–Hoover extended ensemble with a coupling constant of 0.1 ps. Simulations were visualized by visual molecular dynamics (VMD) package.

Gibbs free energy is an important property to describe the thermodynamic state of a chemical system. The free energy difference between two states is the driving force of any chemical reactions. Calculating free energy is essential to the theoretical chemistry research for elucidating the principles behind the behavior of complex chemical system. Gibbs free energy, $G$, a thermodynamic function, can be expressed as:

$$G = U - TS + PV$$

in which $U$ is internal energy, $T$ absolute temperature, $S$ entropy, $P$ pressure, and $V$ volume.

The free energy surface between two states of a chemical reaction (e.g., bonded and unbonded) can be determined by constrained molecular dynamics. A typical scheme consists of
the following steps: (1) selecting a reaction coordinate connecting the initial and final states of a system (e.g., distance between the two molecules), and (2) performing a series of MD simulations (or windows) with the system restrained at various stages along the reaction coordinate by adding a constraint potential. The added potential is usually harmonic, which allows sufficient sampling along the reaction coordinate separated by an energetic barrier between two adjacent states.\textsuperscript{93} The term ‘umbrella’ sampling is named after the shape of this harmonic potential. Umbrella sampling routinely combines with Weighted Histogram Analysis Method (WHAM) to calculate the free energy profile. WHAM reconstructs the free energy profile $A(\xi)$ from histograms, a chart represents date distribution by using bars of different height to show how frequent each different value in a set of data occurs. The histogram in WHAM tracks the probability distribution function $P'(\xi)$ of finding a system at different states along the reaction coordinates $\xi$. The WHAM uses an iterative approach to calculate free energy profiles with an initial guess. Each reconstructed free energy profile provides an improved guess for a biasing potential $U'(\xi)$ used in the next iteration to reconstruct free energy profile. The process continues iteratively until the biasing potential $V(\xi)$ and the free energy profile $A(\xi)$ converge, which can be expressed as:

$$A(\xi) = -k \cdot T \cdot \ln P'(\xi) - U'(\xi) + F_i$$

$$P(\xi) = \frac{\sum_{i=1}^{N_{\text{sim}}} n_i(\xi)}{\sum_{i=1}^{N_{\text{sim}}} \exp \left\{ [F_i - U_{\text{bias},i}(\xi)]/(k \cdot T) \right\}}$$

$$F_i = -K_B T \ln \left\{ \sum_{x_{\text{bins}}} P(x) \exp \left\{ -U_{\text{bias},i}(\xi) \right\}/(k \cdot T) \right\}$$

where $A(\xi)$ is the free energy, $k$ is the Boltzmann constant, $T$ the temperature, $P'(\xi)$ biased probability distribution, $U'(\xi)$ umbrella potential, $F_i$ is the free energy shift from simulation $i$.\textsuperscript{93}
\( N_{\text{sims}} \) number of simulations, \( n(\xi) \) count number in histogram bin, \( U_{\text{bias}, i} \) biasing potential of simulation \( i \), and \( P(\xi) \) is the estimated unbiased probability distribution.

Calculating the free energy surface requires multiple steps: (1) the simulation windows were generated by a simulation to generate configurations along the reaction coordinate; (2) along the reaction coordinate, a series of separate MD simulations (windows) were carried out by constraining the system at a given position from the reaction coordinate; (3) in each simulation window, umbrella potential, a biased harmonic potential, was applied to the system; (4) by covering the reaction coordinate with overlapping windows, a free energy profile curve can be calculated using WHAM.

In each simulation window, umbrella potential, a biased harmonic potential, was applied to the system. For each individual simulation window, a constraint potential with a force constant 9000 kJ·mol\(^{-1}\)·nm\(^{-1}\) for 0.1 ns to equilibrate the system was first applied, then an umbrella potential with a force constant 9000 kJ·mol\(^{-1}\)·nm\(^{-2}\) was deployed for 0.1 ns up to 0.2 ns to obtain probability distribution of the given reaction coordinate. With enough sampling overlaps between simulation windows in the entire reaction coordinate space, a free energy profile curve can be calculated by combining data from each window using WHAM.\(^{165,166}\)

An analysis routine to estimate the errors of the energy profiles was developed using LOESS algorithm in RStudio.\(^{167,168}\) This method took the energy profile and employed the bootstrap technique to calculate the confidential intervals at 95% confidence level. The computed errors are listed as shown in Table 3.1. denoted by brackets. The fluctuation of free energy profile, as shown in Figure 3.4., is consistent with the size of the estimated error bar.

3.2. Results and discussion

Free energy surfaces in Figure 3.4.–3.10. show how the system energy changes as a
function of the distance between oil compounds and surfaces with respect to their centers of mass (COM). For instance, if an oil molecule was adsorbed onto a 2 nm thick calcite surface.

Table 3.1. Desorption energy of single molecule oil droplet and 30-molecule oil drop on calcite and kerogen surface under 300 K$^a$.

<table>
<thead>
<tr>
<th>desorption energy (kJ/mol)</th>
<th>Kerogen with water</th>
<th>Kerogen</th>
<th>Calcite with water</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-polar oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single molecule</td>
<td>17.0 (2.0)</td>
<td>23.3 (3.5)</td>
<td>0</td>
<td>18.0 (5.5)</td>
</tr>
<tr>
<td>Cluster: total</td>
<td>372 (13.8)</td>
<td>438 (13.5)</td>
<td>0</td>
<td>198 (42)</td>
</tr>
<tr>
<td>Cluster: per molecule</td>
<td>12.4 (0.46)</td>
<td>14.6 (0.45)</td>
<td>0</td>
<td>6.6 (1.4)</td>
</tr>
<tr>
<td>Polar oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Single molecule</td>
<td>16.5 (3.3)</td>
<td>39.5 (9.5)</td>
<td>0</td>
<td>33.6 (3.9)</td>
</tr>
<tr>
<td>Cluster: total</td>
<td>210 (11.4)</td>
<td>438 (13.5)</td>
<td>0</td>
<td>222 (36)</td>
</tr>
<tr>
<td>Cluster: per molecule</td>
<td>7.0 (0.38)</td>
<td>14.6 (0.45)</td>
<td>0</td>
<td>7.4 (1.2)</td>
</tr>
</tbody>
</table>

$^a$The ( ) denotes the errors propagated from the output data of WHAM.
under periodic boundary conditions, the COM distance between the adsorbed oil and the calcite surface would be approximately 1 nm. When the oils molecules are close to the surface, the energy increases due to repulsive interactions. When the oils gradually move away from the surface, the energy first reaches a minimum point, at which the adsorption occurs at the surfaces. An absence of the minimum suggests both adsorption and desorption cannot occur at the interface of interest. As the distance continuously increases, the energy increases until the system

Figure 3.5. Free energy surfaces of single molecule of polar or non-polar oil on calcite surface without water (left). Free energy surfaces of cluster of 30 polar or non-polar oil molecules on calcite surface without water (right).

Figure 3.6. Free energy surfaces of single molecule of polar or non-polar oil on kerogen surface with water (left). Free energy surfaces of cluster of 30 polar or non-polar oil molecules on kerogen surface with water (right).
reaches the energy plateau where no additional energy is required to desorb the oil molecules from the surfaces.

3.3.1. Interactions of oil molecules with kerogen surface

The free energy profiles in Figure 3.6. and Table 3.1. show the energy changes as a
function of the distance between oil compounds and kerogen surface in the presence of water.

The desorption energies are $17.0 \pm 2.0$ and $16.5 \pm 3.3$ kJ/mol for non-polar and polar single oil molecule and $371 \pm 12.4$ and $209 \pm 7.0$ kJ/mol for non-polar and polar oil clusters, respectively. In the absence of water, it is challenging to maintain oil molecules as a cluster at or above 300 K. To stabilize the oil cluster, a series of umbrella sampling simulations were carried out under lower system temperatures to extrapolate the desorption energy to 300 K (Figure 3.8.). The desorption energies of the oil clusters on kerogen surfaces are $437 \pm 13.5$ kJ/mol for both polar and non-polar (Figure 3.9.). For the single oil molecule, the desorption energies on kerogen in Figure 3.7. and Table 3.1. are $23.3 \pm 3.5$ and $39.5 \pm 9.5$ kJ/mol for non-polar and polar, respectively.

3.3.2. Interactions of oil molecules with calcite (104) surface

The free energy profiles in Figure 3.10. show how free energy changes as a function of the distance between oil compounds and the calcite (104) surface in water. Unlike the rest free energy profiles, they exhibit a distinct pattern: As the distance increases, the free energy quickly
decreases and then stays at the same value as the molecule is further away from the surface. Such patterns indicate oil cannot be adsorbed onto the calcite surface in the presence of water.

For comparison, the same systems without water were simulated, of which the free energy profiles are depicted in Figure 3.4. and 3.5. The results show that 33.6 ± 3.9 and 18.0 ± 5.5 kJ/mol are required to desorb polar and non-polar oil molecules from the calcite surfaces respectively, and 222 ± 36 kJ/mol and 198 ± 42 kJ/mol to desorb polar and non-polar oil clusters, respectively. A detailed analysis of the trajectory (Figure 3.11.) suggests that the polar molecule

Figure 3.10. Free energy surfaces of single molecule and cluster of 30 polar or non-polar oil molecules on calcite surface in the presence of water.

Figure 3.11. Snapshot of the simulation trajectory of calcite surface interaction with a polar oil molecule in the absence of water
was bound to the calcite surface through the thiol functional group –SH, which confirms a previous study on the adsorption of simple organic molecules on calcite (104). In addition, the thiol group –SH of polar oil appears to favor the sites of Ca$^{2+}$ site of calcite (104) surface, whereas the non-polar oil shows no preference of absorption sites.

3.3.3. Effect of surface composition on the interaction energy

Our study shows that, in general, oil molecules have stronger interactions with kerogen than with calcite regardless of surface environment and oil molecular polarity. Kerogen is an organic compound and usually oleophilic, whose surface property depends on the specific functional groups. The kerogen model in this study contains functional groups such as hydroxyl (–OH) and thiol (sulphydryl, –SH), which inherently exhibit a strong affinity with hydrophilic surfaces while the rest strongly interact with hydrophobic surfaces. On the contrary, calcite, especially the (104) face, is strongly hydrophilic with ionic species Ca$^{2+}$ and CO$_3^{2-}$ on the surface. Therefore, oil molecules can be more easily adsorbed onto kerogen than calcite, giving higher level of energy for oil interactions with a kerogen surface. Another factor that contributes to the difference between kerogen and calcite is the surface area: Calcite has a low surface area which weakens its sorption capacity, whereas kerogen is porous and waxy according to experimental observations. Thus, the effective surface area on kerogen would be much higher than on calcite, leading to a higher sorption capacity.

As a result of their different surface properties, the desorption energy at the kerogen surface is higher than that at the calcite surface: 5.3 to 17 kJ/mol higher for a single oil molecule and 210 to 372 kJ/mol higher for the oil cluster (7.0–12.4 kJ/mol per molecule for the oil cluster). The difference in the desorption energies of both single molecule oil and oil cluster implies that oil recovery from organic phases of reservoir rock can take more energy than from
these highly hydrophilic surfaces of inorganic mineral phases such as calcite.

3.3.4. Effect of molecular polarity

At kerogen surface, molecular polarity plays an imperative role in the energetics. These phenomena can be explained by the dipole interactions. Since there is no free ion in the systems, the intermolecular interactions are dominated by permanent dipole interaction, or Keesom interaction. As shown in Figure 3.12., the thiol functional group (–SH, yellow) of the polar oil prefers to stay in close proximity to the functional groups of kerogen molecules such as amine (–NH–, blue) and hydroxyl (–OH, red) upon contact at the interface, which confirms the expected dipole interactions. Unlike the polar oil, non-polar oil molecules have no dipole moment, therefore a weaker interaction energy than that of the polar oil molecules is expected. Thus, the interactions of the polar oil molecule with kerogen surface is stronger than those of non-polar.172 As shown in the Table 3.1., recovering the polar oil molecule requires energy about two times of

![Figure 3.12.](image)

Figure 3.12. Snapshot of the simulation trajectory of kerogen surface interaction with a polar oil molecule in the absence of water at different time step. (a) and (b) depict strong interactions between polar oil functional group –SH and kerogen functional groups –NH– and –OH, whereas (c) illustrates strong interactions between non-polar carbon chain of polar oil and non-polar benzene rings of kerogen.
the energy of non-polar per molecule in the absence of water. The required energies to recover single polar and non-polar oil molecules are approximately the same in the presence of water. For the oil cluster, our calculation indicates that the minimal amount of energy required to recover the polar oil cluster is comparable to that of the non-polar oil cluster if water is absent. However, in the presence of water, the polar oil cluster requires approximately half of the energy than that to recover the non-polar oil cluster. These results suggest that the effect of polarity is complicated by kerogen surface property and the presence of water.

At the calcite (104) surface, polar oil molecules consistently require higher energy for recovery than that of its counterpart non-polar oil, owing to the molecular dipole of the polar oil and the hydrophilic nature of the calcite surface. Although previous studies suggested that calcite (104) is overall non-polar because the alternating Ca$^{2+}$ and CO$_3^{2-}$ are closely packed and charge balance is maintained,\textsuperscript{173,174} the electrostatic interaction between ionic species at the calcite surface and the functional group at the polar molecule favors the adsorption of the polar oil molecules. Therefore, the required energy to recover the polar oil molecule from calcite is approximately two times of that for the non-polar oil molecule and the energy required by the polar oil molecular cluster is approximately 10% higher than that for the non-polar oil cluster in the absence of water.

3.3.5. Effect of surface water

Our study shows that the presence of surface water reduces the energy minimum to recover oil from all surface conditions. As discussed previously, the calcite surface is hydrophilic, while kerogen is both hydrophilic and hydrophobic. The surface water can easily be attracted to the calcite surface and kerogen hydrophilic functional groups. Both water and polar oil molecules have similar dipole moments 2.27 and 2.9 D,\textsuperscript{136,158} respectively. Water molecules
compete with polar oil molecules for adsorption at surfaces with a hydrophilic character, consequently reducing the energy minimum to recover the oil molecules at the surface. The interactions of waters with the calcite (104) surfaces were much stronger than with kerogen surfaces, suggesting a weaker hydrophilic nature of kerogen surface than that of the calcite surface. The affinity between calcite and water is stronger than that between calcite and oil, resulting in a strong oil-repellent surface of calcite in the presence of water. As shown in Table 3.1., the kerogen surface with water requires much lower energies to desorb oil. For polar oil, the surface water brought a reduction of 50%–60% on energy minimum to recover a polar oil compound and 15% - 30% reduction for a non-polar oil compound. The energy differences between non-polar and polar oil also demonstrate the crucial role of molecular polarity on the fluid–rock interactions. Given the strong hydrophilicity of calcite, the calcite surface becomes oleophobic, jettisoning all the surface oil, in the presence of water. Additionally, the radial distribution of water-surface atom pair distance (Figure 3.13.) shows several peaks for both water–calcite and water–kerogen interfaces, indicating the formation of organized water structures. Among all the RDF peaks within the range of 10 Å, the first peaks for water–kerogen and water–calcite occurred at 1.7 and 1.8 Å, respectively. Overall, the RDF peaks at the water–calcite interface are significantly higher than those at water–kerogen, suggesting strong interfacial interactions between water and calcite. These results provide a fundamental understanding of the decisive role that water plays in oil–rock interactions during oil recovery.

3.3.6. Effect of oil clustering

Our study shows that recovering oil clusters requires lower energy per molecule than a single oil molecule. For instance, the energy minimum to recover a single molecule of polar oil is 4.6–25.2 kJ/mol higher than the energy per molecule of the oil cluster, which is an increase of
37% to 340% of the energy per molecule of the oil cluster. This difference is mainly caused by the number of oil molecules that directly interact with the surface. While the single molecule always interacts with the surfaces, not all the molecules in the 30-molecule clusters directly interact with the surfaces, which lowers the energy minimum per molecule to recover a molecular cluster. Although the oil molecular clusters are too small to be comparable with oils in the porous medium in reservoir rocks, the trend quantified in this study suggests that as the cluster size decreases, recovering the oil confined in the pores becomes more challenging.

![Radial Distribution of Water-Surface](image)

Figure 3.13. Water-surface radial distribution at the equilibrated interfaces under 300 K as a function of the distance between pairs of atoms from surface molecules and water molecules in close proximity.
CHAPTER 4. CONCLUSIONS

4.1. Effect of Solution Chemistry on The Iodine Release from Iodoapatite in Aqueous Environments

The present study focuses on effects by solution compositions on iodoapatite dissolution. The results suggest that the higher ionic strength can accelerate dissolution by decreasing the activity coefficient of reacting aqueous species, thus promoting iodine release from apatite. Non-neutral pH conditions clearly increase the dissolution rate and often lead to precipitations of secondary phases, such as chervetite and hydroxylvanadinite. The secondary phase precipitation at the surfaces hinders the dissolution rate by reducing the available reacting surface area. However, the overall iodine release rates in both basic and acidic solutions are exponentially higher than those in the near-neutral pH conditions, especially in deionized water. Current understanding of dissolution is mostly based on leaching experiments conducted in deionized water. Our investigation on the impact of solution chemistry reveals new complexities of the dissolution kinetics of crystalline waste form during environmental degradation. Unlike fresh water with low ion content, high concentrations of aqueous species commonly found in underground brines can compromise the chemical durability of crystalline waste form in a geological repository. For this specific waste form, maintaining neutral pH and low ion content in aqueous solutions is important to the disposal safety of radioactive iodine. Since iodine is one of the most challenging radionuclides to immobilize, building a comprehensive theoretical framework of iodine immobilization can significantly advance the research in nuclear waste disposal safety.
4.2. Energetics of Interfacial Interactions of Hydrocarbon Fluids with Kerogen and Calcite Using Molecular Modeling

This study demonstrated that molecular dynamics simulation is capable of calculating the free energy surface for fluid–rock interactions involving single oil molecules, oil molecular clusters, and calcite (104) and kerogen surfaces. The results provide fundamental understandings of the interfacial interactions and valuable implications for oil recovery in reservoirs. The main conclusions are as follows.

(1) The hydrophobicity of the surface of reservoir materials has a significant effect on the oil–rock interactions, leading to a higher free energy cost for oil displacement from organic phases of reservoir rock than that from the highly hydrophilic surfaces of inorganic mineral phases such as calcite.

(2) The polarity of oil molecules strongly affects the interfacial interactions at both the kerogen and calcite surfaces. The polar oil molecules require more energy to be recovered from both surfaces than non-polar ones. For complex hydrocarbon fluid systems, having a large portion of polar compounds in the oil poses a great challenge. In order to effectively model the interactions between oil and the reservoir materials and to produce reliable results, an accurate description of the polarity of oil molecules is necessary.

(3) Surface water profoundly influences the interactions between oil molecules and reservoir materials. Because of its large dipole moment, water facilitates the oil recovery process by interacting with hydrophilic surfaces or sites of either organic kerogen or inorganic minerals.

(4) Single oil molecules or small oil molecule clusters dispersed in small nanopores tend to be more challenging to be recovered than large oil molecular clusters due to the stronger interactions of oil molecules with the surfaces.

The success of implementing the free energy methods to study these simple hydrocarbon
systems paves the way for building more realistic simulations of complex systems by varying temperatures, adding fluid components (e.g., electrolytes, methane, carbon dioxide, and large oil compounds) and introducing other major inorganic phases such as clay minerals and quartz.
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Supporting Text: Video links of pertinent simulation trajectories
100 ps MD trajectory of a polar oil molecule interaction with kerogen surface
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https://youtu.be/kmdeLdsBWwQ
100 ps MD trajectory of a polar oil molecule interaction with calcite (104) surface
https://youtu.be/crq9xLuhhk
100 ps MD trajectory of a non-polar oil molecule interaction with calcite (104) surface
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Table C.1 Desorption energies of 30-molecule oil clusters on kerogen surfaces under different temperatures in the absence of water.

<table>
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<th>Polar</th>
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</thead>
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<td>163 [3]</td>
</tr>
<tr>
<td>150 K</td>
<td>260 [5.5]</td>
<td>226 [3]</td>
</tr>
</tbody>
</table>
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VITA

Zelong (Eric) Zhang is a geochemist using materials chemistry to study geochemical phenomena, especially in subsurface energy applications that can improve the sustainability of modern civilization. He received a Bachelor of Science in geochemistry from China University of Geosciences (Wuhan) and a Master of Science in geosciences from Stony Brook University, USA. In college, his interest on interfacial geochemical was sparked by studying the distribution of lipid biomarkers in calcareous speleothem as a paleoclimate record. At Stony Brook, his interest grew into the microscopic level. He focused on the structural characterization of lipid incorporation into calcite using solid-state NMR, a state-of-the-art technique. Seeing that the structural information revealed by NMR was limited, he started to explore different approaches and decided to further his research using molecular modeling, a methodology that can visualize the interfacial processes at atomistic level. He plans to graduate with his Ph.D. in 2020 and pursue a career as a researcher in either corporate R&D or national laboratories. For latest information, please visit https://er1czz.github.io/