

# INTRODUCTION TO THE PROPERTIES OF CLAY MINERALS

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Required materials: montmorillonite, balance, 7 beakers (150 ml), saturated solutions of NaCl, MgCl<sub>2</sub>, and CaCl<sub>2</sub>, squeeze bottle with pure water, ring stand, 1" glass (or Plexiglass) tube, stirrer, rubber stopper with hole for glass tube, 1 large beaker (800 ml), cotton balls, tweezers, quartz sand, funnel, watch with second hand, methylene blue

## INTRODUCTION

"Clay refers to naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when fired or dried." The minerals found in clay are generally silicates less than 2 microns (one millionth of a meter) in size, about the same size as a virus. Clays are very abundant at the earth's surface; they form rocks known as shales and are a major component in nearly all sedimentary rocks. The small size of the particles and their unique crystal structures give clay materials special properties, including cation exchange capabilities, plastic behavior when wet, catalytic abilities, swelling behavior, and low permeabilities.

Clay minerals are used as coatings on paper to produce whiteness and to allow the proper absorption of ink, to extend the life of rubber in tires, in concrete, as catalysts in many industries, to purify oils, in pharmaceuticals, in the ceramic industry to make bricks, chinaware and porcelains, and in many other industries and processes. Clay minerals, and specifically montmorillonite, are used as clay barriers for nuclear and chemical wastes because of their cation-exchange capabilities, low permeability, and long term structural stability.

To understand cation exchange capability, it is necessary to learn a little about the crystal structure of clay minerals in general and montmorillonite specifically. Cation exchange affects the mechanical and physical properties of the clay. The purpose of this laboratory is to illustrate the importance of chemistry on the physical properties of montmorillonite, the clay mineral most often used to isolate dangerous waste materials from the environment.

## STRUCTURAL ASPECTS

Clay minerals are commonly phyllosilicates or layer silicates. These minerals have platy morphology because of the arrangement of atoms in the structure. There are two basic components to the structure: a sheet of corner-linked tetrahedra and a sheet of edge-sharing octahedra. Figure 1 illustrates the linkage of atoms to form both tetrahedra and octahedra, whereas Figure 2 illustrates the linkages of each to form the two varieties of sheets.

**Tetrahedral sheets.** The dominant atom in the tetrahedron is the  $\text{Si}^{4+}$  cation, but the  $\text{Al}^{3+}$  cation can occur also at this site. This is an important point, because the substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  produces a charge deficiency that must be balanced somewhere else in the structure. We will return to the concept of charge deficiency below, although in a somewhat different sense involving octahedra.

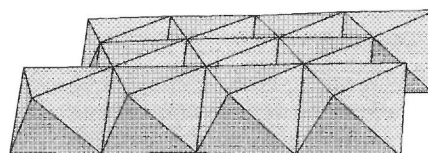
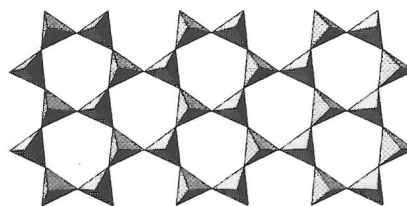
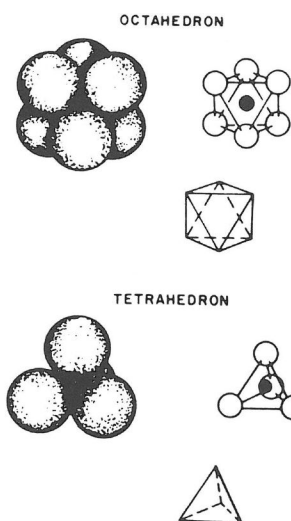
Note in Figure 2 that the tetrahedra link up to form a sheet by the sharing of three corners of each tetrahedron. For each corner that is shared between two tetrahedra, only one oxygen is involved in the linkage. Compare this to the two oxygens involved in two individual tetrahedra. Thus, it takes fewer oxygens to complete a sheet of tetrahedra compared to the same number of individual and unlinked tetrahedra. If we add the number of oxygens around each tetrahedron by "dividing" up an oxygen linking two tetrahedra (so each tetrahedron then has one-half an oxygen), then there are two and a half oxygens per tetrahedron (or 10 oxygens per 4 silicon atoms). Because the O atom has a 2- charge, then a tetrahedral sheet with  $\text{Si}_4\text{O}_{10}$  composition will have an overall charge residual of 4- ( $4 \times 4^+ = 16^+$  vs  $10 \times 2^- = 20^-$ ). Because the overall structure must be charge neutral, another part of the structure, the octahedral sheet, must compensate or compensate in part for this charge residual.

**Octahedral sheets.** The octahedral sheet is composed of edge-sharing octahedra. Different phyllosilicates have different cations in the octahedra. For phyllosilicates with relatively high-charged, trivalent cations (e.g.,  $\text{Al}^{3+}$ ) in the octahedra, it is required that for every two octahedra that contain  $\text{Al}^{3+}$ , there is an empty octahedron. The pattern of  $\text{Al}^{3+}$  and vacant sites is illustrated in Figure 3, and is referred to as a "dioctahedral" sheet. Alternatively, a "trioctahedral" sheet forms where all three sites are occupied, which occurs for octahedra occupied by divalent cations (e.g.,  $\text{Mg}^{2+}$ ). Many phyllosilicates contain a small number of divalent cations in a dioctahedral sheet (e.g.,  $\text{Mg}^{2+}$  substituting in small amounts for  $\text{Al}^{3+}$ ) or, conversely, a small number of trivalent cations in a trioctahedral sheet (e.g.,  $\text{Al}^{3+}$  substituting in small amounts for  $\text{Mg}^{2+}$ ). Where this happens, a small deficiency in charge occurs that must be compensated elsewhere in the structure. As noted above, similar charge deficiencies can develop in the tetrahedral sheet as well.

Nearly all phyllosilicates have hydroxyl ( $\text{OH}^-$ ) ions involved in the linkages to form sheets, in addition to the oxygens. A hydroxyl ion is an oxygen atom with a hydrogen attached. The overall charge of a hydroxyl ion is 1- because the hydrogen atom has a 1+ charge and the oxygen has a 2- charge.

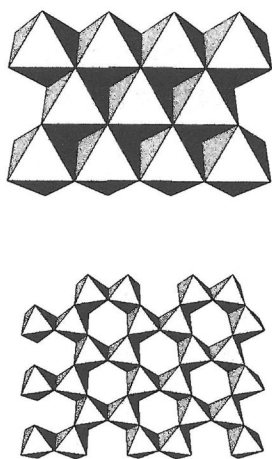
**Layers.** The tetrahedral and octahedral sheets may be considered modular components of a phyllosilicate. It is now necessary to join the two sheets. The lateral dimensions of the two sheets are approximately equal so it is possible to join them together. As we found with the tetrahedral linkages to form the tetrahedral sheet, it takes fewer oxygens to complete the linkage than if we had two individual sheets, because there is a common junction between the two. This common junction is a plane of oxygen and hydroxyls that belongs to both the tetrahedral sheet and the octahedral sheet (Figure 4). For the case of montmorillonite, there are two tetrahedral sheets, inverted relative to each other, and with an octahedral sheet sandwiched between. Thus, some of the oxygens that belong to the tetrahedral sheets also belong to the octahedral sheet. Only the hydroxyl ions do not link directly to the tetrahedra.

REPRESENTING COORDINATION POLYHEDRA

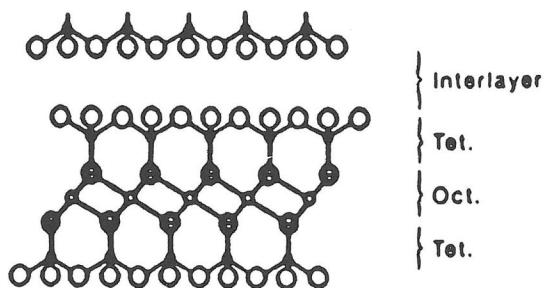


**Figure 1.** Examples illustrating several ways to represent coordination octahedra and tetrahedra. The large spheres are usually oxygen atoms enclosing a "site" where smaller cations may reside. (Figure courtesy of K. Rodolfo)

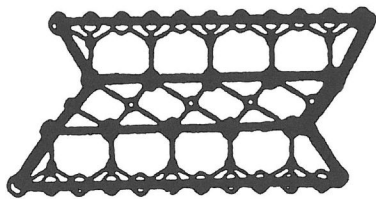
**Figure 2.** Tetrahedra may be linked through a corner oxygen to form a tetrahedral sheet and octahedra may be linked by edge sharing to form an octahedral sheet. (The two sheets have different scales.)



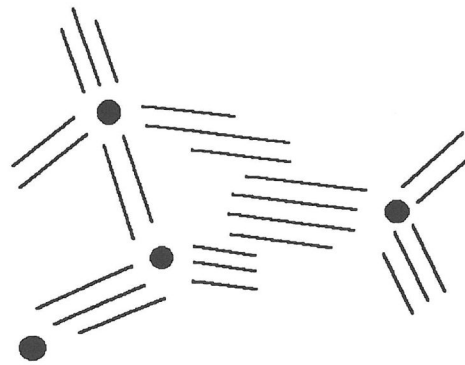
**Figure 3.** Octahedral sheets occur as either trioctahedral (top) or dioctahedral (bottom), depending on whether a vacant site occurs or not. (The two sheets have different scales.)



**Figure 4.** A layer is illustrated in side view. The octahedral sheet is sandwiched between two opposing tetrahedral sheets. (after Koster van Groos and Guggenheim, 1990)



**Figure 5.** Illustration simplifying the sheets for easy drawing. Note the modular components as indicated by the dark lines.



**Figure 6.** Schematic showing how  $\text{Cl}^-$  ions (solid circles) can cause flocculation by adhering to broken (external) edges of clay particles.

Although the tetrahedral and octahedral sheets extend laterally over many hundreds of Angstroms (an Angstrom is  $10^{-8}$  cm), we can simplify the drawing of the layers by using finite widths, as in Figure 4. In turn, we can simplify these representations even further by drawing modular units that represent tetrahedra and octahedra (Figure 5) and by leaving out the circles and lines that represent the atoms and bonds (not illustrated). As long as we understand and agree to this drawing as a representation of the structure, then we can use these diagrams as a convenience.

**Charge balance and the layer.** Assuming for simplicity that we do not have any substitutions in an aluminous dioctahedral layer when the tetrahedral cations, octahedral cations, oxygens, and hydroxyl groups are all taken into account, the resulting chemical composition of the layer is  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ . If we examine the charges for this layer we find that there is complete charge balance (e.g., for positive charges:  $2 \times 3^+ + 4 \times 4^+ = 22^+$  vs for negative charges:  $10 \times 2^- + 2 \times 1^- = 22^-$ ). A phyllosilicate of this composition is known in nature and is called pyrophyllite.

The composition of the layer in montmorillonite, however, is less ideal, with chemical substitutions of a small amount of Mg for Al in the octahedral sites. Thus, the layer has a composition close to  $(\text{Mg}_{0.4}\text{Al}_{1.6})\text{Si}_4\text{O}_{10}(\text{OH})_2$ , where 0.4 Mg has substituted for some Al in the octahedral sites (compare the layer chemistry to that in the preceding paragraph). If we examine the charges in this layer, we find that there are 0.4 more negative charges than positive charges (e.g.,  $0.4 \times 2^- + 1.6 \times 3^+ + 4 \times 4^+ = 21.6^+$  for positive charges vs  $10 \times 2^- + 2 \times 1^- = 22^-$  for negative charges). This may not seem like much to you, but it makes a world of difference in the behavior of montmorillonite compared to other phyllosilicates. All crystal structures must be charge neutral. Thus, the net negative charge of 0.4 on the layer must be compensated, and montmorillonite does this by having positively-charged material (and  $\text{H}_2\text{O}$ ) between the layers. This region is called the "interlayer" space (Figure 4).

**Interlayer material.** It does not really matter what is in the interlayer, as long as it is positively charged and atomic or molecular in size. Thus, it is possible to place cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , or  $\text{Mg}^{2+}$  in the interlayer, or even organic molecules. Often, depending on the nature of the cation, polar  $\text{H}_2\text{O}$  molecules enter the interlayer. For example, copious amounts of



H<sub>2</sub>O go into the interlayer with Na, whereas many fewer H<sub>2</sub>O molecules enter the interlayer with Ca. Overall charge balance is always maintained, however, because H<sub>2</sub>O is neutral. Also, charge balance is maintained with the number of cations entering the interlayer space, as in the case where half as many Ca cations enter the interlayer than Na, because the charge on Ca is twice that of Na. In addition, it is fairly easy to replace interlayer cations with other material, as long as there is a large amount of that material in the immediate environment. For example, an aqueous (water) solution containing many Na cations around a montmorillonite grain will readily allow for Na to exchange for K, if K is in the interlayer. Therefore, these cations are often called "exchangeable cations". The fact that exchangeable organic molecules can enter into the interlayer explains why montmorillonite is useful to purify oils, since oil contaminants with a positive charge will enter the interlayer. However, non-polar and neutral oil contaminants may not enter the interlayer very readily.

To understand how cation exchange works, it is necessary to define "internal" vs "external" surfaces of a clay particle and to determine how they attract cations and anions. The internal surfaces are the two planes of atoms on either side of the interlayer space at the base of the tetrahedral sheet. External surfaces are the broken edges of the layer. Because there are no broken bonds on the internal surfaces and the negative charge on the layer originates well within the layer (at the octahedral sheet), the internal surfaces attract cations and other positively charged particles. In contrast, however, the external surfaces generally attract negatively charged anions because the cations (e.g., Si<sup>4+</sup>, Al<sup>3+</sup>) closest to the broken surface within the clay require the negative charge to compensate.

Cation exchange is most readily achieved by dissolving a salt in water so that the cation dissociates from the anion. Thus, for example, NaCl will dissociate to form Na<sup>1+</sup> and Cl<sup>1-</sup> ions in water. The Na<sup>1+</sup> is then available to enter the interlayer to replace whatever cation happens to be present, provided that the concentration of Na in solution is sufficiently high. Natural montmorillonite generally contains a mix of cations, including Na, Ca, K, Mg, Al, etc. End-member compositions (e.g., pure Na-exchanged montmorillonite or pure K-exchanged montmorillonite) have specific and unique properties, so it is useful to make different end-member composition by cation exchange.

If only Na<sup>1+</sup> is present in solution, then the individual clay particles would float freely in the water, which is called "dispersion". However, the negative anions (Cl<sup>1-</sup>) in solution attach to the external surfaces of the clay layers and cause "flocculation" or the clumping of particles (Figure 6). As the clay flocculates, it falls to the bottom of the glass or beaker.

A cation exchanged clay in a salt solution can be made to disperse by washing in pure water and removing the Cl ions (to be replaced by polar H<sub>2</sub>O molecules), since the Cl ions are only weakly bonded to the edges. Because the Na is relatively tightly bound within the interlayer, washing the clay will not affect the Na cations. Usually, it takes several washings (sometimes up to six) to remove fully the Cl. Na-exchanged montmorillonite generally requires fewer washings than other cation exchanged montmorillonites to achieve dispersion. Depending on what experiments or processes are planned, sometimes it is more convenient to work with either a dispersed or a flocculated clay.

## EXPERIMENTAL PROCEDURES

### Part I.

The purpose of this part of the laboratory is to illustrate the cation exchange capabilities of montmorillonite and the effect of cation exchange on the physical properties of the clay. We will cation exchange  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  into the interlayer of the clay.

1. Weigh 2 g. of montmorillonite and place it into a 150 ml. beaker.
2. A "saturated" solution is one in which no additional solid can be dissolved in water. Your instructor has prepared a saturated solution of NaCl. Decant (pour off just the fluid portion, making certain that no solid is poured also) approximately 30 ml. of saturated NaCl solution into the beaker with the clay (label the beaker: Clay + Na). Stir briefly for 10-15 seconds and then set aside.

Repeat the same procedure for clay +  $\text{MgCl}_2$  solution and clay +  $\text{CaCl}_2$  solution.

3. Allow each beaker to stand until most of the clay settles to the beaker bottom (about 5 minutes). The fluid may remain murky. The high chloride (Cl) content of the fluid prevents dispersion. Let's now remove the Cl ions by washing with water.
  - a. Decant the fluid from the clay--be very careful not to lose too much clay.
  - b. Add water to the clay residual so that it is at the 60 ml. level on the beaker and stir. Again, allow the clay to settle for about 5 minutes. Are there any differences between the way the Na-montmorillonite appears compared to the other two?

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- c. Decant each beaker for a second time. Again, be careful not to lose the bulk of the clay in each beaker. (It may be necessary to decant fluid, allow to settle for a bit longer, and then to decant again.) No add another 60 ml of water. Stir and allow to settle for about 5 minutes. Re-examine the clay water mixes and discuss the differences.

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4. Decant as much fluid from each clay/water mix as possible, being careful not to lose the clay.

Set the beakers containing the wet clay aside for Part II.

## Part II.

The purpose of this part of the laboratory is to examine the effect on permeability of different compositions of montmorillonite clay. We will examine the flow of water and salt water through a column of (a) sand and (b) montmorillonite + sand mix.

1. Place three or four cotton balls at one end of the glass column and use a rubber stopper with a hole to seal that end. Place the small glass tube in the stopper, so that water will be able to flow from the stoppered end without forming a reservoir. This is the bottom end. Leave the top end open. The purpose of the cotton is to allow the fluid to drip from the hole without the loss of clay or sand.
2. Place sand (enough to fill the glass column half way) in the large beaker and add water until the sand is wet. Pour off any excess water. Using the funnel, fill the column from the top end with the wet sand. It helps to tilt the column, so that the sand works its way down the side of the glass column. Use the squeeze bottle to wash the sand down the glass, but use water sparingly so that the sand does not stratify (form layers of equal size sand grains). Avoid having large (air) voids in the sand column. Fill the column only halfway. Mount the column on a ring stand, with a beaker at the column base to catch water. Allow any excess water to drip out of the column and, once the dripping stops, empty the beaker.
3. Add 50 ml. water to the column and time how long it takes to pass through the column (i.e., how long it takes to recover about 50 ml. in the beaker at the column base). The actual amount of water that is collected will vary depending on how wet the initial sand was. However, the collected amount will be approximately 50 ml. and the flow will be essentially complete.  
time = \_\_\_\_\_
4. Repeat step 3 with 50 ml of saturated NaCl solution (NOT the clay-water mix).  
time = \_\_\_\_\_
5. Remove the sand from the column and place it in the large beaker. Add water to the sand, stir, and then decant. Wash the sand in this way several times to remove the NaCl. Try to eliminate any excess water.
6. Decant the residual water from the Ca-exchanged montmorillonite from Part I. Add one-half of the amount of clay to the wet sand and stir in well. It is best to try to stir and fold the clay and sand mix by hand. It is important that you make a sincere effort to stir in the clay uniformly throughout the sand.
7. Place the clay/sand mix into the column. As before, place a cotton ball at the bottom first. Also, it is permissible to add a small amount of water to aid in getting the mix to flow into the funnel, but use water sparingly. It may be necessary to decant any excess water off the top of the column. (Do NOT allow the clay in the excess water to settle on the top of the column. Therefore, decant this excess water off.)
8. Add 50 ml. pure water in to the column top and determine the amount of time it takes to collect in the beaker at the bottom. time = \_\_\_\_\_
9. Repeat the experiment by timing 50 ml. of NaCl saturated fluid. time = \_\_\_\_\_
10. Now add 50 ml. of water to the top of the column and record the time it takes to drain. time = \_\_\_\_\_  
Empty the beaker. Repeat with 50 ml. more water. Again time the results. time = \_\_\_\_\_  
Empty the beaker before continuing. Finally, repeat a third time. time = \_\_\_\_\_

11. Add a small amount of methylene blue dye to 50 ml. of water. Add this solution to the top of the column and determine the amount of time it takes to collect 50 ml. in the beaker at the column base. What do you find?

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If time permits:

Each group of students should report the times for 50 ml. flow of saturated NaCl solution through the sand column, and times for saturated NaCl solution and three times for pure water in the sand + clay column. Discuss the possible reasons for the variations in times between each set of measurements.

Discussion after completing the experiments:

1. What was the purpose of adding water to the column in Part II, Question 10? Remember, we used Ca-exchanged montmorillonite in the experiment and added NaCl-saturated water to the column first.
2. Na-exchanged montmorillonite is found naturally and in large quantities in bentonites. Bentonites are extensive beds derived from volcanic ash (natural glass) deposits that have recrystallized as montmorillonite. This material is used in many industrial processes and for clay liners in chemical and radioactive waste disposal sites
  - a. How effective would the clay liner be if the ground water contained appreciable NaCl? ...only pure (fresh) water?
  - b. What would you have to know about the nature of the chemicals in a chemical waste dump, if montmorillonite is to be used as a clay liner. What would the effect of different chlorides have on the effectiveness of the liner?

## LOW LEVEL RADIOACTIVE WASTE DISPOSAL: DISCUSSION

Background. The Lilly Light Company was active from 1946 to 1952 in making luminescent light dials from thorium in West End Chicago, a town of about 20,000 in 1946. During this period, the company employed about 300 women, who painted numbers on the watch dials with radioactive paint. It should be remembered that this period was before the time when radioactivity was considered potentially harmful. In fact, X-ray machines were commonly used in shoe stores to determine if the shoe-size was correct by simultaneously X-raying the foot in the shoe, and radiation therapy was a common treatment for acne.

The Lilly Light Company maintained over 100 buildings in West End Chicago. Almost all were contaminated by thorium and related mine tailings. The contamination consisted generally of particles of thorium dispersed throughout large volumes of construction material. Thorium ( $^{230}\text{Th}$ ) has a half life of 80,000 years, and the general "rule" for more common radioactive waste is that disposal sites should be constructed to maintain radioactive materials for about 10 half lives. Although radioactivity from low level waste should be obviously avoided, an equally important problem is where radioactive particles become airborne as dust. Once inhaled, such particles remain trapped in the lungs to damage tissue over long periods.

In 1952 the Lilly Light Company filed for bankruptcy and was purchased by the Nosean Mining Company, as part of a larger take-over of several companies. The Chairman of the Board of Nosean considered briefly the manufacture of Nosean "Nite-glo Facial Tissues", by combining the concept of thorium-based luminescence with softness and strength, to produce a tissue that will glow in the dark on every night table in the U.S. This scheme failed to gain momentum, and Nosean concentrated its efforts elsewhere, although the company remained in control of the assets of the Lilly Light Company.

Over the years since the bankruptcy of Lilly Light, the town (now city) developed around the abandoned buildings. The buildings, which covered many city blocks, were protected by an aging chain-linked fence. The fence was routinely breached by children. The community was becoming concerned that the property had become an "attractive nuisance" for the neighborhood children and, furthermore, it was concerned about the rapidly deteriorating buildings, several of which already had collapsed roofs. In addition, the land had become an "eyesore", and property values around the area were depressed.

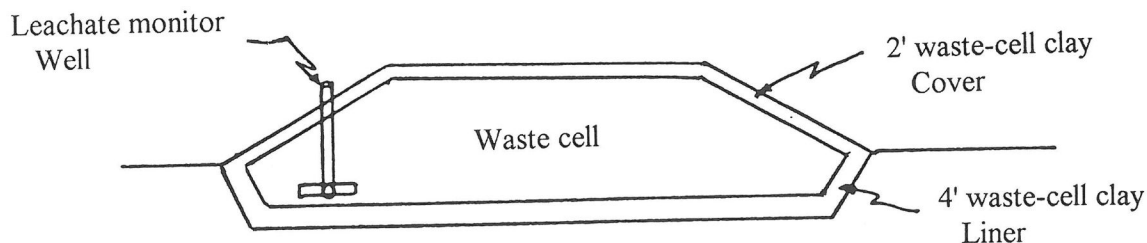
In 1978, the State of Illinois petitioned the U.S. Nuclear Regulatory Commission (NRC) to decommission the site. Because thorium production and use was involved, the NRC had jurisdiction over the site. Although the Nosean Mining Company did not gain greatly from its purchase of Lilly Light and had no involvement in the use of thorium on the site, it had legal responsibility as property owner of the land. The City of West End Chicago was involved in the litigation as an "interested party".

The NRC ordered Nosean Mining to examine the site and to suggest remediation. It was generally understood that the site would be decommissioned--Nosean did not want a long-term commitment for maintaining the site, the NRC had an ever-burgeoning number of sites in the U.S. and did not want long-term jurisdiction if an alternate approach could be found, and the City and State wanted to remove the blight so property values would rise.

Site conditions. Nosean found that the vast number of buildings were contaminated with thorium dust and particles. Contamination included building materials (wood beams, brick, etc.), soil around the buildings, and soil and clay from retention ponds apparently used in the processing and concentration of ore. By 1981, Nosean workers were ordered to wear protective suits to avoid contamination, and the old fences were replaced with newer chain-linked fences. Warning signs were placed around the site. There was concern that as contaminated buildings collapsed and deteriorated further, more thorium particles would be exposed to wind and rain, thereby spreading to areas away from the site. There was some evidence that this had already happened. However, thorium migration downwards to the water table under the former retention ponds was very minimal because thorium oxides are not very soluble.

Remediation. Nosean picked a plan to dispose of the low level radioactive waste at the Lilly Light plant site. It was argued that, although sites may be available downstate, transport of the large volumes of waste would create greater danger than disposal at the plant site. For example, according to Nosean Mining, unacceptable amounts of dust would be created at the site by loading onto trains and trucks, further dust would be made airborne during shipping and unloading, and the containment of water used for dust abatement would be difficult to handle. It would also cost the company nearly \$60 million for transportation and more to acquire land downstate. Some estimates were as high as \$87 million. On-site disposal, on the other hand, would only cost an estimated \$20 million.

Nosean Mining extensively described the characteristics of the site at West End Chicago. It is underlain by glacial till, including kaolinite, sands and gravel. The water table is not near the surface. The containment cell was first described as illustrated in Figure 1. It consists of a large clay cover and "manufactured" clay lining of locally derived clay. Because the site will be decommissioned after it is assured that the cell has "stabilized", Nosean Mining suggested that the City would be able to use the top surface as clay-based tennis courts.



**Figure 1.** The initial proposal for waste disposal at the West End Chicago site, circa 1982.



**Table 1.** National siting criteria for shallow-land burial of low-level radioactive waste (U.S. Nuclear Regulatory Commission, 1981) as printed by Hawley, J.W. and Longmire, P.A., Site Characterization and Selection, in C.C. Reith and B.M. Thomson, *Deserts as Dumps? The Disposal of Hazardous Materials in Arid Ecosystems*, Univ. of New Mexico Press, 1992, p. 76.

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1. The disposal site shall be capable of being characterized, modeled, analyzed, and monitored.
  2. Within the region or state where the facility is to be located, a disposal site should be selected so that projected population growth and future developments are not likely to affect the ability of the disposal facility to meet performance objectives.
  3. Areas must be avoided having economically significant natural resources that, if exploited, would result in failure to meet the performance objective.
  4. The disposal site must be generally well drained and free of areas of flooding or frequent ponding. Waste disposal shall not take place in a 100-year flood plain, coastal high-hazard area, or wetland.
  5. Upstream drainage areas must be minimized to decrease the amount of runoff which could erode or inundate waste disposal units.
  6. The disposal site must provide sufficient depth to the water table that groundwater intrusion, perennial or otherwise, into the waste will not occur.
  7. Any groundwater discharge to the surface within the disposal site must not originate within the hydrogeologic unit used for disposal.
  8. Areas must be avoided where tectonic process such as faulting, folding, seismic activity, or volcanism may occur with such frequency and extent to significantly affect the ability of the disposal site to meet performance objectives or may preclude defensible modeling and prediction of long-term impacts.
  9. Areas must be avoided where surface geologic processes such as mass wasting, erosion, slumping, land sliding, or weathering occur with such frequency and extent to significantly affect the ability of the disposal site to meet performance objectives or may preclude defensible modeling and prediction of long-term impacts.
  10. The disposal site must not be located where nearby facilities or activities could adversely impact the ability of the site to meet performance objectives or significantly mask the environmental monitoring program.
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**Table 2.** Performance objectives, waste-management assumptions, and recommended siting criteria from K.L. Falconer, L.C. Hull, and S.A. Mizell (1982) Site selection criteria for shallow land burial for low-level radioactive waste, in R.G. Post, Waste Management '82, Volume 2. Low-level waste: Proceedings of the Symposium on Waste Management at Tucson, Arizona, Arizona Board of Regents, and as reprinted in C.C. Reith and B.M. Thomson, Deserts as Dumps? The disposal of Hazardous Materials in Arid Ecosystems, Univ. of New Mexico Press, 1992, p. 77-8.

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**Performance Objectives**

1. The annual dose from radionuclides released from any shallow land burial site to persons outside the site boundary shall not exceed 25 mrem/yr-thyroid, 25 mrem/yr-any organ, for a performance period of 500 years.
2. Waste shall not be disposed of in a shallow land burial site that would result in an unacceptable dose to an inadvertent intruder after an institutional control period of 100 years has ended.

**Assumptions about Waste Management Systems**

1. The site will be selected, designed, operated, and closed to meet performance objectives. Zero release is not achievable.
2. Performance objectives can be met by utilizing both natural and engineered barriers.
3. After the institutional control period, the site will be suitable for normal surface use but will not be designed to prevent human excavations into the waste.
4. Waste form will not jeopardize site performance.

**Site Selection Criteria**

1. *The site should be of sufficient area and depth to accommodate the projected volume of waste and a three-dimensional buffer zone.*

To meet site performance objectives for low-level radioactive waste disposal, the site and its operation must not limit the activity of humans beyond site boundaries. A three-dimensional buffer zone will allow waste attenuation within the site boundary such that performance objectives are met. The essential information required to determine outer boundaries of the site (i.e. the buffer zone) includes the rate of change of radionuclide concentration as a function of distance from the disposal facility along all migration pathways and the concentration and quantity of radionuclides in the waste source. The depth to which the buffer zone extends depends on the hydrologic, geologic, and climatic setting of the disposal facility and whether waste is buried in unsaturated or saturated materials.

In environments where infiltration does not reach the zone of saturation, such as areas where evapotranspiration plus runoff equal or exceed precipitation, solutes dissolved from upper soil horizons are deposited in a zone of accumulation. Material leached from the waste would be deposited in the zone of accumulation and would not reach the saturated zone. Between the zone of accumulation and the capillary fringe is a zone of low geochemical activity. The buffer zone boundary could be in this inactive zone if sufficient leeway is allowed for potential climatic changes or enhanced infiltration through the disposal trenches.

In very arid climates, little or no water is available for leaching, and a thick zone of low geochemical activity separates buried waste from an underlying saturated zone. This environment would present a minimal probability of release by groundwater pathways, and the lower buffer zone boundary could be placed at a moderate distance below the disposal horizon.

2. *The site should allow waste to be buried either completely above or below the transition zone between the unsaturated and saturated zones.*

The reliability of performance prediction may be significantly decreased by burial of waste in the transition zone and greater radionuclide release rates may result from the increased geochemical activity associated with this zone. To determine compliance with this criterion, it is necessary to examine the water table elevation, the range of both seasonal and long-term water table elevation, the range of both seasonal and long-term water table fluctuations, height of the capillary fringe, thickness of excavatable material, and, if waste is buried below the transition zone, the hydraulic characteristics of earth materials in the saturated zone.

3. *The site should be located where flooding will not jeopardize performance.*

Where burial occurs above the water table, flood waters can transport waste material and/or saturate the waste, increasing leachate formation and accelerating subsurface water flow. Flooding can also interfere with site operations irrespective of the zone of burial. Locating burial sites outside areas that require extensive engineered protection will ensure that no increase in the probability of flooding occurs during the performance period of the site because of failure of engineered barriers.

4. *The site should be located where erosion will not jeopardize performance.*

During the required performance period of the site, erosion by wind and water must not cause intrusion on the buffer zone and/or waste cover such that it (a) uncovers the waste, (b) increases surface radiation levels above regulatory limits, and/or (c) significantly shortens radionuclide release pathways. Waste that is uncovered is susceptible to transport from the site, but erosion does not have to uncover the waste to shorten migration pathways significantly. During closure, certain engineered structures, such as trench caps, will likely be emplaced to improve waste containment. Erosion of these emplaced structures could decrease the performance capabilities of the site. Allowances for predicted rates of erosion during the site performance period should be incorporated into site design, operating, and closure criteria.

Plant cover and moisture availability are the most important factors governing the rate of erosion by both wind and water. Where average annual precipitation is very low, natural vegetation may be sparse or absent, allowing high wind erosion rates and high water erosion rates whenever precipitation does occur.

5. *The site should be located in areas where hydrogeologic conditions allow reliable performance prediction.*

Confident characterization of the hydrogeologic system in which a waste disposal site is located enables determination of potential migration pathways, estimation of radioactive contaminant movement rates in the subsurface environment, and design of a monitor network to collect data that can be used to confirm performance predictions of radionuclide transport. Major hydrologic characteristic of the site that must be examined include: subsurface geology, hydrologic budget, direction and magnitude of ground water flow, permeability type and diffusion properties of the system.

6. *The site should be located where geologic hazards will not jeopardize performance.*

Significant land disturbances may destroy site integrity and increase the likelihood of radionuclides entering the biosphere. In addition, site hydrology may be altered to the extent that performance predictions are no longer applicable. Specific geologic events that must be considered include earth movement associated with seismic activity, mass movement, land subsidence, and volcanic activity. The results of these events in the geologic past may so complicate the hydrogeologic system that predictions of site performance cannot be confidently obtained.

7. *The site should be selected with consideration given to those characteristics of earth materials and water chemistry that favor increased residence times and/or attenuation of radionuclide concentrations within site boundaries.*

Leachate migrating from buried wastes may carry radionuclides and other contaminants picked up from the waste. Showing the movement of contaminants relative to the movement of water will provide more time for radioactive decay to decrease radionuclide concentrations. Properties of earth materials and water chemistry that favor the removal of radionuclides from solution by sorption or precipitation and that favor retention on or in solid phases, will retard the movement of radionuclides. Nuclide concentration will decline more rapidly with distance from the waste if geochemical processes actively remove radionuclides from leachate than if only hydrodynamic dispersion is acting.

8. *The site should be selected with consideration given to current and projected population distributions.*

The minimum distance a site can be located from the population cluster must be determined by considering the size of the population and the effects of potential accidental and chronic radiation released during operations. A site located close to population centers could interfere with their expansion, as well as increase the likelihood of human intrusion into the waste after institutional control has ended.

9. *The site should be selected with consideration given to current and projected land use and resource development.*

Site selection must represent a balanced choice in land use, in that siting represents a commitment in land use to future generations. Historical, current, and potential land uses at the site and the adjacent areas should be prime considerations in complying with this criterion. Land uses which represent a higher priority in comparison to low-level waste disposal should be evaluated.

10. *To the extent consistent with other criteria, the site should be selected with consideration given to location of waste generation, access to all-weather highway and rail routes, and access utilities.*

A certain risk exists from the transport of radioactive waste from points of generation to final disposal. This risk is a function of the waste form, nuclide content, vehicle safety, transportation systems, and distance traveled. By considering major points of waste generation and transportation routes in site selection, this risk can be reduced. Locating a site with regard to waste generators and transportation systems also minimizes the cost of land disposal. Additional economic factors that can be controlled through site selection include access to utilities, materials for site construction, operation and closure, and public services.

11. *The site should be selected consistent with federal laws and regulations.*

Federal laws that a disposal site must comply with include but are not limited to: Clean Air Act (PL 95-95), Federal Water Pollution Control Act (PL 95-217), Safe Drinking Water Act (PL 93-523), National Environmental Policy Act (PL 91-190).

12. *The site should not be located within areas that are protected from such use by federal laws and regulations.*

Federal laws which preclude, by intent, the selection of low-level waste disposal sites within the boundaries of areas protected under them include but are not limited to: Wilderness Act of 1964 (PL 88-577), Wild and Scenic Rivers Act (PL 90-542), Endangered Species Act of 1973 (PL 93-204), National Wildlife Refuge Act of 1966 (PL 89-669), Laws establishing National Parks, Historic Properties-Preservation (PL 89-665), Archeological and Historical Preservations Act of 1974 (PL 93-291).

## NOTES TO THE INSTRUCTOR

The concept of this laboratory originated in 1993 from the need to develop an environmental geology course. The overall objective of the course was to teach a broad understanding of earth processes and systems so that students could become informed consumers of scientific information. One portion of this course required an applied or environmental mineralogy component, with sufficient introductory material that a consistent background could be provided even if the course is taught by different instructors. Also, the laboratory needed to be simple, relatively inexpensive, easy to maintain and set up, capable of being completed within a two-hour period, and comprehensible for students with only minimal backgrounds in chemistry, since the course was not intended just for geology majors. Although this exercise was originally designed for an environmental geology course, it is applicable to many courses, including hydrology, mineralogy, sedimentology, geomorphology, physical geology, etc.

The resulting environmental mineralogy laboratory illustrates several important general mineralogical concepts. Although not always explicitly stated in the laboratory text, these concepts include cation sites and cation exchange, solid solution, charge neutrality of the chemical constituents in phases, and the effect of chemical composition on the physical properties of phases. Other concepts are more appropriate for clay mineralogy, such as the effect of salts on the behavior of clay swelling, plastic behavior of clays, and permeability.

Although this laboratory exercise is self-contained, it was not meant to stand alone. The laboratory leads not only to possible discussions of the scientific concepts given above, but also of how natural materials may be used to isolate or remediate chemical or nuclear waste. For example, courses may include discussion involving how to isolate low-level radioactive waste by using a clay containment system; we use an example near Chicago where low-level radioactive waste was to be sited within city limits. The discussion involves background information and past legal action, site conditions, a design of a proposed containment cell, national siting criteria, proposed performance objectives, and about 25 topics and questions to explore. This discussion is included here also, although with changes to names and details to protect the identity of the participants.

***Special comments on the experiments and experimental procedures.*** It is noteworthy that the montmorillonite used in this laboratory must be of high purity. For example, cat litter and othersimilar sources are generally not of sufficient quality for these experiments. We use a high-purity montmorillonite<sup>1</sup> available commercially, but other sources may provide material of high quality.

Part II of the laboratory considers the flow rate of water and Na-rich brines through a column of a montmorillonite + sand mixture. The times required for flow (Questions 8, 9 and 10) are dependent on the particle size of the sand used, the amount of montmorillonite added to the sand, and the quality of the montmorillonite used in the experiments. Pore sizes in the sand must be sufficiently small to trap some of the montmorillonite and to allow the montmorillonite to seal upon expanding. A sand with grain sizes ranging up to fine-medium has worked well, and a poorly sorted sand may be better than a well sorted sand. Also, Question 6 of Part II must be modified for the appropriate amount of added montmorillonite. The instructor should test the mixture so that the first experiment in which water drains through the column takes about 3-4 minutes (Question 10, Part II).

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<sup>1</sup> unmodified Supercol<sup>®</sup>, available from American Colloid Company, 1500 W. Shure Dr., Arlington Heights, IL 60004, USA. A gallon of unmodified Supercol<sup>®</sup> will last for years. American Colloid has provided these quantities free of charge as a service to the educational community. Please offer to purchase the material, however.



An important point in Question 7 of Part II is that montmorillonite must not form a layer on the top surface of the column. Clay is an effective sealant, and if a clay layer is allowed to form, water is impeded from flowing through the column. Decanting excess water above the column often prevents a clay layer from forming to seal the column surface. Likewise, to prevent clay concentrations from forming, it is imperative that the student thoroughly mix the clay into the sand (for Question 6, Part II).

Sand obtained commercially may already contain clay. To check for clay material, place some sand in a large beaker with water and stir. If the resulting water appears cloudy, the sand contains a clay fraction, which must be washed from the sand before proceeding with the experiments. Successive stirring of the sand with clean water will remove the clay.

**Anticipated results.** Part I illustrates how cation exchange may affect the physical properties of the clay. Cation exchange takes place almost immediately upon stirring the montmorillonite in the saturated solutions of NaCl, MgCl<sub>2</sub>, or CaCl<sub>2</sub>. The wait time of 5 minutes is for the purpose of settling. The Na-exchanged clay, which contains H<sub>2</sub>O in the interlayer also, does not settle to the same extent as the other exchanged montmorillonites. As more Cl is removed by washing, the Na exchanged montmorillonite will disperse. This effect may be apparent within one or two washings. If the clay is washed sufficiently (four or five times), however, the use of a ultrahigh speed centrifuge will be required to bring the clay to the bottom of a container.

Part II examines the property of permeability through a sand column vs composition of the montmorillonite. Parallel experiments are done to isolate the effect of permeability of the sand column using pure water and then NaCl saturated solution, followed by the same fluids with a sand + Ca-exchanged montmorillonite column. The NaCl saturated solution (Part II, Question 4) takes substantially longer to flow through the sand column than pure water, presumably because of its different ability to wet the sand grains.

The student (Question 9, Part II) introduces NaCl saturated fluid into the column containing Ca exchanged montmorillonite, and this sets up a Na exchange. However, because of the Cl present, the (now Na exchanged) montmorillonite does not disperse. Adding pure water in Question 10 washes the Cl (and excess Na and other cations having been exchanged from the clay) from the sand, thereby causing dispersion which closes the pore throats of the sand. Question 10 suggests that three washings are necessary, but this may vary and it may only be necessary to do two washings (less commonly, four washings). Variations in the number of needed washings are common, since the flow of water in the column cannot be controlled. In any case, if the students are waiting around watching a diminishing flow rate, then the point has been made.

Note that it takes only a small amount of montmorillonite to affect a considerable amount of sand. Also, brines passing through sands with some clay, followed by fresh water, clearly can greatly affect the permeability of the sands. Not only is this an important consideration in remediation work in the environmental industry, but it is also important in the petroleum industry and in the understanding of quick clays, stability problems, and many other engineering-related problems.

Question 11, which involves the introduction of methylene blue to the column, illustrates the ability of montmorillonite (+ sand) to adsorb other materials, and thus it acts as a "filter". The blue color is readily adsorbed in the top couple of centimeters of the column. Methylene blue is an organic molecule with an associated positive charge, and it is adsorbed quickly by the clay. An alternative experiment, in case class time is a concern, is to add the methylene blue directly to a beaker containing montmorillonite + water. The clay will adsorb the dye very quickly.



***Additional classroom experiment.*** A short class demonstration to illustrate clay dispersion and swelling behavior are not included in this exercise, but it is appropriate for an introduction to the properties of clay minerals. Clay dispersion is best illustrated over several days so it is best to set up this demonstration in one class period and then to return to it at intervals up to a week.

Take two 150 ml. glass beakers and fill each about 3/4 with water. In one beaker add about 3 tablespoons of sand or soil (provided the soil does not have a significant clay component). In the other beaker, add a similar amount of montmorillonite (use the same montmorillonite as in the laboratory exercise). Stir the soil/water mix, but it is not necessary to stir the montmorillonite/water mix (if there is a time constraint, stir the montmorillonite very gently for a brief time). Allow both beakers to stand for two or more days. Larger beakers can be used with greater amounts of clay and water. Unlike the soil/water mix where the soil settles to the bottom of the beaker, the clay particles will disperse throughout the beaker of water. Materials generally do not behave this way! If the water is allowed to dry from the beaker with montmorillonite, the result will be a mass of hardened clay (clay + interlayer water) many times the volume of the initial 3 tablespoons.

### **SUGGESTIONS FOR THE LOW LEVEL RADIOACTIVE WASTE DISPOSAL DISCUSSION**

The class may be divided into three groups, advocates for Nosean Mining Company, advocates for the citizens of the City of West End Chicago, and advocates for the NRC. The discussion leader can be the (impartial) judge. As judge, you may ask questions, but do not expect to render a "decision". The discussion should be considered "open-ended".

Topics and questions to explore:

Is there anything conceptually incongruous about disposal-site use for recreational use? Could recreational use actually accelerate deterioration of the cell? If snowmobile or motorcycle use are allowed, how could this affect the cell cover?

How may freezing and thawing affect cell cover integrity? How may drying and wetting affect the cell cover?

What may be the effect of borrowing animals, such as badgers, have on the integrity of the site? Consider both the effect on the cell cap and in the interior of the cell (void spaces). Does this suggest that such a site should be left unmonitored?

What are the negative effects of vegetation with extensive root systems? Are there any positive effects? Should vegetation grow in the disposal site without monitoring? Are there any effects from decomposing organic matter?

If monitoring is a wise idea, for how long should it be done? What are the criteria set forth by the NRC.

What is the "bath tub" effect? Does the engineering of this cell promote or lessen the possibility of the bath tub effect? What must be done to prevent the effect?

How would the designers of the cell determine if the cell fails? Do the leachate wells presently suggested test for failure? How would you design a cell to test for possible failure?

How may water run-off possibly affect the cell cover? How does erosion (e.g., wind, water, ice, etc.) in the Chicago area proceed? What will be the impact of raindrops during

intense summer storms be on an unprotected clay cover? How may an extensive drought affect the cell integrity? Describe gully erosion, mass movement.

What site characteristics are at odds with the criteria set forth by the NRC? Discuss the criteria set forth regarding population, potential land use, and potential population increase.

What may be the effect of possible air pollution found in the Chicago area, such as acid rain (sulfuric acids)?

Although the cell contents will be artificially compacted during emplacement, how may additional natural compaction affect the cell integrity?

Discuss more ideal locations and climates for waste disposal. What would be considered "ideal" to you? What criteria did you use to decide on an ideal location?

What are the aesthetic objections for the West End Chicago site that might be offered by the citizens of the City and State? If the current siting proceeds, will the objectives of the City and State be met?

Should there be any criteria regarding slopes on the cell? How may this prove important?

For more advanced discussions:

Have the students design a waste disposal cell.

Discuss ways that geology may be used in the design of a "natural site" depository in conjunction with a well designed cell or cover.

How would low level waste disposal differ from high level waste disposal?

How would low level waste disposal differ from hazardous chemical waste disposal?

Discuss the rationale behind using a clay cover--Is such a cover to prevent all water from entering the cell or to limit water? How should the cell character differ or be related to liner characteristics?

What are slurry trenches and how may their use limit seepage? Discuss the purpose of redundant liners and leak detection systems.

Discuss possible biointrusion barriers to prevent burrowing animals or penetration of roots. Also consider the design of drains, swales, aprons, and infiltration barriers.

How would you design a marker to serve as a warning to future generations? Remember that the curses of the pharaohs were not particularly effective in stopping thieves and English language markers may be equally ineffective. Remember also that the limestone blocks on the pyramids, which represented quality building material, was stripped from the pyramids shortly after they were built.

What sort of performance assessments should be made on the site?