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MINERAL REPLACEMENT REACTIONS ENABLED THROUGH
ELECTROKINETIC FLUID FLOW WITHIN PORES

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ABSTRACT

Pseudomorphic mineral replacements involve a change in the composition or structure of a mineral without a change in the shape and size, as well as pore formation in the product phase. Here we explore pseudomorphic mineral replacements to determine the reaction process, focusing on how fluid flows affect the kinetics of the process. Though the thermodynamics of the phenomenon is well understood, the kinetics of this process have yet to be adequately represented. This work challenges the widely accepted diffusion-limited, coupled dissolution-precipitation reaction process, and it explores the question of whether convective flows emerging from concentration gradients are driving the pseudomorphic mineral replacement process. The question was approached experimentally using confocal and transmission microscopy. Quantum dots were intentionally trapped within a potassium bromide (KBr) crystal and extracted using saturated potassium chloride (KCl) *via* mineral replacement. The results showed that the 20 nm blue quantum dots were extracted within time scales significantly shorter than predicted by diffusion. We attempted to extract 4 μm particles, however no extraction occurred at first. SEM imaging showed that over time, the pores sealed. A flow-through system was then created, and it was found that replacement rates and pore cross-sectional area both increased as external flow rates increased. The data thus indicated that dissolution and precipitation occur at separate fronts, in order to set up a concentration gradient which drives electrokinetic flows in and out of the mineral pores, through diffusioosmosis. Understanding that these concentration-driven flows play a large role in the replacement process, we were able to determine flow rates at which optimum mass transfer occurs and extract 4 micron particles trapped within a KBr mineral. Understanding this reaction process further will enable a more holistic understanding of more

geologically relevant systems and allow for more efficient extraction of oil and gas from rocks and minerals. This system served as an effective nexus between chemical engineering fundamental principles and geological settings.

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BACKGROUND

The phenomenon of pseudomorphic mineral replacement has long been observed in nature from bone decay¹ to weathering² to the seemingly simple replacement of minerals by other minerals.³ The thermodynamics of this process are well understood and presented in literature.³ Conversely, the reaction process and mechanism of this process have been somewhat mysterious. It has been generally accepted that the reaction must progress through a diffusion-based process involving a coupled dissolution and precipitation front.³

However, recent experiments and calculations have shown that the time scales for a dissolution-limited mechanism may not adequately describe the process. This observation has spurred the consideration of fluid flow based models that challenge the widely accepted coupled dissolution-precipitation reaction process and present an alternative depending heavily on convective flows in the system. This work seeks to compare these two reaction processes and their respective driving forces.

Primary Objectives of This Thesis

The principal questions of this thesis are as follows:

1. Does the widely accepted diffusion-limited, coupled dissolution-precipitation mechanism adequately describe the reaction process of pseudomorphic mineral replacement reactions? In other words, is the reaction process surface-controlled or transport-controlled?

2. How do convective flows come about within the mineral pores during pseudomorphic mineral replacements?
3. What implications does a convective flow based model have technically? Specifically, can pseudomorphic mineral replacement be used in the extraction of materials trapped inside of a rock or mineral?

Background on Mineral Replacement

The distinction between surface-controlled and transport-controlled (or diffusion-controlled) reactions is an important one to a chemical engineer, particularly in the field of catalysis.⁴ A surface controlled reaction is a reaction that is rate-limited by the speed at which a step occurs on the surface of a material.⁵ In heterogeneous catalysis, this occurs as a fluid reactant or intermediate adsorbs to or desorbs from the surface of the solid catalyst.⁴ Quite oppositely, a transport-controlled reaction's rate is limited by how quickly the species in the reaction diffuse.⁵ This same distinction is also important in "mineral replacement." Mineral replacements involve the re-equilibration of a mineral with its surroundings (typically a fluid), resulting in the alteration of the chemical or structural makeup of the mineral.³ These processes involve a few key aspects: dissolution and precipitation, a mobile fluid interface, and porosity development in the product phase.⁶ In some cases, the external volume of the original mineral is preserved, and in this situation the process is labeled "pseudomorphic."⁷ A schematic of pseudomorphic replacement can be seen in Figure 1. Other processes classifying as mineral replacements are diagenesis,⁸ metasomatism,⁹ and metamorphism,^{10,11} all of which include the aforementioned key aspects of a mineral replacement reaction. It is also possible for mineral

replacements to occur where the elements making up the mineral are unchanged, but the chemical structure is changed (such as the replacement of aragonite by calcite).¹²

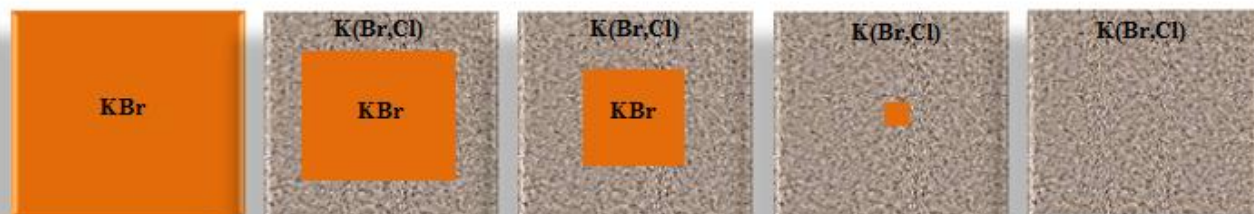


Figure 1. Schematic of pseudomorphic replacement. This schematic shows the replacement system explored in this thesis. Upon coming in contact with aqueous saturated KCl, a KBr crystal will transform from the outside in, into a new, porous K(Br,Cl) phase. This process conserves the external shape and size of the parent crystal.

While this phenomenon may seem esoteric to a typical chemical engineer, understanding mineral replacement, particularly in regards to whether it is surface or transport controlled, has far-reaching scientific, geological, and industrial consequences.¹³ Processes such as bone decay,^{1,14,15} environmental weathering,^{2,16,17} and gas and oil extraction via fracking^{18,19} all contain fluid-mineral interfaces. Furthermore, the understanding of mineral replacement reactions and the flows therein can provide new options in the design of catalytic materials and photonic devices. Mineral replacement reactions have even been found to drastically reduce the radioactivity of aqueous solutions through the uptake of Radium.²⁰ Mineral replacement is also known to affect groundwater and soil chemistries, and can be used to remediate polluted soils.^{21,22,23} Though the discussion of the reapplication and relevance of mineral replacement study to all practical processes is beyond the scope of this work, this thesis will draw specific focus to the extraction of materials trapped within minerals.

While significant research has been completed to understand mineral replacement thermodynamically,^{3,6} the exact mechanism, specifically the reaction process is not known. Certain theories suggest that solid state diffusion is responsible for the replacement of one mineral by another.²⁴ Solid state diffusion, however cannot adequately describe the mechanism behind mineral replacements, as these reactions occur at much shorter time intervals than predicted by solid state diffusion.²⁴ The current mechanism widely accepted within literature is a “dissolution-precipitation” mechanism.^{3,6,7} In this mechanism, the parent phase dissolves, and the product phase precipitates at approximately the same location (the dissolution and precipitation fronts are less than 100nm apart).

Estimates based on simplified Fick’s 2nd law ($\text{time} = \text{length}^2 / \text{diffusion coefficient}$) indicate that the pseudomorphic replacement of a 2 mm long crystal should take on the order of 1000 seconds, which agrees well with experimental evidence.^{25,26} This calculation leads one to believe that the diffusion driven dissolution-precipitation mechanism is accurate. However, the current dissolution-precipitation mechanism ignores convective and electrokinetic fluid flows. This thesis explores the failings of the coupled dissolution-precipitation mechanism, and it shows that fluid flows within the pores of a replacing mineral hold the key to understanding the transport-controlled reaction process of replacement, hence the previous questions.

Background on Electrokinetic Flows

Understanding the fluid flows within a replacing mineral requires the use of electrokinetic theory. Despite a large body of research on mineral replacement, no replacement systems have yet been studied from an electrokinetic standpoint. This thesis seeks to incorporate

electrokinetic theory into the study of mineral replacement, with an emphasis on diffusiophoresis.

Diffusiophoresis is the motion of particles dissolved in a fluid as a result of a concentration difference, a phenomenon first observed by Derjaguin et al.²⁷ Often times, such as in the case of the potassium bromide, potassium chloride, and water (KBr-KCl-H₂O) replacement system studied in this thesis, the dissolved particles carry a charge. Since different particles have different diffusion coefficients, the particles will travel at different rates. If the ions are both charged and diffusing at different rates, a net electric field will form to prevent charge separation and the risk of electrical discharge. The theory behind diffusiophoresis hinges upon the formation of an electric double layer, where aqueous ions form a finite, small, and oppositely charged layer around them upon attracting species of opposite charge.^{28,29}

Diffusiophoresis encompasses a number of different mechanisms with well-understood physics, including chemiophoresis and chemiosmosis, along with the aforementioned electrophoresis and electroosmosis.³⁰ Electrophoresis is the motion of a charged particle in one direction and the surrounding fluid in the other direction, caused by a net electric field. Similarly, chemiophoresis is the motion of a particle in one direction and the surrounding fluid in the other direction, caused by a difference in electrolyte concentrations. In this case, the particle will move towards the higher electrolyte concentration, as the fluid around it re-equilibrates.²⁹

Electroosmosis occurs as a result of a stationary, charged surface underneath the fluid.²⁹

Although this stationary surface will not move, the electrical double layer just above the surface, caused by the surface charge, will move, causing particle and/or fluid motion.²⁹ Chemiosmosis, similarly to electroosmosis, involves motion at a charged surface, but as a result of an electrolyte

concentration difference.²⁹ Throughout this thesis, the combination of chemiosmosis and electroosmosis will be referred to collectively as “diffusioosmosis.” Figure 2, below shows an illustration of the types of diffusiophoresis. Diffusioosmosis has seen relatively little technological application, but has fairly recently been used in colloidal transport and DNA translocation/entrapment.³¹

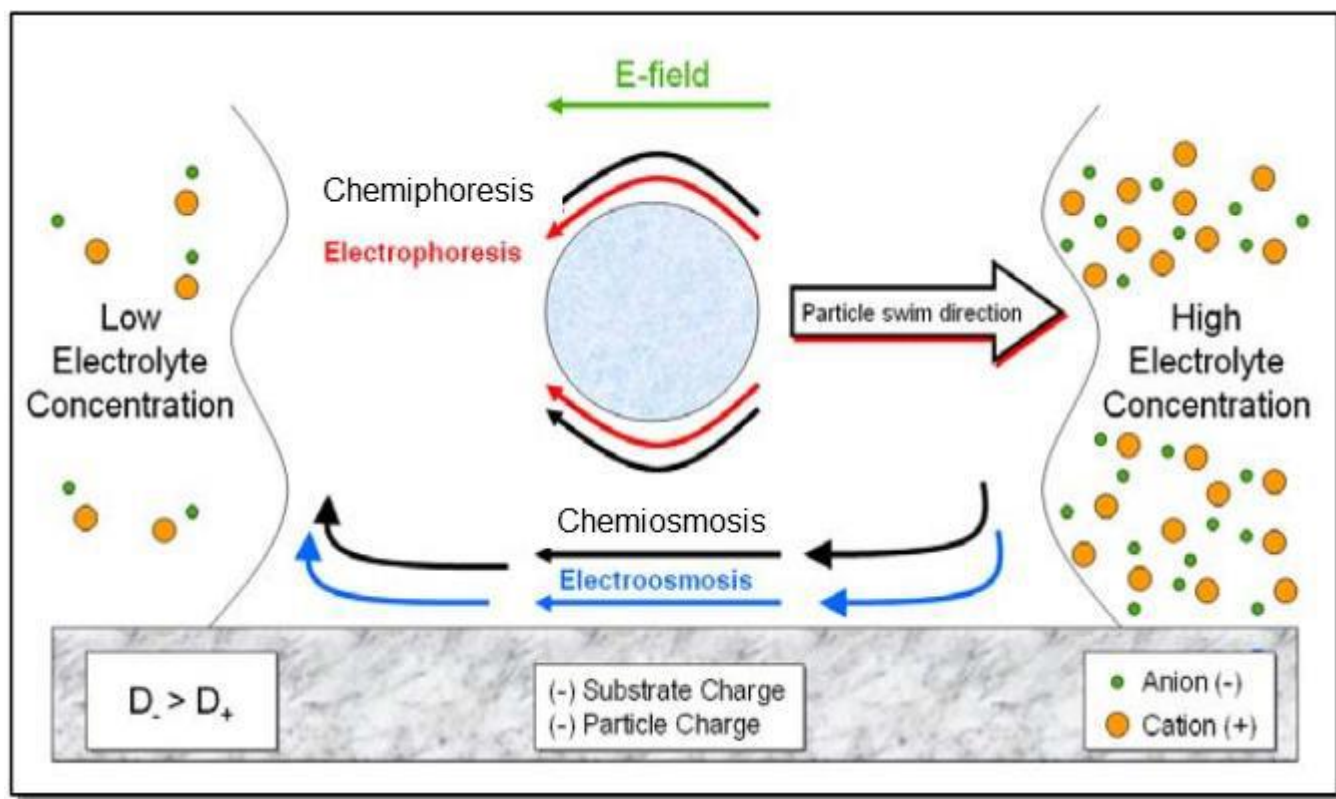


Figure 2. Schematic of diffusiophoretic system²⁹ wherein the diffusion coefficient of the anion is greater than that of the cation. In this system, the particle and substrate have a negative charge. It is important to note that if the diffusion coefficient magnitude or particle/substrate charge were reversed, the electrophoretic and electroosmotic flows would be reversed, while keeping the chemiphoretic and chemiosmotic flows the same.

The basis of electrokinetics can be summed up in the Poisson-Nernst-Planck equations (Equation 1), where c_i is the molar concentration of species i , t is time, u is velocity, D_i is the diffusion coefficient of species i , z is the valence of species i , e is elementary charge, k_B is Boltzmann's constant, T is the temperature, ϕ is chemical potential, and ϵ is the fluid permittivity. This set of equations is derived from conservation of mass for an incompressible fluid, the Nernst-Planck flux density equation, the Einstein relation, the gradient of chemical potential, the Poisson Equation, as well as a few other assumptions and approximations.³²

$$\begin{aligned} \frac{\partial c_i}{\partial t} + u \nabla c_i - \nabla \cdot \left[D_i \left(\nabla c_i + \frac{z_i e c_i}{k_B T} \nabla \phi \right) \right] &= 0 \\ -\nabla \cdot (\epsilon \nabla \phi) &= \sum_i z_i e c_i \end{aligned} \quad (\text{Equation 1})$$

This thesis draws specific focus to electrokinetics and electrophoresis, and it has been well-established that the electrophoretic velocity of a particle can be found using Equation 2.^{29,33,34}

$$u = \frac{\epsilon \zeta_p E}{\eta} \quad (\text{Equation 2})$$

In Equation 2, u represents electrophoretic velocity, ϵ represents the fluid permittivity, ζ_p represents the zeta potential of the particle, η represents the fluid viscosity, and E represents the electric field. The electric field for this system can be found using Equation 3, where k_B is Boltzmann's constant, T is the temperature, z is the valence, F is Faraday's constant, e is

elementary charge, D_+ is the diffusion coefficient of the cation, D_- is the diffusion coefficient of the anion, and c is molar the concentration.²⁹

$$\mathbf{E} = \frac{k_B T}{z F e} \left(\frac{D_+ - D_-}{D_+ + D_-} \right) \frac{\nabla c}{c} \quad (\text{Equation 3})$$

Equation 2 is derived from the Nernst-Planck Equation (combination of Fick's First Law of diffusion, Ohm's Law, and Newton's Law). Equation 2 ignores convective effects on the electric field, because at the relatively low Peclet numbers seen in this experiment the convective term is negligible. It is important to note that an electric field, and therefore electrophoretic velocity, only exists when a concentration gradient is present.

Diffusiophoresis has been studied heavily in idealized systems.³⁵ However, in certain special cases, such as the self-generation of diffusiophoretic flows, diffusiophoresis can play a very important role in driving fluid flow, providing an internal driving force within the system.³¹

MATERIALS AND METHODS

KBr-KCl-H₂O Replacement System

The mineral replacement system chosen for this thesis was the KBr-KCl-H₂O system, which is well-studied in literature and exhibits KBr replacement by aqueous saturated KCl.^{36,37} While perhaps not the most geologically relevant system (although KCl is found in nature as sylvite and halite³⁷), this system was chosen for its simplicity, the availability of data on the components of the system, and for its quick time scales (on the order of minutes as opposed to days or years). This thesis uses the KBr-KCl-H₂O model salt system as a proof of concept for pseudomorphic replacements in general. Concepts within this thesis can be reapplied to more complex and geologically relevant systems, such as replacement of calcite by fluorite, replacement of leucite by analcime, and replacement of pentlandite by violarite.³

Materials

Our saturated solutions and solid crystals were made from well-characterized starting materials. Salt solutions were made using powdered potassium chloride (KCl) and potassium bromide (KBr) obtained from Sigma-Aldrich, and de-ionized water (Millipore Corporation Milli-Q system, 1.8 M Ω -cm specific resistance). Saturated solutions contained 420,000 ppm and 678,000 ppm of KCl and KBr, respectively, in de-ionized water. Crystals of KBr (part # 0002-4539) and KCl (part # 0002-4538) were obtained in random cuttings from International Crystal Laboratories, NJ, USA.

Trapping Quantum Dots and sPSL Particles inside KBr Crystals

In order to demonstrate mineral replacement's applicability as a method to extract substances trapped within the structure of a mineral, small particles were intentionally trapped inside of KBr crystals. These particles were "Quantum Dots" (Qdot® 655 ITK carboxyl quantum dots, excitation/emission: 635 nm/655 nm) obtained from Life Technologies, and fluorescent surfactant-free sulfate-functionalized polystyrene latex microspheres (sPSL, $a = 4.0 \mu\text{m} \pm 2.1\%$, $w/v = 2\%$, excitation/emission: 580 nm/605 nm) obtained from Interfacial Dynamics Corporation (Portland, OR). These particles were chosen for their emission/excitation wavelengths, as well as their relatively small size allowing them to be incorporated into the crystal structure of KBr. Both types of particles were also used to trace flow paths within the KBr-KCl-H₂O replacement system.

Using powdered KBr and de-ionized water, 5-10 mL of saturated KBr in deionized water was created. Then 5-8 μL of Quantum Dots or sPSL tracer particles were added to the solution, and the solution was allowed to sit for approximately two days. At the end of this time, KBr crystals had grown to a size of 1-2 mm³. Inspection under an optical or confocal microscope confirmed that these crystals contained Quantum Dots or sPSL microspheres randomly incorporated into the crystal's structure.

Fabrication and Setup of Batch Reactor and Flow Cell

A petri dish batch reactor was created to observe the KBr-KCl-H₂O system underneath an inverted confocal or optical transmission microscope. A hole was cut into the bottom of the petri dish (Cell E&G, part # PDH00001-200) to provide a replaceable surface. A glass coverslip (VWR, part # 48368-062, 22 mm x 22 mm) was used as the replaceable surface, and was attached using paraffin wax and a cotton swab. Paraffin wax was chosen, as it creates a leak proof seal and does not undergo a chemical reaction with any of the components of the KBr-KCl-H₂O replacement system. To observe replacement in the batch reactor, a crystal (typically KBr), approximately 9 mm³, was placed on the replaceable glass coverslip and 0.5 mL of saturated solution (typically KCl) was added to the reactor.

The flow cell reactor (Figure 3) was made of 0.2” thick polycarbonate (Lexan 12” x 24” sheet obtained from Home Depot) cut into a 1” x 2.5” rectangle. A 1 cm x 2 cm hole was cut into the center of the material using a Dremel (model # 220-01 and tips). The Dremel was then used to sand a pathway for small, polyethylene tubing (BD Intramedia, ID = 0.03” and OD = 0.048”) fitted to BD single-use needles (22 gauge with OD = 0.02825”, part # BD305155, obtained from VWR). UV adhesive (NOA 61, obtained from Norland Products) was used to attach a typical glass slide (VWR, part # 48300-025) to the bottom of the polycarbonate. The apparatus was then placed under a UV lamp for 10 minutes to seal the glass slide to the polycarbonate. Paraffin wax was applied to the outside of polyethylene tubing to attach the tubing to the sanded pathway.

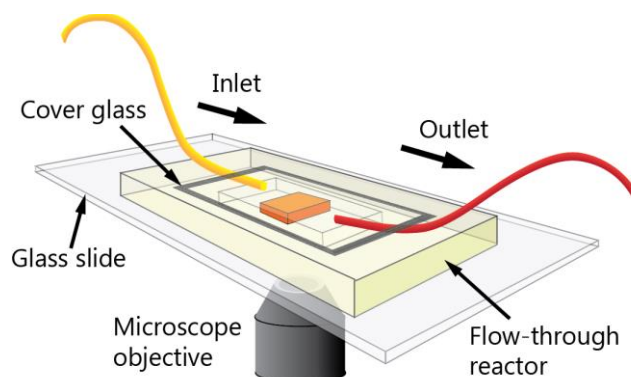


Figure 3. Schematic of flow cell reactor. Saturated KCl flows from a syringe pump through the left (yellow) tube, fills the center area containing a KBr crystal (shown in orange), and flows out the right side (red) tube, where the effluent solution is collected. A paraffin wax seal keeps the saturated KCl from exiting anywhere except through the output tube.

Before use, a crystal was placed in the hole drilled into the polycarbonate, and secured there using paraffin wax. Then, paraffin wax and a glass coverslip (VWR, 22mm x 40mm) were used to seal the compartment. Saturated solution (typically KCl) was flowed into the compartment at various flow rates (0.1-2 mL/min) using a calibrated syringe pump (Kd Scientific 780210) with BD syringes (10-60mL, B-D 2201 PrecisionGlide® Needles).

Observation and Characterization of Replacement Systems

Bright-field observation of particle motion was made on a Nikon inverted microscope (Eclipse TE2000-U) fitted with an optical light source and CCD camera (Q-Imaging). Nikon NIS Elements Imaging Software (V. 4) was used for both particle and replacement rate measurements and tracking. A Leica TCS SP5 laser scanning confocal microscope (LSCM, Leica Microsystems, lasers: Argon, HeNe543, HeNe633, 70.77 μ m pinhole) was used for imaging and

recording motion of sPSL microspheres and Quantum Dots. Typically 4x and 10x objectives were used with the transmission and confocal microscopes.

A Leo 1530 field emission scanning electron microscope (FESEM) provided by the Penn State Nanofabrication Facility and a Hitachi S-3000H scanning electron microscope (SEM) provided by Penn State Material Characterization Laboratory were used to obtain electron microscopy images. Energy dispersive spectroscopy (EDS, Oxford Instruments, Palo Alto, CA) was used to elementally map the composition of the crystal before, during, and after replacement. Since the EDS elemental analysis was done in conjunction with SEM the chemical composition of specimens could be determined qualitatively. SEM and FESEM images were taken at an accelerating voltage of 3-5 kV and working distances between 3-7 mm.

X-ray Diffraction (XRD) (PANalytical Empyrean, Netherlands) was done on our crystal samples using Cu K α radiation before and after the replacement process to determine the crystalline structure and identify their phase composition.

UV-Vis spectroscopy (PerkinElmer, LAMBDA 35) was used to determine whether quantum dots or sPSL microspheres exited the flow-cell reactor, by scanning an effluent sample from λ =500-700 nm and observing absorbance indicating the presence of Quantum Dots or sPSL microspheres.

Sample Preparation for SEM

In a batch reactor, the KBr crystals were allowed to undergo replacement with saturated KCl for different time intervals and were then washed with benzene (as salts do not dissolve in apolar solvent) and left to air-dry. In a flow-through reactor, benzene was injected through the

syringe pump to halt the replacement process. The cover glass was then removed and the crystal was left to air-dry. For observing the pores, the samples were placed facing up under the SEM and the FESEM. However, to observe the extent of the replacement process and the dead-end pores formed during the replacement process, the crystals were cleaved into two halves and the newly created side was placed facing up under the SEM and the FESEM. Batch and flow-through reactor samples were also washed (with benzene) and air dried before being taken for XRD.

Analyzing/Tracking of Mineral Replacement Data

The inbuilt tracking module in Nikon AR software (used with transmission microscope) was used to quantify the replacement front distances and replacement speeds as a function of time. Since the confocal microscope software did not have such tracking capabilities, videos from this microscope were analyzed using “Tracker” from cabrillo.edu.

Image intensity profiles were analyzed using ImageJ software (National Institutes of Health).

RESULTS & DISCUSSION

KBr-KCl-H₂O Batch Reactor System

In order to observe the mineral replacement process, we captured a video of mineral replacement in the typical KBr-KCl-H₂O batch reactor system. Despite a large body of mineral replacement research, no videos of these reactions exist in literature, to the author's knowledge. The KBr-KCl-H₂O replacement video obtained, shown in Figure 4 as a time-lapse image, shows rapid, pseudomorphic replacement. As the video progresses, a dark band develops from the edges of the crystal toward the center. This dark band represents the new K(Br,Cl) phase that is formed as the KBr crystal is replaced. This band can be seen clearly, due to the different refractive indices of the KBr and the product K(Br,Cl) phases. If allowed to react fully at ambient conditions, in approximately 2 hours, the crystal will have a uniform K(Br,Cl) phase.



Figure 4. Time-lapse image of KBr crystal replacing in batch reactor with saturated KCl solution. The dark rim represents the newly formed K(Br,Cl) product phase.

It has been well-determined in literature that mineral replacement occurs at rates far too fast for solid state diffusion²⁴ which tracking the replacement front confirmed. We also analyzed the crystal structure using powder XRD. The diffraction patterns confirmed that the crystal underwent a change from KBr to a solid solution of K(Br,Cl). While it was necessary to visualize and characterize this transformation, it was equally important to find the reaction process. The laws of thermodynamics state precisely how to predict the outcome of this re-equilibration process; however, kinetics is the controlling factor in deciding the evolution and the progress of

this reaction mechanism. To better understand this, we used KBr crystals with encapsulated QDs under a confocal microscope in order to quantify the dynamics of the process.

KBr was synthesized with quantum dots trapped within the crystal structure, as per the Materials and Methods section of this thesis, in part to test if diffusion was the dominant mechanism in the KBr-KCl-H₂O replacement system. If the replacement were occurring via a diffusion dominated reaction process, the trapped Quantum Dots should diffuse out in a matter of hours, as the diffusion coefficient for these particles is on the order of $\sim 10^{-11} \text{ m}^2/\text{s}$. However, the results showed rapid extraction of Quantum Dots, as is indicated by the rapid decrease in the blue color within the KBr crystal in Figure 5(c). This rapid extraction indicates that the force driving the quantum dots out of the crystal is not diffusion. In 10 minutes, the Quantum Dots travelled approximately 500nm. If the Quantum Dots had moved by diffusion alone, covering this distance should have taken approximately 7 hours. When placing a KBr crystal with Quantum Dot inclusions into saturated KBr solution in the batch reactor, no decrease in the color intensity was seen, indicating no extraction in the control system.

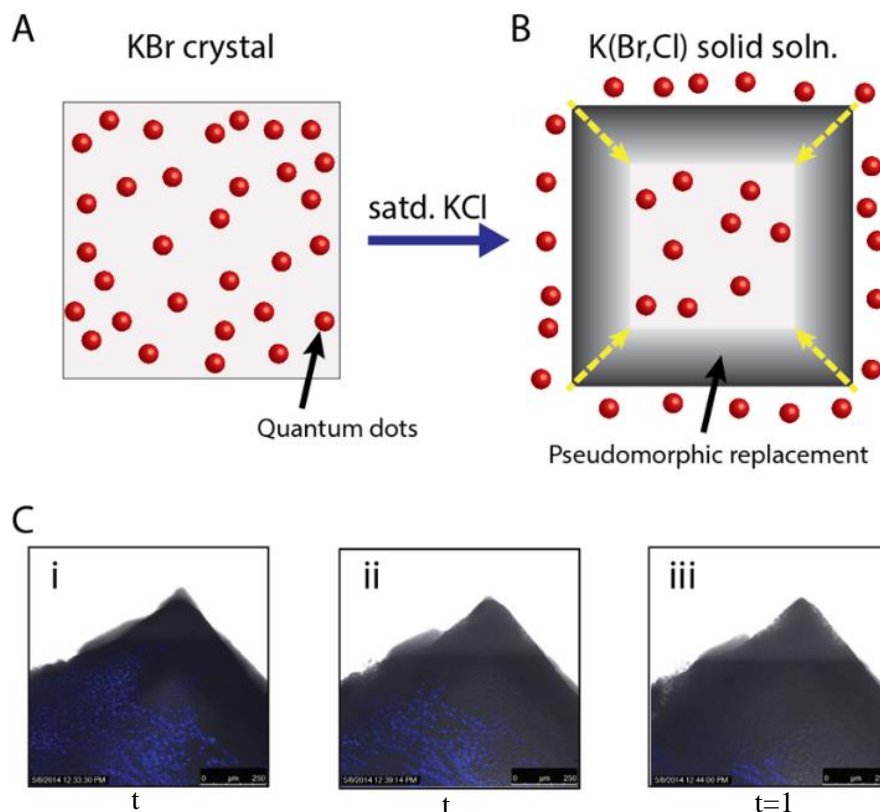


Figure 5. Extraction of Quantum Dots from KBr crystal in batch reactor. (a) Schematic showing KBr crystal with trapped Quantum Dots. (b) Schematic showing conceptual extraction of Quantum Dots trapped inside of KBr. (ci-ciii) Time-lapse image of KBr crystal with entrapped Quantum Dots in a batch reactor with saturated KCl solution. These images are overlays of transmission and confocal microscope images. The blue color shows where Quantum Dots are present. When hit with 635 nm light, the quantum dots emit 655 nm light. The confocal microscope was set to detect light emitted in a small range near 655 nm and display this light as a blue color. As can be seen in (c), the blue color is fading over time, from the outside in, indicating extraction of the Quantum Dots.

A key characteristic of pseudomorphic mineral replacement reactions is development of porosity, as a result of a less dense product phase being formed. Since KCl is less dense than KBr, as the replacement front develops in the KBr-KCl-H₂O replacement system the crystal becomes less and less dense. To make up for this constantly decreasing density, but a constant external volume, pores develop within the crystal. Mechanistically, these pores are a result of the

difference in atom sizes of Br^+ and Cl^- ions, as well as varying KBr and KCl solubilities. These pores are necessary to allow replacement on the inside of the crystal.

Using SEM microscopy, these pores were imaged (Figure 6). Comparison of pores from crystals that had replaced for different amounts of time in the same system showed a change in pore size from nanometer scale to 100s of microns within 10 minutes. While pores from crystals that had replaced longer had larger diameters, the pores began to close. This partial pore closing is evident when comparing Figure 6d and 6e. Replacement continues as pores continue to expand under the surface of the crystal, but the outside of the pore has begun closing. The opening and partial closing of pores observed with SEM imaging shows that the dissolution and precipitation fronts must be separated. In the batch system, this separation is typically on the order of 100 microns.

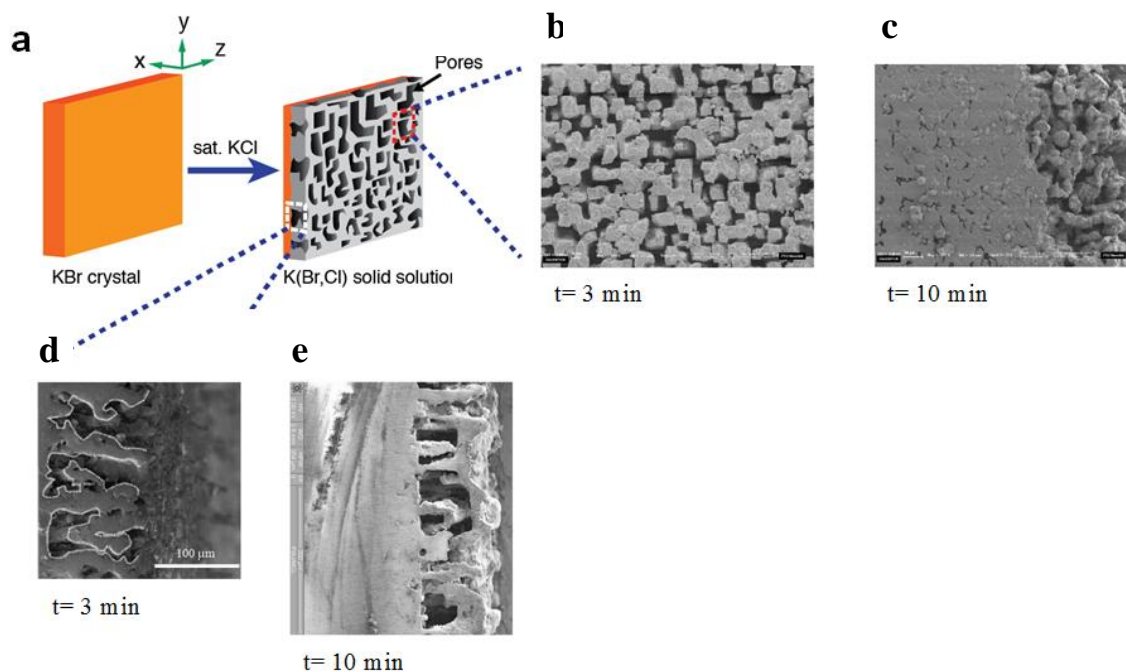


Figure 6. Porosity development during mineral replacement. (a) Schematic showing porosity development as replacement occurs. (b) and (c) Front-view SEM image of pores in product phase of partially replaced KBr at 3 and 10 minutes, respectively. (d) and (e) Side-view SEM image of pores in product phase of partially replaced KBr at 3 and 10 minutes, respectively. Comparison of (b) to (c) and (d) to (e) show the partial pore closing on the surface of the crystal, while underneath the pore's size is expanding.

Observations from these SEM images led to doubts in the proposed dissolution-precipitation mechanism, as this model is unable to explain the sealing of pores. If the reaction were occurring via a single-front dissolution-precipitation, pores could not be sealing at one end while entering deeper into the crystal at the other end. These images and the observations of the extraction of Quantum Dots from a KBr crystal led to the hypothesis that convective, specifically diffusiophoretic and diffusioosmotic, fluid flows existed within the crystal's pores.

In mineral replacement reactions, mass transport plays a critical role. There are two regimes in which mass transport takes place, and here we analyze their effect on the eventual rate of mineral replacement process. Firstly, the external mass transport regime where advection of saturated KCl solution over the crystal surface ($Re > 1$, $Pe \gg 1$, laminar flow) gives rise to external mass transport, and secondly, the flow through the pores ($Re \ll 1$, $Pe \sim 1$, viscous flows) where internal mass transport dominates. The extensive solution for these two approaches is beyond the scope of the current thesis. However, here I present a succinct analysis behind the interplay of these transport processes and their effect on the rate of replacement.

In the external mass transport domain, the mass transfer can be simplified to a L  v  que problem.³⁸ The L  v  que problem is an idealized situation which accurately describes the limiting case in many relevant applications such as fluid flow, heat transfer, and catalysis.³⁸ Since reaction (or heat transfer) is assumed to occur infinitely fast, the solution represents an asymptote that real-world experiments will approach.³⁸ In order to determine if convective flows could be ignored in the mineral replacement system, Peclet numbers, Pe , were analyzed on the idealized L  v  que system shown in Figure 7.

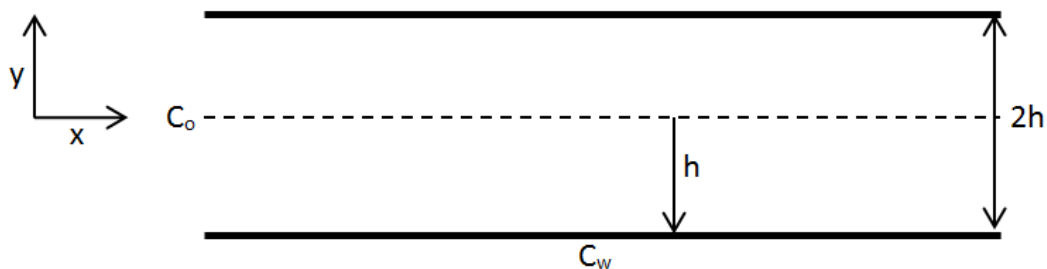


Figure 7. Idealized system used for L  v  que solution and Peclet number analysis

The L  v  que system assumes the flow is fully developed and laminar, that the width of the channel into the paper, W , is much greater than h , and that symmetry along the axis exists such that contributions from the z direction is negligible (the problem is effectively two-dimensional). Since the fluid is fully developed and there is a pressure drop across the ends:

$$v_x = v_y = 0 \quad (\text{Equation 4})$$

$$v_x(y) = \frac{dx}{dt} = v_o \left(1 - \frac{y^2}{h^2}\right) \quad (\text{Equation 5})$$

Using Fick's 2nd Law to find the concentration gradient:

$$\frac{dc}{dt} = \frac{dx}{dt} \times \frac{dc}{dx} = D \left(\frac{d^2c}{dx^2} + \frac{d^2c}{dy^2} \right) \quad (\text{Equation 6})$$

Assuming $Pe \gg 1$, the diffusion along the x -axis is negligible and $\frac{d^2c}{dx^2} = 0$. By using this assumption, as well as combining Equations 5 and 6, we find:

$$v_x(y) \frac{dc}{dx} = D \frac{d^2c}{dy^2} \quad (\text{Equation 7})$$

Solving for the velocity and then the flux of ions (J , #ions/m²·s) over the crystal surface, it can be found that:

$$J \propto Pe_l^{1/3} \quad (\text{Equation 8})$$

For this system, the relevant Peclet number is Pe_l , the Peclet number along the length of the channel. Mathematically, this value can be computed using Equation 9.

$$Pe_l = \frac{\text{Convective rate (x)}}{\text{Diffusive rate (x)}} = \frac{\text{Diffusive time (x)}}{\text{Convective time (x)}} = \frac{l^2 / D}{h / (Q / hW)} = \frac{Ql^2}{Dh^2W} \quad (\text{Equation 9})$$

Using values from one specific flow-through experiment where $Q = 2 \text{ mL/min}$, $W = 5 \text{ mm}$, $D \approx 10^{-9} \text{ m}^2/\text{s}$, and $l/h \approx 0.5$ the Peclet numbers are calculated to be $Pe_l = 1.5 \times 10^6$. Therefore, convective rates relative to diffusive rates are not small enough to be ignored when determining the mechanism and reaction process of mineral replacement. Although beyond the scope of this thesis, COMSOL modeling was completed using the Sherwood (Sh) and Damköhler number (Da) to show *via* scaling analysis that mass transfer increased as flow through the system increased. More information about the modeling can be found in the manuscript submitted on the subject matter of this thesis.³⁹

As a result of the failures of the dissolution-precipitation mechanism, a new reaction process was proposed involving electrokinetic flows in transient dead-end pores (Figure 8).

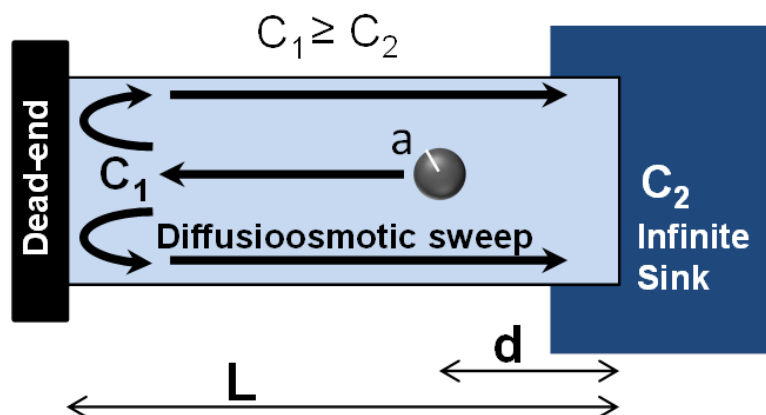


Figure 8. Schematic of proposed electrokinetic replacement reaction process. The concentration differences between the bulk solution outside of the pore, and the liquid inside of the pore drives diffusiophoretic flow through the center of the pore. This fluid flowing into the pore is balanced by fluid flow toward the outside of the pore via a diffusioosmotic sweep along the edges of the pore. This reaction process is based upon convective, electrokinetic fluid flows within the pores, treating the end of the pore as a transient dead-end pore. The reaction process is able to account for both quick extraction of materials from inside of the pores to the outside of the pores, as well as pore sealing over time.

The proposed reaction process involves two countercurrent convective flows within the pore. Convective flows are driven either by pressure gradients or electrokinetics. Since the pores have a dead-end, conventional pressure driven flows are not possible, therefore flows must be electrokinetic. Through the center of the pore, diffusiophoresis drives fluid flow carrying K^+ and Cl^- ions towards the center of the crystal. This flow is a result of the concentration difference of the saturated KCl in bulk liquid outside of the pore and the concentration of the fluid within the pore, as well as the liquid at the end of the pore, which is undersaturated with respect to KCl, but significantly more saturated with respect to KBr than the bulk fluid. In order to balance the flow of mass into the pore, a diffusioosmotic flow along the stationary walls of the pore develops, carrying liquid containing K^+ and Br^- ions outside of the pore. This flow pattern is very similar to

the dead-end flows explored by Kar.²⁹ Unlike the diffusion based dissolution-precipitation mechanism, this mechanism is driven by convective, electrokinetic fluid flows.

The convective flows in this model explain the extraction of quantum dots at speeds greater than those predicted by diffusion, as the particles are carried out of the pore via diffusioosmosis. This model also reconciles the closing of pores during the replacement process, because it proposes that dissolution and precipitation occur at different fronts. This distance between fronts is a key difference between the proposed electrokinetic scheme, compared to the coupled dissolution-precipitation mechanism. Without separate fronts, the driving force for electrophoresis (a concentration difference) would not exist.

In order to determine if a concentration gradient existed, replacement was carried out using saturated KBr in the fluid phase instead of saturated KCl. In this system, no concentration gradient exists, since saturated KBr would be in the solution throughout. Not surprisingly, no replacement occurred without a concentration gradient.

KBr-KCl-H₂O Flow-Through Cell System

In order to test the hypothesized electrokinetic replacement mechanism, a flow-through cell experiment was designed, as described in the Materials and Methods section. A flow-through system was chosen, because increased flow rate of the bulk solution should not affect replacement rates if the reaction is occurring through a diffusion dominated mechanism. However, if the reaction occurs via a convective flow dominated reaction process, a change in replacement rate should be seen as a result of a change in flow rate.

Real-time videos of KBr-KCl-H₂O replacement in the flow-through cell were taken at various flow rates. Figure 9 shows time-lapse images from a video of replacement occurring in the flow-through cell reactor, with a saturated KCl flow rate of 1 mL/min. One interesting observation is that the outer boundary of the crystal shrinks throughout the replacement. Therefore, outside of the static batch reactor environment, pseudomorphic replacement does not occur in the KBr-KCl-H₂O system, an observation not previously reported in literature.

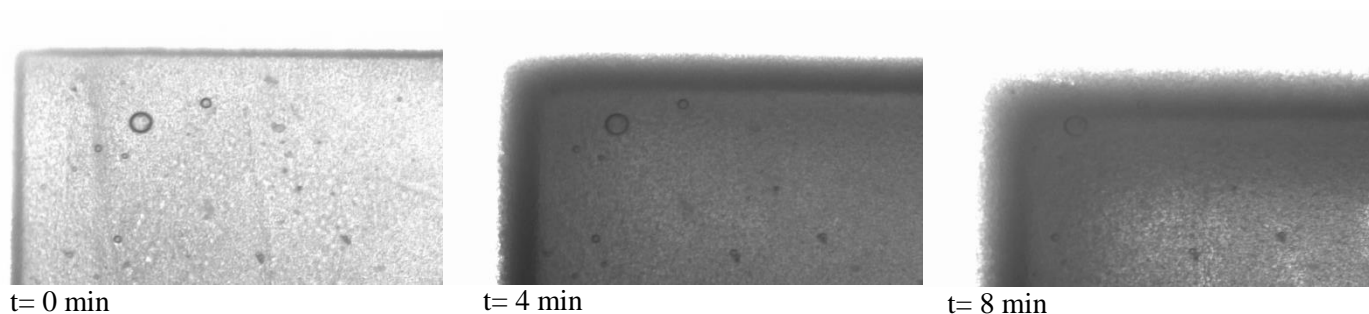


Figure 9. Replacement of KBr by K(Br,Cl) in a flow-through cell reactor at flow rate of 1 mL/min saturated KCl. (a) KBr crystal just after KCl solution begins flowing (b) KBr crystal 4 minutes after KCl begins flowing (c) KBr crystal 8 minutes after KCl begins flowing. As replacement occurs in the flow-through system, the overall volume of the crystal shrinks, as is evidenced by the shrinking external border of the crystal in the figures above.

Carrying out KBr-KCl-H₂O mineral replacement reactions at various flow rates in the flow cell reactor yielded very different results in terms of pore formation and mineral replacement rates, as can be seen in Figure 10. As the rate of flow through the reactor increased, the rate of replacement also increased, indicating that an increase in the cell flow-through rate increased the convective fluid flow rate within the pores of the crystal. It was found that at a flow rate of 2 mL/min or faster, the replacement front traveled at an approximately constant speed. Therefore, optimum mass transfer occurs at flow rates of 2 mL/min or faster.

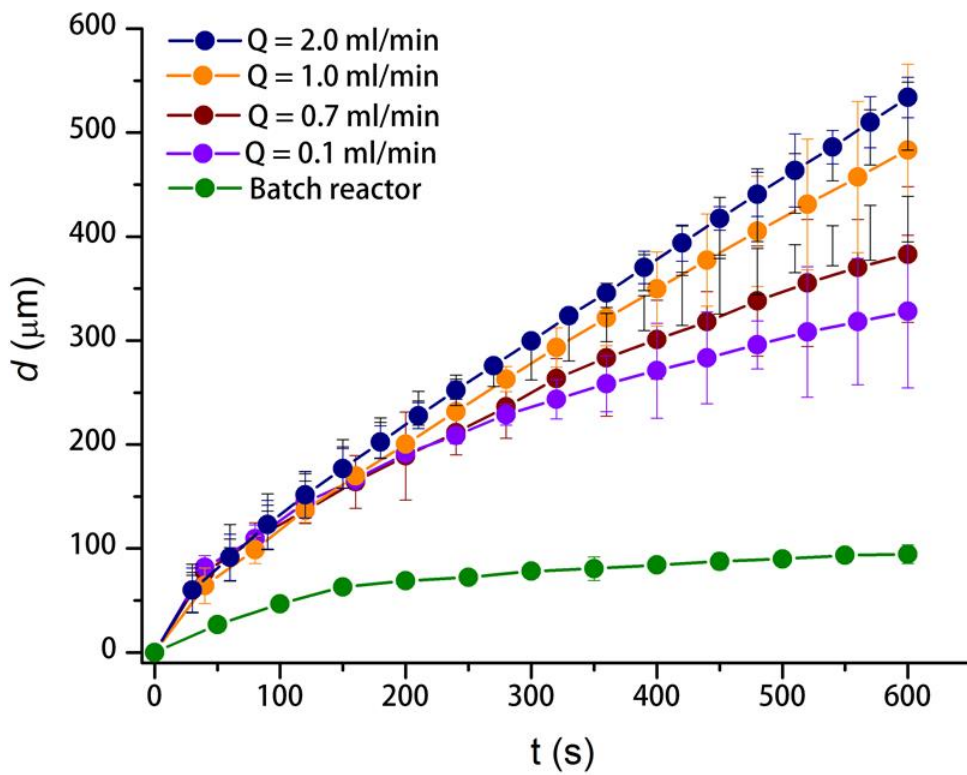


Figure 10. Experimental replacement rates in a flow-through cell reactor at various flow rates, Q . Video analysis was completed using NIS AR tracking software.

Study of the KBr-KCl-H₂O mineral replacement system in a flow-through reactor allowed a more holistic understanding of not only how the process occurs, but also ways this process can be exploited. Based on the diffusion driven assumption of the dissolution-precipitation mechanism, the mineral replacement process would not be useful as a method to extract trapped materials (such as oil and gas) from within rocks or minerals, since these materials would diffuse out slowly if at all. However, the newly proposed electrokinetically driven reaction process has far-reaching implications for using these flows as an extraction technique. It was experimentally determined that pore sealing could be stopped by using controlled fluid flow conditions. Mineral replacement processes like that in the KBr-KCl-H₂O replacement could be extremely useful for in-situ mining processes, such as hydraulic fracturing. Mineral replacement could be used to increase porosity in shale and sandstone formations with low permeabilities to enhance extraction yield. Similar improvements could be made in processes where leaching of specific elements, particles, or gas is desirable.

An example of this extraction process is shown in Figures 11 and 12, showing 4 μ m sPSL particles extracted from a KBr crystal. We could not extract these particles in the batch reactor system, as a result of the partial pore closing. However, when the flow rate of the flow-through cell was increased to 2 mL/min, the pore sealing was reduced sufficiently to allow particles 4 μ m in diameter to exit. While the Quantum Dots served as an effective proxy to determine if mineral replacement could be used as an extraction technique, sPSL particles are a more realistic example, as they have a larger diameter, 4 μ m. sPSL particles also have a diffusion coefficient two orders of magnitude smaller than Quantum Dots, thus indicating that sPSL particles should take even longer than Quantum Dots to be extracted from the crystal. Estimates from Fick's 2nd

law indicate that this extraction should take on the order of one day.^{25,26} Both types of particles were extracted at approximately the same rate, further confirming a convective flow based reaction process.

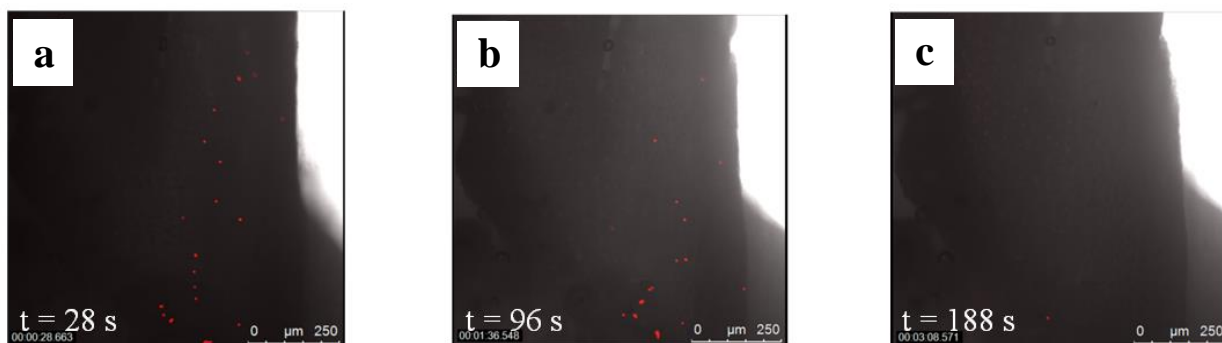


Figure 11. Extraction of 4.0μm sPSL particles from KBr crystal. Experiments were completed in flow-through cell reactor at saturated KCl flow rate of 2mL/min under confocal microscope. (a) 28 seconds after KCl began flowing (b) 96 seconds after KCl began flowing (c) 188 seconds after KCl began flowing. The red dots show the locations of sPSL particles, which could be seen exiting one at a time as the process occurred. Within 10 minutes, all of the sPSL particles were extracted from the crystal. This process should have taken on the order of 1 day to occur via simple liquid diffusion.

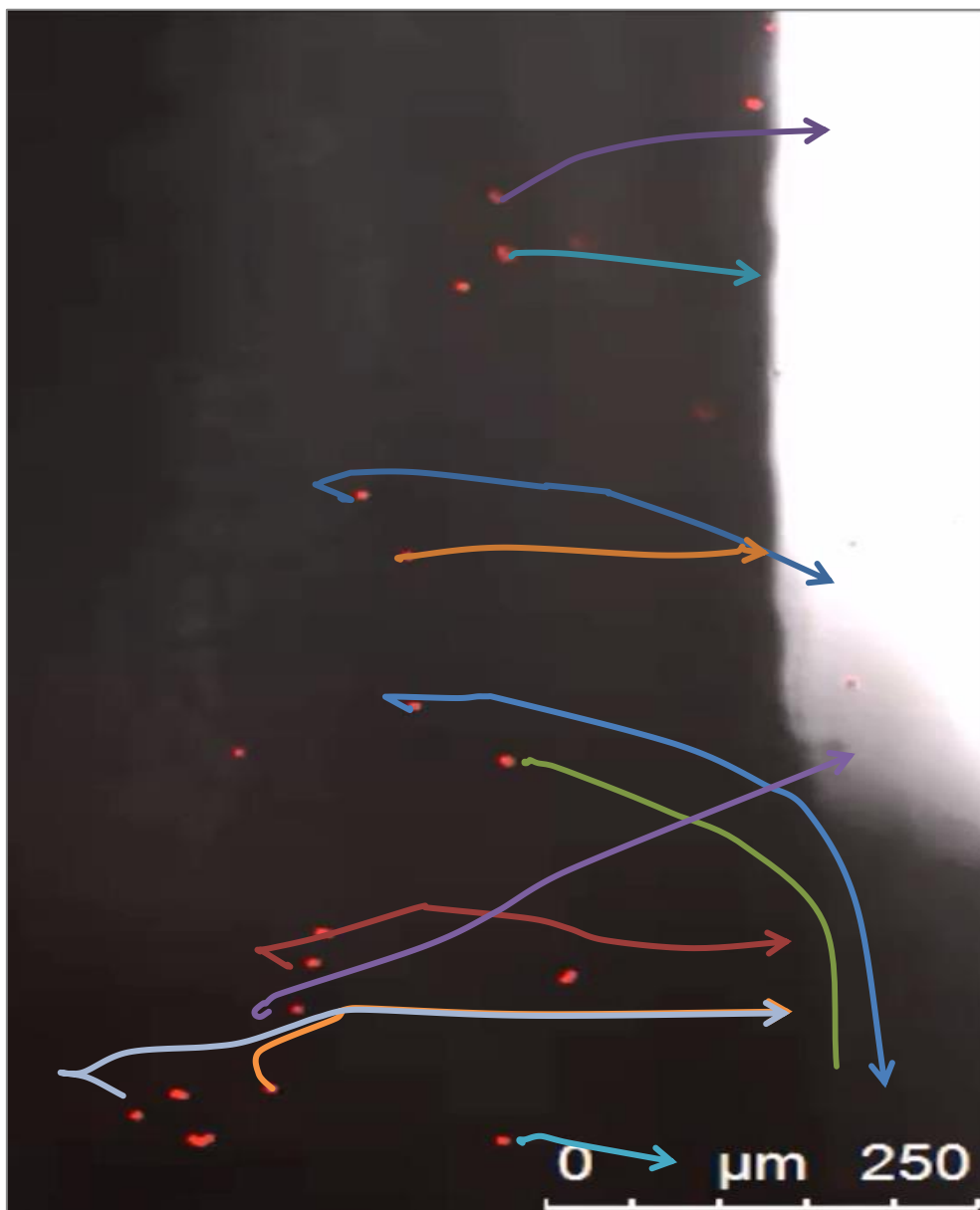


Figure 12. Tracked extraction of 4.0µm sPSL particles from KBr crystal. The particles were tracked using Tracker and overlaid on the microscope image to show the path of the particle.

Extraction of Quantum Dots in a flow cell was also tested, in order to experimentally prove that the materials inside of the crystal were, in fact, leaving the crystal structure and entering the liquid phase. Figure 13 shows a UV-Vis scan of the effluent of the flow-through cell

after Quantum Dot extraction compared with scans of saturated KCl, with varying amounts of Quantum Dot solution present. Although no clear peaks were seen representing Quantum Dots in the effluent sample, the absorbance of the effluent sample was higher than the absorbance of the samples containing no Quantum Dots, indicating that these particles were present in the effluent stream.

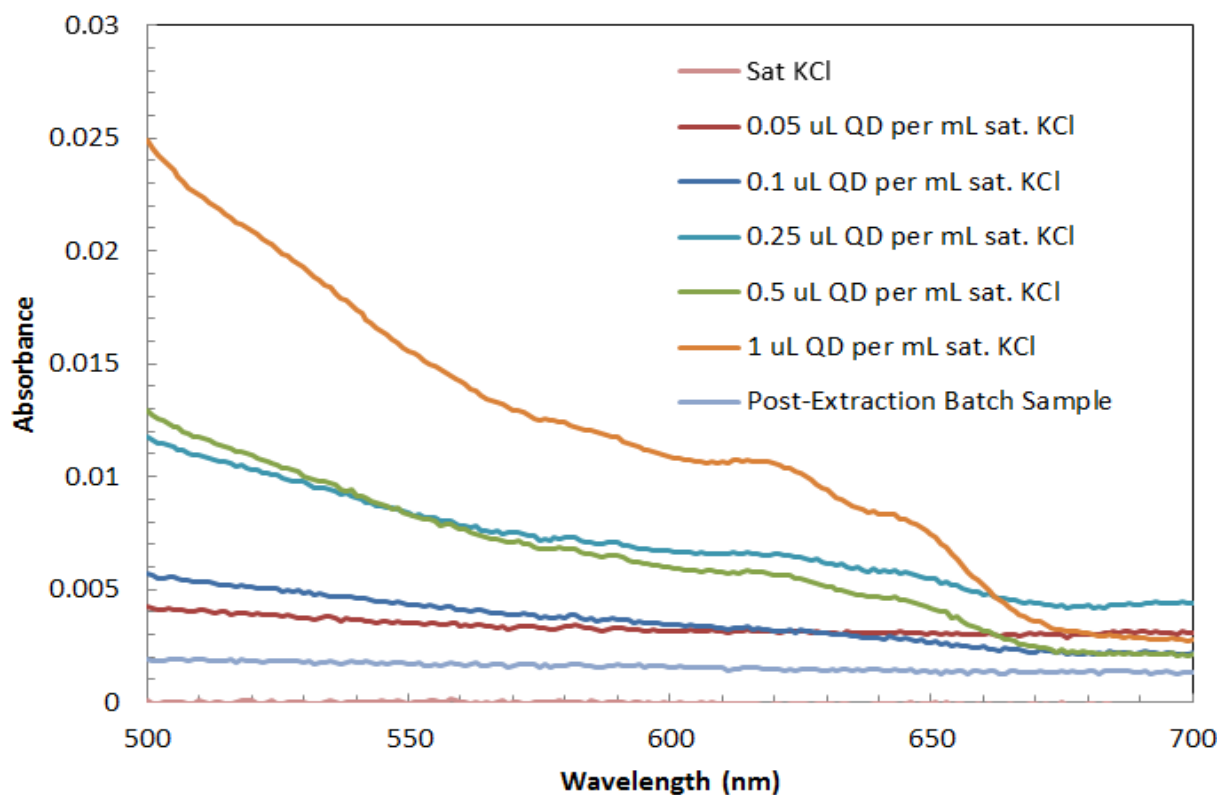


Figure 13. UV-Vis results of flow-through cell extraction of Quantum Dots.

We also attempted extraction of Quantum Dots by flowing saturated KBr. We found no additional absorbance from this effluent sample, indicating that saturated KBr did not extract Quantum Dots.

CONCLUSION

This thesis challenges the classic view that pseudomorphic mineral replacement occurs through a diffusion-based mechanism. Mineral replacement in the KBr-KCl-H₂O system was found to occur through an electrokinetic, convective fluid flow based reaction process. Unlike the coupled dissolution-precipitation mechanism often cited in literature, this mechanism is not diffusion limited and depends heavily on fluid flow rates outside of the crystal. The convective flow based reaction process is also able to account for experimentally observed pore closing, as dissolution and precipitation occur at separate fronts. This reaction process involves a diffusiophoretic flow in the center of a pore, carrying Cl⁻ ions toward the center of the crystal, as well as a diffusioosmotic sweep along the walls of the pore carrying Br⁻ ions.

It was found that increasing external fluid flow rates increased the replacement rate, with optimum mass transfer occurring at saturated KCl flow rates around a KBr crystal of 2 mL/min and above. Quantum dots and sPSL tracer particles trapped within a KBr crystal were extracted through the use of mineral replacement, thus confirming the applicability of mineral replacement as a means of extracting materials trapped inside of rocks and/or minerals.

While perhaps not the most geologically or industrially relevant system, a convective flow based mechanism has far-reaching implications in bone decay, environmental weathering, and particularly in oil and gas extraction. Further research can be done to apply mineral replacement in oil and gas extraction to increase the efficiency and yields of extraction by extending pores deeper into rocks and minerals.

Further research must be done to explore questions raised in this thesis to determine the effects of external fluid flow on increasing replacement rates in other systems, such as the uptake of radioactive radium by barite. Research must also be completed in other salt systems (such as NaCl and KCl, a potential cation exchange) to determine the applicability of this reaction process to other systems, and research should be completed to study the zeta potential of the pore walls.

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EDUCATION

The Pennsylvania State University, Schreyer Honors College, Class of Spring 2015
Bachelor of Science in Chemical Engineering with Honors in Chemical Engineering

WORK EXPERIENCE

ExxonMobil - Research and Engineering Intern Summer 2014

- Optimized and updated solvent dewaxing filter model to initiate recovery of nonconforming product valued at over a million dollars
- Created thermodynamic heat balance model to determine the proportion of wax melted due to wash section of rotary filter drum
- Coordinated international site testing to validate new/updated models
- Compiled Best Practice on eliminating pour point giveaway due to melted wax

Procter and Gamble - Papermaking 5/6M Summer Engineer Summer 2013

- Studied energy inefficient systems and made technical recommendations to increase efficiency. Scoped projects totaling \$50,000 per year in savings
- Initiated and managed \$69,000 per year fiber savings project by aligning requirements across various departments
- Coordinated glue optimization test, compiled formal report, and proposed new glue centerline, resulting in \$38,000 per year in savings
- Led redesign and installation of faulty stair unit as well as other safety initiatives

GE Aviation LEAP - 1B Externals Intern Summer 2012

- Analyzed part clashes using engineering software and tools to determine the most efficient placement of external parts
- Created material selection matrix for High Pressure Turbine Active Clearance Control mounting concept
- Paired parts and connectors appropriately using comparative analysis resulting in my design entering the Digital Pre-Assembly

Penn State Mineral Replacement Research advised by Dr. Darrell Velegol 2013-2014

- Conducted experiments on the application of geological/chemical phenomena to real-world challenges. Experimental research provides the basis for honors thesis

UNIVERSITY ACTIVITIES

The Statesmen A Cappella Group
• **Today Show** performance in May 2013
Campus Crusade for Christ Member
Pennharmonics A Cappella Group
• Varsity Vocals International Collegiate Competition of A Cappella – Team Finalist

LEADERSHIP POSITIONS

The Statesmen, Administrative Director 2013-2015

- Manage group schedule, rehearsal agenda, and practice times weekly
- Lead group discussions regarding performances, disciplinary action, and auditions
- Oversee all other leadership roles and backfill as needed

Schreyer Honors Orientation Mentor 2012-2013
High School Class President 2008-2011

HONORS

Genentech Outstanding Student Award – Penn State University 2013
Evan Pugh Scholar Award - Penn State University 2014
Sparks Award - Penn State University 2013
The President's Freshman Award - Penn State University 2012
National High School Musical Theatre Awards participant (on Broadway) 2011