



Review Article

A comprehensive review on clay swelling and illitization of smectite in natural subsurface formations and engineered barrier systems

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ABSTRACT

For the safe disposal of high-level radioactive waste using Engineered Barrier Systems (EBS), bentonite buffer is used by its high swelling capability and low hydraulic conductivity. When the bentonite buffer is contacted to heated pore water containing ions by radioactive decay, chemical alterations of minerals such as illitization reaction occur. Illitization of bentonite indicates the alteration of expandable smectite into non-expandable illite, which threatens the stability and integrity of EBS. This study intends to provide a thorough review on the information underlying in the illitization of bentonite, by covering basic clay mineralogy, smectite expansion, mechanisms and observation of illitization, and illitization in EBS. Since understanding of smectite illitization is crucial for securing the safety and integrity of nuclear waste disposal systems using bentonite buffer, this thorough review study is expected to provide essential and concise information for the preventive EBS design.

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1. Introduction

According to International Energy Agency, nuclear energy currently provides 30% of the world's power and 11% of the world's electricity [1]. This is achieved through 450 active nuclear reactors globally with 60 more being constructed. 98 of those reactors operate in the US, supplying about 19% of US electricity while generating over 80,000 metric tons of nuclear waste till date [2]. In South Korea, 24 operating plants have accumulated 14,000 metric tons at a rate of about 750 tons per year [3]. Most of the low and intermediate level wastes are temporarily stored in shallow underground repositories at the reactor sites. For the high-level nuclear waste, the global consensus is to store them in deep geological repositories at depths of 200–1,000 m [2,4].

In general, the repository for high-level nuclear waste has two main functions: confinement and retardation. Confinement requires completely isolating the waste from the biosphere, while retardation requires slowing down any eventual release of radionuclides from nuclear wastes [5]. This is achieved by using a multi-barrier approach, comprised of the natural barrier (the host rock), and the engineered barrier, typically made up of a bentonite buffer

and a metal canister. Bentonite is chosen for several adequate properties including low permeability, adsorptive properties due to large specific surface area, and its high swelling potential [6]. It must be able to swell and contain the radionuclides, heal, or seal any openings within the repository, and maintain low hydraulic conductivity. Low hydraulic conductivity ensures that diffusion is the dominant fluid transport mechanism [5]. This requires a hydraulic conductivity between 10^{-14} – 10^{-11} m/s and a minimum swelling pressure of 0.1–1.0 MPa [4,5,7]. Published literature primarily reports the swelling pressure for common bentonites proposed for repository concepts to be greater than this: 2–6.5 MPa Gyeongju bentonite [8,9], 10–40 MPa for MX-80 and Montigel [10], 105 kPa–5 MPa for GMZ bentonite (D. [11], and 1.8 MPa for FEBEX bentonite [12]. Values for MX-80 (a 65–82% Na-montmorillonite) and Montigel varied widely because the tests were conducted for varying dry densities. For hydraulic conductivities, experimental values show that most bentonite variants are in the range of 10^{-14} – 10^{-13} m/s [4,7,13].

However, some of these properties (like the swelling potential) are affected when it is exposed to high temperatures. In particular, the transformation of the swelling smectite in bentonite into illite is a major concern, because of the non-expandability of illite. Studies have shown that within 1000 years, the illitization of bentonite can lead to 1–8% loss in smectite volume fraction at 100 °C, and 1–27% at 200 °C [14]. Hence, studying and understanding the illitization

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Table of abbreviations

DC	Dissolution and Crystallization
DECOVALEX	Development of COupled models and their VALidation against EXperiments
DGR	Deep Geological Repositories
EBS	Engineered Barrier System
FEDEX	Full-scale Engineered Barrier EXperiment
I–S:	Illite-Smectite
OR	Ostwald Ripening
RO	Intermediate randomly interstratified phase
R1	Regularly interstratified phase
R2	Regular and periodic phase
SEM	Scanning Electron Microscope
SST	Solid-State Transformation
TEM	Transmission Electron Microscopy
THMC	Thermo-Hydro-Mechanical-Chemical
XRD	X-Ray Diffraction

phenomenon is a major focus of current state-of-the-art studies on the reliability and safety of Engineered Barrier Systems (EBS). In this regard, this paper aims to provide a thorough review on the illitization of smectite. Section 2 provides the information of clay mineralogy; section 3 provides the review on the mechanisms of smectite-illite transformation; section 4 provides the review on the illitization in the EBS.

2. Clay mineralogy

2.1. Basic clay mineralogy

Some of the earth's most important properties can be attributed to its clay content [15]. Properties such as cation exchange, shrink-swell properties, permeability, and various mechanical moduli can be attributed to the clay content [16–18]. Often, these macro properties can be explained by understanding the underlying micro and crystal structure of clay minerals [15]. The microstructure and charged surfaces dictate the reactivity of clays and the deformations (T. [19], which are comprised of particles, aggregates, and clusters (T [20–23]).

The particles are made up of hydrous aluminum silicates, arranged as sheets, with a typical dimension of 0.005 mm [24]. Because of this, they are often categorized as members of the phyllosilicates group of minerals (from “phyllo” meaning “leaf”). Each structural unit of a clay mineral is made up of tetrahedral or octahedral sheets [1]. The tetrahedral sheets are made up of a sequence of tetrahedra connected by shared oxygen atoms, while the octahedral sheets contain octahedrons made up of four oxygen atoms and two hydroxyl ions shared by various cations [1,25,26]. Depending on how the tetrahedral and octahedral sheets are juxtaposed, clays are classified into 1:1 (also called T-O clay) and 2:1 layered structures (also called T-O-T clay), respectively. 1:1 layer has octahedral and tetrahedral connections at the apices, while the 2:1 layer has one octahedral layer sandwiched between two tetrahedral layers [18,27,28]. A typical structure is shown in Fig. 1. They are among the most studied class of clay minerals, primarily because of their swelling properties.

2.2. Smectite

Smectite is a group of expandable 2:1 phyllosilicate clay minerals, which are unique in their ability to swell upon hydration, low

porosity, high surface area, and high cation exchange capacity [29]; H [30,31]. Minerals within this group include dioctahedral smectites (montmorillonite, nontronite, and beidellite) and trioctahedral smectites (hectorite, saponite, and stevensite) (Sparks, n.d.; [32,33]). Within this group, montmorillonite is most widely used for engineering purposes. It is used as an additive in drilling mud and as buffers for nuclear disposal primarily because of its low permeability and high sorption capacity [33]. It can retard the transport of radionuclides by adsorbing the metal ions, either through ion exchange or by surface complexation [34,35]. Additionally, their swelling property enables them to contain the radionuclides under high temperatures. The swelling is caused by the interaction between the charged layer and the cations contained in the surrounding solution [36,37]. Different types of swelling can be identified by understanding how the layer and cations interact.

2.3. Types of clay swelling

Clay swelling occurs in two ways—via crystalline stepwise formation of mixed layers and osmotic swelling [38–41]. Crystalline swelling was first observed [42] and is known to occur in all clay minerals. It involves a stepwise phase transition, in which the water molecules line up between unit layers resulting in an increased interlayer spacing [43]. Here, hydration occurs on the external particle interfaces and in the interlayer spaces. The adsorbed waters are known to form one, two, three and even four distinct layers in the interlayer as confirmed by experiments and simulations [38,39,44–47]. Crystalline swelling can sometimes result in the separation of layers which can be observed in X-Ray Diffraction (XRD) analysis [48]. It depends on multiple factors, such as dry density, swelling conditions, nature of the interlayer cation, and water activity [49–52].

Osmotic swelling occurs in minerals containing exchangeable cations in the interlayer at higher water content [43,48]. It results from an osmotic migration of water molecules from the surrounding water to the interlayer. It is driven by the cation concentration differences between the clay surface and the pore water, and continues until equilibrium is reached [10,53]. The repulsion between the electrical diffuse double layers on clay surfaces also aids its development [48]. Often, it is the principal cause of instability, because it results in much larger volume increases in the interlayer than crystalline swelling [43]. Monovalent smectites such as Na-montmorillonite are known to reach clay platelet separation distances of 40 Å and more for very dilute suspensions [54–56]. For divalent smectites (Ca- or Mg montmorillonite), less osmotic swelling occurs, because of the stronger ionic forces that reduce double layer repulsion leading to a maximum platelet separation distance of 19 Å [48,55,57]; W [58]. Only Ca-montmorillonite is known to accommodate more water outside particles due to the inter-particle osmotic swelling caused by osmotic forces on external surfaces [59,60]. Hence, both the interlayer spaces and the external particle surfaces are important in swelling [48]. This reiterates the importance of the clay structure in explaining its behavior and explains why some of the swelling capability is lost when smectites are transformed to illite.

3. Smectite-illite transformation (illitization)

Illite is a 2:1 micaceous clay mineral that precipitates naturally in oversaturated conditions [61]. It is the primary component of many argillaceous sediments and is produced from the thermogenic transformation of kaolinite or smectite in natural systems [62]. During this transformation, K⁺ is fixed within the interlayer leading to a covalent bond with the Oxygen atoms [63]. This ensures that the interlayer swells to a lesser extent than the original

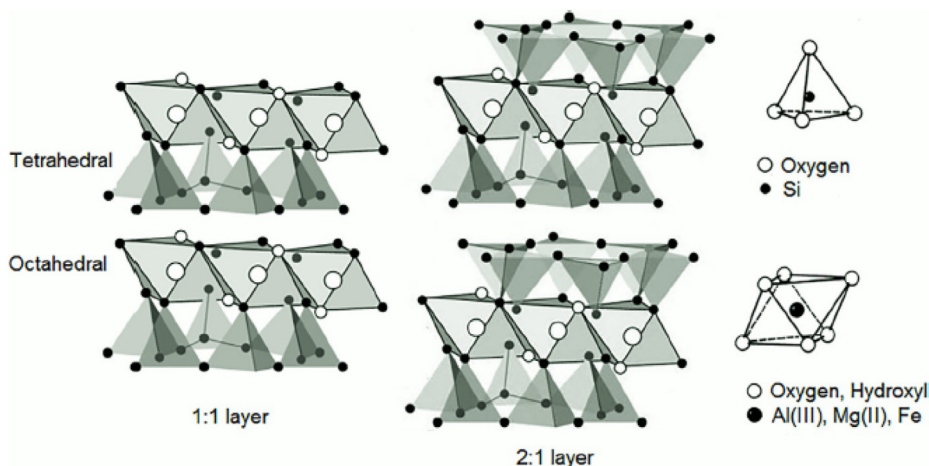


Fig. 1. Schematic representation of both configurations 1:1 layer and 2:1 layer for clay minerals [27].

smectite. Because of its lower expandability, it is assumed to be the non-expanding member, when it is present in illite-smectite (I–S) layers series [64]. Hence, understanding its formation is crucial for predicting the performance of bentonite barrier systems.

Mixed layers illitization is the gradual transformation of smectite layers to illite, via a sequence of intermediate steps [65]. proposed that smectite illitization follows an Ostwald's step rule, in which the easiest phase forms first, and the reaction continues stepwise until equilibrium. This means that in a smectite system, if all minerals are equally exposed to the same conditions necessary to form illite, the transformation would be heterogeneous. Several authors have corroborated this and indicated the existence of two or more structurally and morphologically distinct crystals [66–68]. [69] observed that smectite illitization proceeded in the phases of intermediate randomly interstratified (Reichweite R0) and regularly interstratified (R1) layers during burial diagenesis. In hydrothermal experiments, similar trends are observed with illite-smectite (I–S) becoming less expandable (more illitic) at elevated temperatures [70,71]. It becomes R1-ordered at about 30–40% expandability, R2-ordered (regular and periodic) at 15% expandability, respectively [67]. [68] made additional observations of flake-shape crystals for smectite-rich R0 forms, lath-shaped R1, and hexagonal shaped at 0% smectite (illite).

In natural sedimentary and geothermal systems, this appears as a depth-dependent evolution. In such systems, randomly interstratified mixed layer (I–S) are often observed at the top, while it becomes progressively illitic (more ordered) with burial [72]; D [64,65,68,73,74]. In certain studies, the depth-dependent evolution was correlated with other properties: temperature [64], geologic time [75], K^+ concentration in fluid (W.-L. [76], and water/rock ratio [70]. The ordering is often inferred from XRD measurements or directly observed in high-resolution Transmission Electron Microscopy (TEM) [66,77]; D. D [78].

In earlier studies, different methods of measurements also led to different explanations for the crystal structure of I–S, based on XRD results (see Fig. 2) [79]. explained the crystal structure using a Markovian model as being made of MacEwan crystallites made up of both smectite and illite layers [66]. It views the I–S layer as being large. Alternatively, the fundamental particle model, based on the analysis of TEM results, posits that I–S are made up of thinner repeating crystallites [80]. Here, the smectite expansion occurs due to activity at the interfaces between the fundamental particles [66,81]. Most explanations of clay behavior use the fundamental

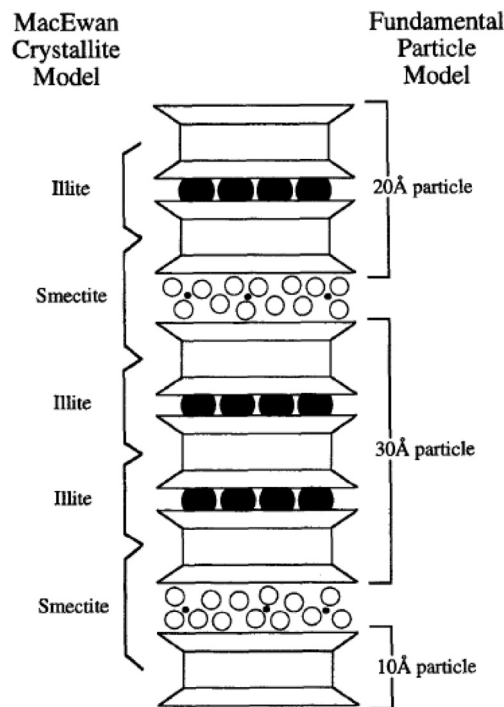


Fig. 2. Mixed-layer I–S represented as a MacEwan crystallite and as an aggregate of fundamental particles [66].

particle model. As such, it has become more common than the Markovian model and is adopted here.

The smectite illitization process is slow but systematic due to the lower energy barrier, compared with kaolinite illitization which involves a higher energy barrier and requires an external source of K^+ to occur [61]. Smectite illitization is the most important clay mineral reaction when studying the diagenesis of sedimentary rocks and is often used as a geothermometer [82]; W.-L [75,76]. It has been observed in several natural systems and laboratory experiments [83]; D. [84]; D. D. [85]; D [65]. The laboratory experiments are often set up to mimic the processes postulated to have caused illitization. As such, a brief look at the natural occurrence of illitization is needed to understand the choice of experiments.

3.1. Natural occurrence of illitization

Illitization has been observed in several geologic formations. In the Gulf coast [72], showed the progressive formation of I–S from smectite with depth of burial. Similar observations were made by Ref. [86] for lower cretaceous shale in British Columbia and [87] for the east Slovak basin. D [88], reported that Gulf Coast smectite illitization occurred at 150 °C.

Other authors focused on modeling the kinetics of the illitization process in geological reservoirs [61]. modeled illite as muscovite mica to understand the control factors of illitization. They studied the model reactions in marine sandstone/shale formations between 50 and 200 °C. They reported that organic matter maturation could also influence the reaction rate by increasing the Gibbs free energy of the illitization. Their results illustrated the importance of the sequence of timing of geological processes on the formation of illites [68]. chose to describe their I–S series using a two-step reaction model, because a one-step reaction model could not fit data from different wells. They used the difference of ordering in splitting the series into distinct units of ordered and un-ordered I–S layers. The first reaction involved the disordered I–S layer, while the second reaction (ordered I–S) proceeded based on the result of the first. The kinetic model they obtained showed the stronger dependence on time than on temperature [68]. Their rationale for using a two-step reaction was because the one-step model was unable to fit the smectite data (from XRD) used to derive the reaction model. Additionally, they posited that the presence of distinct crystalline forms and a change in the illite component within a smectite-illite sequence supported the existence of two-step reaction sequence [89,90].

[91] studied illitic clays from seven North American bentonites and three North Sea sandstones. The samples were examined by XRD, TEM, and Scanning Electron Microscope (SEM) and found varying levels of illitization. While the bentonite clays were both randomly and regularly interstratified, the sandstone illites were all regularly interstratified. They explained their observation based on a dissolution of smectite and precipitation/growth of illite particle theory. Their experiment showed that I–S found from different deposits, where shales and sandstones had different composition trends. This was confirmed by Refs. [92,93]; and [94]. [92] explained that these compositional differences lead to differences in reaction kinetics.

In summary, an experiment to study illitization should involve subjecting the samples to high temperatures (150–200 °C) for long time. Local variations of the smectite and cations in pore fluid are also significantly affecting the illitization of smectite. These findings have influenced the design for the published experimental studies of illitization.

3.2. Experimental observation of illitization

Several hydrothermal reaction experiments have been conducted to mimic the natural formation of I–S. They each focused on specific problems.

- conversion rates [88],
- the effect of interlayer cations (D. [95],
- octahedral substitution [96],
- tetrahedral substitution (Huang and Otten, 1987),
- solution chemistry [97],
- kinetics of layer charge development [98],
- kinetics of illitization [77]; D. [65,99,100]; W.-L. [68,75,76,101],
- importance of temperature on illitization [67].

In all of these experiments, understanding the reaction kinetics

of illitization is paramount. This is because, several uses of bentonite in engineered systems rely on adequate knowledge of the onset of illitization and the factors affecting it. Factors such as temperature, time, salinity, and solid-liquid ratio have all been studied in illitization experiments.

[65] conducted hydrothermal experiments on beidellite to determine the reaction rate of smectite illitization. They concluded that the illitization rate follows first-order kinetics. This model has been found to be inadequate in modeling field observations because the illitization of synthetic smectite was found to be much less than that of natural smectite [88]; W.-L [76]. Consequently [75], proposed a sixth-order kinetic equation based on field studies. They observed mixed layer I–S minerals composed of 80% illite which had been subjected to temperatures between 70 and 250 °C for ten years to 300 My. Because the completion degree of illitization was not 100%, considering the time involved, they suggested that illitization was kinetic-controlled and not equilibrium-controlled. This agreed with the Ostwald step rule proposed by Ref. [65]. Their model was first order with respect to the pore fluid activity ratio (e.g. K^+/Na^+), and fifth order with respect to the smectite mole fraction, respectively. They stated that the sixth order model had little or no physical-chemical significance and that the actual kinetic law was likely of a lower order [75]. Notwithstanding, the sixth order equation has been widely used for modelling natural smectite illitization [99].

[76] derived an experimental model by subjecting Na-saturated Wyoming bentonite under the temperatures of 250–325 °C at 500 bars of pressure. The bentonite was saturated with 0.1 M–3 M KCl solutions. Their results show that both Ca^{2+} and Mg^{2+} retard illitization, with Mg^{2+} being a more dominant retarder. TEM study showed morphological changes in the smectite like those reported by Ref. [102] in natural hydrothermal environments. They assumed a concentration of K^+ in reservoir brine and used their model to predict the extent of smectite illitization in several basins of different depths and ages.

Interestingly, neither of these three models (W.-L [68,75,76], had the same forms or parameters. To test their versatility and general utility [100], used them to calculate the timing and extent of illitization in four distinct environments (Denver Basin, Gulf Coast, the Salton Sea Geothermal System, and Paris Basin) with significantly varying ages, geothermal gradients, and K^+ activities. None of the models was successful in all four basins, further reiterating the need for customized characterization and modeling for distinct smectites [100]. echoed the importance of temperature and K^+ in the illitization, but critiqued the lack of consideration for Al, Si, pH, and the dissolution of K-feldspar in the systems.

[73] investigated the illitization by subjecting smectites to 250–400 °C temperatures, saturated with 1 M KCl solution at a solid/solution mass ratio of 1:10. The reactions lasted between 5 and 120 days. TEM data showed a progressive replacement of expandable layers into illite with diverse corresponding changes in morphology, interlayer K content, and Al for Si substitution [73]. In both the experimental models and natural systems, illitization appears to be controlled by temperature, pressure, time, and chemical conditions [73].

However, experimental studies have shown that it was dependent on multiple factors such as solid to liquid ratio, pressure, pH, di- or tri-octahedral nature of the smectite, K^+ availability and time. By varying these, several experiments have succeeded in creating illite in the laboratory [67]; D. [103]; D. [65,73,104]; W. L. [105]; W.-L [70,76,106]. One aspect that is not fully answered is the question of the exact temperature at which illitization occurs. The studies of [107–109] have shown that illitization was possible even at room temperature, contrary to earlier studies which opined it occurs at >100 °C. Similar observations were made by Ref. [67] who observed

illite in batch reactors of beidellite at 35–80 °C. However, most nuclear repository designs still assume 200 °C as the temperature for studying the effects of illitization on engineered barrier systems [110].

3.3. Mechanisms of illitization

Fundamental phenomena of illitization of smectite are not fully understood yet, such as the effects of temperature, time, and K^+ content on the rate of illitization, the stoichiometry of the transformation (conservation likelihood of aluminum), and the mechanism of the transformation [64,100]. The mechanism of illitization is important, because it determines how the reaction can be modeled. It dictates the thermodynamic relationship between minerals and the detailed reaction kinetics (D. D. [78]; D. D [111]. Several mechanisms of illitization have been proposed from the previous researches [112].

- (1) solid-state transformation (SST) [83,99,101,113–117],
- (2) dissolution and crystallization (DC) [77,118]; D. D. [62,71,78,81,91,119–124], and
- (3) Ostwald ripening (OR) [125].

Fig. 3 below illustrates these three mechanisms.

SST involves a layer-by-layer solid state replacement of smectite with illite. The process occurs in close topotactic contact with fluids acting as catalysts and transport media for the process [83]. Because it is a gradual process, one expects gradual changes in mineralogy, crystal structure, and chemical composition [83]. They are characterized by small scale changes in the order of 1 nm, which may be detected by TEM, analytical electron microscopy, and electron diffraction [83]. It is readily seen through XRD as a series of interstratified phases of I–S [77,100]. Studies that have observed SST often do so in low permeability environments such as bentonite [62,99,126,127], shale and bentonite [114], and mudstone [117,128]. In their studies, the authors reported the compositional data

showing that illite layers formed in earlier steps were conserved, gradual change in I–S interlayer ordering and the absence of morphological changes due to illitization [129]. [83] studied the mixed layer I–S in 28 diagenetic North American and European bentonite samples. By integrating XRD analysis is of polytype, chemical, thermal, morphological (atomic force microscopy), and oxygen isotope analysis, they found the illitization occurred via SST. The strongest indication of this was the absence of morphological changes. However, they observed significant lattice restructuring, albeit in a less systematic and less extensive way as would be typical of a DC mechanism.

In the second mechanism, smectite is changed to illite via a dissolution-precipitation process in which fundamental smectite particles are transformed to fundamental illite particles [130,131]. This involves the progressive dissolution of smectite in the reaction front while the new phase is precipitated *in situ*. Other authors posited that DC occurs via an Ostwald ripening process (D. D. [85]; D. D [78,132]. The fundamental particle changes in both DC mechanisms require TEM to be visualized. In DC, the smectite is completely dissolved followed by the precipitation of I–S or illite with the smectite and illite particles existing separately. Consequently, there are significant changes in clay structure and texture as the structural memory of the original smectite is lost [83]. DC mechanisms are believed to occur in high permeability environments such as hydrothermal systems, because liquid is required for dissolution [125,133–135]. [73] stated that the actual illitization mechanism was a DC process following an Ostwald step rule with intermediate metastable I–S phases. Table 1 below summarizes the differences between the stated mechanisms.

In summary, most authors now agree that more than single process is possible as controlled by rock permeability which is likely to change during high temperature illitization [127,133,135–138]. [73] explains that in the early stages of dual mechanism illitization, K^+ sorption and fixation occurs in the interlayer of smectite leading to R0 structure due to an increase in layer charge [139]; D. [103]; D [70,101,104,106,121,140,141]. In later time, ordering is changed to $R \geq 1$ by a continuation of the first reaction [106,121,140,141]. Alternatively, the loss of swelling could lead to improved permeability and flow of fluids to promote the smectite dissolution and precipitation of ordered I–S [70,71,73]. [85] proposed a similar dual mechanism in which I–S transitions from SST to DP with depth in the Gulf of Mexico. For hydrothermal I–S from Japan [102], described SST by K-fixation, followed by DC, and then OR [66]. However, OR has been discarded as an illitization mechanism [142,143].

4. Illitization in engineered barrier systems (EBS)

4.1. EBS for nuclear waste disposal

Countries using nuclear power face the challenge of nuclear waste disposal. To safely dispose nuclear waste, repositories are designed to completely isolate the waste from the biosphere, while slowing down any release of radionuclides for hundreds of thousands of years in the event of a failure of the barrier [5,144]. To fulfill these functions, wastes are emplaced in Deep Geological Repositories (DGR).

DGRs are engineered structures between the depth of 200 m and 1,000 m [4]. Minimum depth ensures that it is not impacted by erosion depending on the environmental conditions and disposal concept, while burial beyond 1,000 m is uneconomic. DGRs are designed to ensure that there is no impact on the background levels of radioactivity in the disposal environment for geologic time. To fulfill the critical isolation role, DGRs incorporate a system of natural and engineered barriers known as the multibarrier approach,

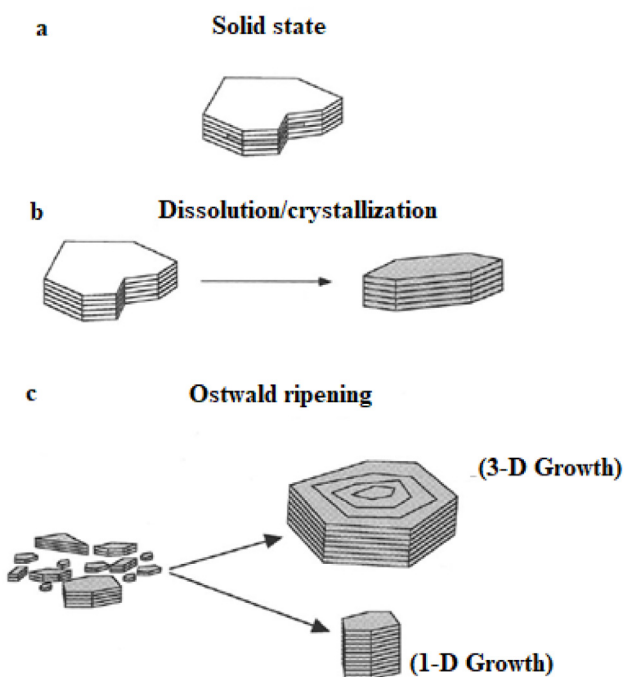


Fig. 3. Different mechanisms for the hypothetical illitization. (a) Solid state transformation. (b) Dissolution and crystallization/precipitation. (c) Ostwald ripening [66].

Table 1
Typical trends of different illitization mechanisms [66].

Mechanism	Chemistry	Texture	Crystal structure
SST	Gradual chemical changes proportional to extent of illitization	<ul style="list-style-type: none"> No major change in size and shape of platelets Smectite interlayers may grade laterally into illite interlayers. 	Gradual structural changes (interlayer ordering and polytype)
DC	Permits abrupt chemical changes.	<ul style="list-style-type: none"> Permits formation of euhedral crystals. Smectite crystals can be physically separated from illite crystals. 	Permits abrupt structural changes between parent and child crystals.
OR	Constant chemical composition for overgrowth and template	<ul style="list-style-type: none"> Permits formation of euhedral crystals. Crystal coarsening 	Permits abrupt structural changes between template and overgrowth.

which is illustrated in Fig. 4 [4,145].

The multiple barrier concept is the basis of geological disposal of radioactive waste and is implemented in some repository concepts [146,147]. Different countries have unique designs of how the multibarrier is set up [1,144]. It involves the combination of natural and/or engineered barriers to provide containment and radionuclide retardation. The stability of the barrier significantly depends on its weakest link or component [148].

The natural barrier system (NBS) is comprised of the host rock (usually crystalline or argillaceous rock), which is the geologic formation hosting the DGR. In the US, several shale or argillite basins with adequate disposal options have been identified [149,150]. The engineered barrier system (EBS) includes the solid matrix of the nuclear waste, the metallic canister surrounding the waste, and the backfill/buffer placed around the canisters to seal any cavities that may form in the future [4,151,152]. The material used for each component is selected based on several factors including the geological setting, the interactions between the natural host rock and EBS materials, the heat generation by the waste, interaction of materials with ionizing radiation, materials corrosion, materials degradation due to microbial activity, and the potential of materials to generate gasses because of irradiation, corrosion, or microbial activity [4]. The main objectives of the EBS are [147].

- to reduce corrosion rate of canisters,
- to limit hydraulic flow and transport,
- to limit the radionuclide migration from the waste-form to the far-field (biosphere).

Firstly, corrosion of canister must be considered. Ideally, the EBS canister should be made of noncorrodible material such as gold or platinum, but due to the economic feasibility, other metal canisters like stainless steel, carbon steel, copper, titanium, and nickel alloys are generally preferred for EBS canisters [4,144]. When metals are selected for canisters, knowledge of their corrosion across thousands of years must be ascertained [146].

Secondly, the behavior of the buffer material across expected conditions needs to be characterized. The buffer/backfill acts as both a physical and a chemical barrier to radionuclide migration [147]. The buffer material controls hydrochemistry (like pH), provides stability and protection for the waste, and limits radionuclide migration. The materials are designed to fill any voids that may arise in the repository [4]. For low and intermediate level wastes, the buffer may be made of porous cement, which is designed for extended pH-buffering, positive corrosion protection especially for mild steel, and its ability to immobilize radionuclides [147,153]. However, the high pH could be a disadvantage particularly due to the degradation of the buffer smectite at high pH [153].

For high level waste, the buffer is made up of compacted expansive clay, typically bentonite or a mixture of bentonite and sand, because of the bentonite's high swelling capacity, low permeability, high adsorption capacity, and radionuclide retardation properties [144,154,155]. The major challenge with using bentonite is the potential loss of its swelling properties when it is heated. Under high temperature and K^+ concentration, the bentonite might transform into illite [144]. While illite is a strong adsorbent for radionuclides like Cesium, it swells less than the parent smectite [63]. Recent modelling studies have confirmed that temperatures as high as 200 °C may affect the swelling stress via

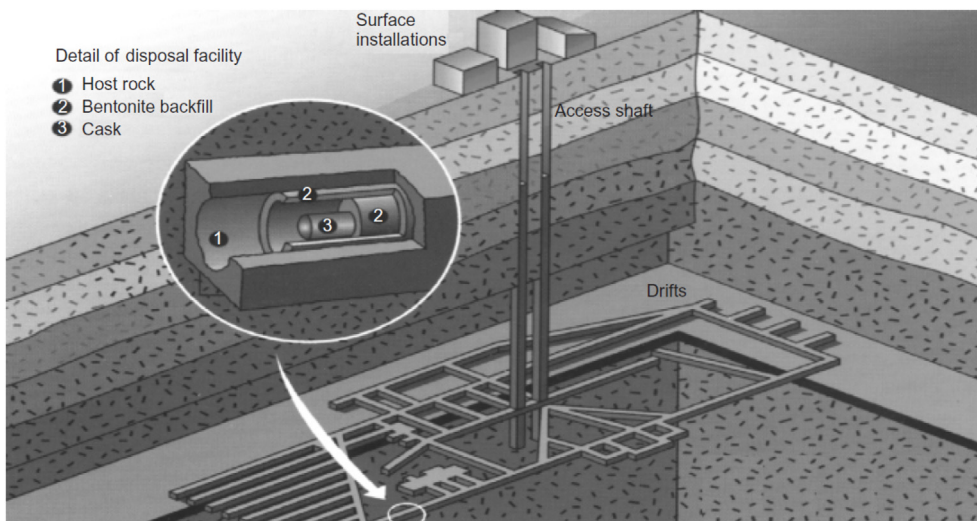


Fig. 4. Conceptual schematic of a deep geological repository for high level nuclear waste [12].

illitization [110,156,157]. Such repository temperatures would result from the continuous expulsion of heat from the radioactive waste. In a recent study [156], states that the buffer material should be engineered to control the peak temperature for thermal management to limit heat transfer to the far-field rock. This can be achieved by mixing the bentonite with graphite or graphene oxide (Y.-G [158]. Hence, understanding the different physics occurring as well as their impacts on bentonite swelling are crucial for the safety assessment of DGRs [155].

4.2. Use of bentonite for EBS buffer

Bentonite and bentonite/sand buffers are selected primarily for EBS systems because their low permeability ensures that the dominant transport mechanism of fluid in the barrier would be diffusion, with little or no advection [5]. Additionally, they possess self-sealing, high swelling, high cation exchange capacities, and redox (reducing) properties [4,5]. This is due to the large proportion of montmorillonite in bentonite which is both expansive and active in ion exchange [4]. The swelling property is especially crucial as bentonite is often used in blocks, pellets, or plinths depending on the repository design [4,159]. Upon saturation, the bentonite swells causing high pressure (or strain depending on the confinement conditions) that reduces the permeability and hydraulic conductivity to diffusion-dominant levels. Bentonite should swell enough to impede flow of radionuclide or water but not to a swelling pressure that would jeopardize the safety of the repository [160]. Experimental studies indicate that for various bentonites, conductivities range from 10^{-13} – 10^{-14} m²/s [4,161].

In addition, the high cation exchange capacity of bentonite enables it to exchange mobile radionuclides and adsorb them in its pores which significantly retards mobility [4]. Radionuclides may be held on bentonite through adsorption, surface precipitation, surface cluster formation, coprecipitation, or diffusion into an existing mineral structure [1]. Usually, bentonite adsorbs the cations either by ion exchange at permanent sites or by surface complexation [1,35]. Over the operation of the repository, the bentonite barrier must retain this radionuclide adsorption and swelling capabilities [162,163]. They should be retained irrespective of several thermo-hydro-mechanical-chemical (THMC) phenomena that may occur. The performance of the bentonite under these phenomena must be understood for adequate prediction of the long-term safety of the geological repositories.

Consequently, several studies have characterized the diverse bentonites for use in engineered barrier systems [164–168]. Impacts of the brine salinity and cation content on its swelling and physicochemical properties have been studied [155,169,170]. [171] reported swelling pressure of 1500 kg/m³ MX-80 bentonite dropped by 75% when the ionic strength of saturating NaCl was increased from 0 M to 3 M, while it dropped by only 40% when it was saturated with CaCl₂ for similar conditions.

Furthermore, temperature affects the rate and quantity of illitization. In bentonite buffers, temperatures less than 100 °C are recommended for long term stability [3]. The temperature distribution would depend on the rock properties, rate of heat generation from the nuclear waste radiation, and the design of the repository. To minimize thermal degradation, the bentonite buffer needs to have a thermal conductivity, which is high enough to rapidly conduct the heat to the host rock [172]. Based on their modeling scenarios [110], showed that illitization led to 1–8% loss in smectite mass fraction at 100 °C, and 1–27% at 200 °C, respectively. Thermal pressurization also led to higher stresses in the case of 200 °C, compared with the case of 100 °C. The simulations were run for 1000 years using Kunigel-V1 bentonite (pH of 8.40) as the buffer material and the Opalinus clay (pH of 7.40) as the host rock.

However [173], concluded that the 100 °C limit often used in repository designs was over-conservative. They found no significant changes in the hydraulic properties even at 120 °C.

[14] warned that laboratory and mockup test results needed to be taken with caution, because the conditions deviated significantly from actual repository conditions. They were critical of the timing of re-saturation versus maximum temperature, water availability, and mechanical constraints in the experiments. In their summary, they stated that.

- Chemical change of EBS bentonite is complex with debatable implications.
- Illitization and the corresponding change in swelling capacity were inconclusive from studies.
- Long-term high temperature experiments will be required to fully understand the role of illitization in EBS and the impacts of the countless variables influencing it.

4.3. Laboratory and field scale studies of EBS illitization

Several laboratory and repository scale experiments have been performed to understand the behavior of the bentonite EBS under several THMC processes. Results from them have greatly improved simulation tools for the application in these days [174]. Some studies have explored the impact of salinity on compacted bentonite swelling [175–178]. They reiterated the change in swelling properties of bentonite due to the chemical reaction with the swelling pressures decreasing with an increase in pore water salinity [179]. Heated clay samples for one year after saturating the samples with varying solutions: initially distilled water, 10,000 ppm of CaCl₂ solution, and 50% artificial ocean water respectively. They found that K- and Na-feldspar dissolved slightly at 130 °C but were completely dissolved at 200 °C, the hydraulic conductivity increased 2–3 orders of magnitude, while the swelling pressure was unchanged [122]. Observed no chemical alteration after heating Ca- and Na-smectite at 150 °C for two months. The saturating solutions were comprised of 0.01 M NaOH (pH 12), 1 M K₂CO₃ and mixtures of 1 or 3 M KCl with 10^{-4} or 10^{-2} M KOH [155]. Found that exposure to the ground water in outer Ontario (with a total dissolved solid of 300 g/L) and temperatures of 23 °C, 40 °C, and 80 °C was sufficient to affect the swelling ability of MX-80 bentonite. Even the surface area, pore diameter, and pore volume significantly decreased after the reaction. They stated that temperature alone was not significant, but that the loss in swelling was correlated with the changes in the water chemistry.

The problem though is that laboratory conditions are often ideal, sometimes closed, and unrepresentative of the geological repository conditions. To reduce the gap, several underground research laboratories have been constructed: the Opalinus clay rock at the Mont Terri rock laboratory in Switzerland (1987); the Tournemire site in France (1996); the Callovian–Oxfordian clay rocks at the Centre de Meuse- Haute-Marne site in Bure, France (2004); and the Boom clay rock at Hades, Mol site in Belgium (1980) [148]. Most of them started as part of the DEvelopment of COupled models and their VALidation against EXperiments (DECOVALEX) in nuclear waste isolation project [180]. Recently, three principal projects are ongoing in Europe: Mont Terri in Switzerland, Centre de Meuse-Haute-Marne in France, and Hades at the Mol site in Belgium [148,181]. Various tests are regularly conducted at these sites including the Engineered Barrier experiment conducted at the Mont Terri underground laboratory and Full-scale Engineered Barrier Experiment (FEBEX) test performed at the Grimsel Test Site prior to its dismantling in 2015 [182]. Such tests provide direct observation of EBS THMC behavior and realistic data for validating

diverse simulators.

FEDEX project is an EBS demonstration project based on the Spanish reference concept for nuclear waste disposal. It includes two large-scale tests: the in-situ Grimsel test in Switzerland and the CIEMAT mock-up test in Spain [183]. It started in 1997 and was the first long-term full-scale experiment with thermo-hydro-mechanical variables recorded ever since [184–188]; X [150,189]. Similar experiments have been conducted over the years including in-situ heating experiment (HE-E experiment) since 2011 in Mont Terri; ATLAS experiment in the Mol rock laboratory; the TER experiment at the Bure site; and the HE-D experiment in the Mont Terri underground research laboratory in Switzerland FEDEX; the Prototype Repository experiment in Äspö rock laboratory in Sweden; and the Full-Scale Emplacement Experiment in the Mont Terri laboratory [190]; X [189]. At Mont Terri alone, over 138 individual experiments have been conducted between 1996 and 2016 but almost none has focused on illitization [151].

[14] warned that laboratory and mockup test results be taken with caution, because the conditions deviate significantly from actual repository conditions. They were critical of the timing of re-saturation versus maximum temperature, water availability, and mechanical constraints in the experiments.

5. Summary and conclusion

For the safe disposal of nuclear waste using EBS, bentonite buffer is used because of its high swelling capability and low hydraulic conductivity. Illitization of bentonite involves the chemical alteration of expandable smectite into non-expandable illite. This paper provides a thorough review to provide the concise and summarized information underlying in the illitization of bentonite, by covering basic clay mineralogy, expandable smectite, mechanisms and observation of illitization, and illitization in EBS. Understanding of smectite illitization is considered critical for the safe design of nuclear waste disposal systems using bentonite buffer, and this thorough review study is expected to provide detailed information for the considerations to be made in safe EBS design.

Based on the study, the concluding remarks can be made as follows.

- The process of smectite illitization is caused by the fixation of K^+ ions within the interlayer of smectite. This creates a covalent bond between the K^+ and the Oxygen in the interlayer. This makes illite to be of lower swelling potential than the original smectite.
- Illitization is not entirely disadvantageous. While illite is a lower swelling clay, it is a very strong adsorbent for radionuclides, particularly Cesium.
- There is a consensus that illitization proceeds either by a solid-state transformation or dissolution-recrystallization process. In models however, the dissolution precipitation approach is used for implementation.
- Data for reaction models of illitization are often based on experimental values. While there are large scale field trials of various EBS concepts ongoing, no data has been provided concerning the transformation of smectite to illite. There is concern that this may be because of field trials lasting for relatively short time.
- A major concern in illitization modelling is the source of K^+ for the transformation. Most authors have assumed it comes from K-feldspars within the bentonite. Few authors have treated it as being sourced from the groundwater imbibing from the host rock.
- Illitization is dependent on multiple factors. While most studies have focused on temperature and time, others have revealed

that the chemistry of saturating solution, as well as the specific bentonite are also crucial. The consensus is that temperatures above 200 °C are required. However, studies have reported illitization at much lower temperatures (<50 °C). Hence, temperature is not by itself a conclusive factor in determining illitization. As such, it is highly recommended that adequate characterization be conducted for each bentonite to be used as generalization might be misleading.

Author contributions

Lotanna Ohazuruike: Investigation, Roles/Writing – original draft.

Kyung Jae Lee: Funding acquisition, Project administration, Resources, Software, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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