Clay as sealing material in nuclear waste repositories

Nuclear waste from thermal plants poses a lasting risk to the biosphere because of its long radioactive life. The planned definitive storage place for it is in deeply buried repositories. Such repositories would need to be both impermeable to water, and plastic during deformation, in order to avoid the formation of cracks that may allow water in. One of the clay minerals, smectite, has these two properties and is an ideal candidate as a sealing material or even host rock for nuclear waste repositories. The chemical stability of smectite in the repository environment is sufficient to maintain good sealing properties during the active life of the relevant radionuclides.

Nuclear waste: the problem

Nuclear power has some evident advantages over other sources of energy, and also one very clear disadvantage: nuclear waste. This waste is of the type termed ‘high-level nuclear waste’, to differentiate it from the ‘low-level nuclear waste’ resulting from other types of applications, where the resulting products are radioactive for a relatively short period of time (tens of years). This article refers only to the high-level type. Nuclear waste contains part of the initial uranium or plutonium fuel and the products of their decay. The radioactivity of this mixture is still high—the core of the problem—and the life of the waste varies from hundreds of thousands to a few million years. It is therefore necessary to maintain this material, confined from the biosphere for at least a hundred thousand years, when its radioactivity will reach that of natural uranium. The most widely accepted concept of a nuclear waste repository is that of a deeply buried one, which places the waste at a great distance from the biosphere. However, it is necessary to ensure that it will remain there. The challenge then, is to build repositories that will remain stable and without any leaks for such long periods of time.

Characteristics needed in a safe repository

The main enemy of a safe nuclear waste repository is water. The waste is in the solid state and, if buried away, it would remain there unless transported by some agent. This agent is usually water, which can transport the radionuclides in dissolved form or in colloids or small particles. We can therefore establish that a basic characteristic of a safe repository is for it to be impermeable, that is, water should not be able to penetrate it. At this stage it is appropriate to consider the physical form in which the waste will be taken to the repository and buried. The nuclear material will be condensed as a glass and introduced in metal canisters very resistive to corrosion. The amount of waste in the canister and the design of the canister will be such that the radioactive decay produces a maximum temperature on the outer surface of the canister of approximately 100 °C. The metal canister is the first protective barrier and is designed to last about 1000 years in favourable conditions of low fluid presence, mobility and corroding power. Thus, the required characteristics of the facility where the waste will be buried are as follows:

1. It should be able to adsorb the small amount of water that might be present in a ‘dry’ repository;
2. It should hinder any water flow to or from the repository;
3. It should be able to transmit the heat generated in the canisters to allow heat dispersion and avoid steep temperature gradients (these gradients are dangerous because they can physically or chemically destabilize the emplacement and trigger undesired processes);
4. It should have plastic behaviour that allows it to deform without the formation of fissures,

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response to the stress created in the surrounding rock by the drilling and to possible future tectonic movement;
5. It should be able to alter the chemical composition of the interstitial water to minimize its corrosive power; and
6. If water reaches the canister and corrodes it, the emplacement should be able to retain the radionuclides in the water, avoiding their transport away from the repository.

One of the above characteristics is plasticity to absorb mechanical stress. Obviously, tectonic stress will be avoided by choosing emplacements in tectonically inactive areas. However, the long life of the repository makes it advisable that eventual movements are considered a possibility. There are several ‘concepts’ of nuclear waste repository that fulfil the above characteristics to varying degrees. One possibility is to locate the repository within a salt dome, which provides a very plastic medium and anhydrous environment, given the hygroscopic character of salt. The other two possibilities use clay as the plastic and anhydrous material protecting the canisters. In one case, the repository is located in a large clay formation; in the other, the location is a large rock formation with no or few, unconnected fissures, where clay is used as a lining between the rock and the canisters to provide for the characteristics indicated. This article deals with the latter type, specifically why clay is such a good candidate as sealing material. In one case, the repository is located in a large clay formation; in the other, the location is a large rock formation with no or few, unconnected fissures, where clay is used as a lining between the rock and the canisters to provide for the characteristics indicated.

Why clay does the trick

Why is it that clay is impermeable, plastic, able to buffer water chemistry and to adsorb and retain radionuclides? All these properties are connected with the unique structure and chemical properties of clay. Some clarification is necessary here, as clay is a term encompassing a large group of minerals with structural and chemical similarities but with different physical and chemical properties. The clay mineral that most fulfils the characteristics listed above is smectite, a clay which, despite having a rather large range of chemical compositions, maintains basic physical and chemical properties that are valuable to its role.

Smectite is a layer silicate, that is, a mineral rich in silicon, with a layer structure. The layers extend much more in their length and width (tens of nanometres) than they do in their thickness (a fraction of a nanometre). These layers stack and create the smectite crystals. The number of layers in the crystals is small, ranging from two to a few tens of layers. Thus, the crystals look like thin lamellae, a few tens of nanometres thick, with lateral dimensions of a few micrometres. The layers are formed by two sheets of tetrahedra sandwiching a sheet of octahedra. The polyhedra have oxygen atoms in their apices and cations in their centres. Silicon is the major cation in the tetrahedral sheets and aluminium, iron and magnesium are the major components found in the octahedral sheet. These cations are interchangeable in the octahedral sheet, and also small amounts of aluminium exchange for silicon in the tetrahedral sheet. The result of this chemical exchange between cations with different electric charge (silicon 4+, aluminium and iron 3+, magnesium 2+) is that the layers have a residual negative electric charge. To compensate for this, other cations penetrate the space between the layers and exchange for those originally there. The cations in the smectite interlayer space are hydrated, that is, they are surrounded by water molecules in such a way that the cations and the water keep the interlayer space expanded. The layers are not touching each other and they can admit large amounts of water between them, so much so that when in contact with sufficient water they keep expanding until eventually the layers become completely separated entities. This is the interplay between the electrostatic attractive force between the layers and cations, and the ‘repulsive’ force generated by water penetration. This situation causes
the interlayer space to be accessible to the external fluids and to the cations dissolved in the water, and this is why they can penetrate this space and displace the cation species that are located there.

Desirable smectite

How is it that these characteristics of smectite produce its desirable properties for use in nuclear repositories? Once the canisters containing nuclear waste are in place surrounded by smectite (whether from a smectite-rich geological formation, or from an engineered barrier lining the space between the canister and the host rock), the tendency of smectite to hydrate will lead it to absorb water until complete saturation. The spontaneous saturation process may be non-homogeneous and it is advisable that a pre-saturation is carried out before the repository is closed, to facilitate the homogeneous adsorption of water. As water is adsorbed, smectite expands, and because the clay is contained within a limited volume, it closes all fissures around the canister until it creates a space that cannot admit any more water. Thus the clay becomes completely impermeable. The only possible water movement is that of the diffusion of the water adsorbed on the clay, but this is extremely slow and unlikely to have any effect on the canister. The expanded smectite becomes very plastic, as it is formed from very small particles or crystals and a large amount of water that fills the space between layers and the pores between particles. The consistency of this mixture can be compared to that of plasticine, with the important difference being that clay has an interior pressure that causes it to expand and occupy any void space in contact with it.

Only water adsorbed on the clay or in pores between crystals will be in contact with the canister. All the water adsorbed in the clay is firmly held within it. Water movement will be a very slow diffusion process across a thick layer of clay. The thickness of the clay lining in rock-hosted repositories will be about one metre. Smectite has an extremely large surface area (approximately 600 m²/g) that will interact with the percolating water. This intense interaction will have the effect of buffering the chemical conditions of the water, for example moderating the pH, and reducing the corrosive power of the fluids, thus protecting the metal canisters. However, in the possible scenario of a corroded canister which is penetrated by water, and where the glassy nuclear waste is being leached and transported away from the canister, the last defence mechanism comes into play. Smectite can exchange cations in its interlayer space. The exchange process depends on several variables such as the concentration of the incoming cation in the fluids, the electric charge of the cation, the cation radius and overall hydration state. Most of the radionuclides in the waste have a favourable cationic electric charge when in solution that will allow them to be retained selectively by the clay. On their way out, the fluids would exchange their lethal load of radioactive ions for the harmless type that we drink in our water everyday.

A practical question after considering the great performance of smectite is: where do we find it? Is it abundant? The answer is that it is very abundant and we find it everywhere: smectite is a very common mineral in sediments and soils. However, there is a catch: it is frequently mixed with many other minerals and often these sediments do not have the physical or chemical properties needed in the repositories. In the case of repositories within clay formations, it is necessary to use geological formations with a sufficiently high smectite proportion. In repositories hosted in other types of rocks, the clay sealing around the metal canisters has to be very rich in smectite. The ideal candidate for clay sealing is a rock called bentonite. This rock is a product of the alteration of volcanic ash. It frequently contains from 80 to (almost) 100 per cent smectite. Bentonite is an abundant rock and the preparation of bentonite as a lin-
Inexpensive mechanical processes.

Clay stability

The next step is a consideration of the durability of the smectite seal. We know that smectite is stable in near-surface conditions, because it is present in sediments that are many millions of years old. However, is smectite also stable in the conditions of the repository? The answer is yes and no. This is because the conditions in the repository are not homogeneous. The clay in contact with the surface of the metal canisters will experience a maximum temperature of approximately 100°C, but this maximum temperature quickly decreases away from the canister. Besides this, the temperature is not constant: it will increase very quickly at the beginning and then decrease slowly as the radioactivity decreases. Smectite in the close vicinity of the canister will not be stable. We know that at temperatures above approximately 60°C smectite transforms into illite, another clay mineral of very similar composition, but without the permeability, plasticity and adsorption properties of smectite. However, this transformation process is very slow, and certain chemical conditions are required for it to happen. The questions are then: can we avoid the chemical conditions favouring the transformation to illite and is the reaction sufficiently slow to render the repository safe?

Smectite transforms into illite via a loss of silicon (as dissolved silica), a retention of potassium that displaces all the other cations in the interlayer space and expulsion of the interlayer water, and collapse of the interlayer space. After this reaction takes place, the clay does not adsorb water or ions. However, the reaction needs a potassium supply. The simplest way to prevent this reaction is to put the repository in a host rock with interstitial fluids that contain little or no potassium so that the reaction cannot take place. This might not always be possible, but luckily there are also ways to retard any possible potassium exchange. Smectite will release sodium and take up potassium much more easily than it will release calcium and magnesium in exchange for potassium. So, if the original clay contains large amounts of calcium or magnesium rather than sodium, it will be much less likely to take up potassium. What if potassium ions slowly make their way towards the clay near the metal canisters? How long will it take for the reaction to happen? This is an extremely difficult question, precisely because the reaction is so slow that it is very difficult to measure its rate. However, this reaction rate has been studied by numerous scientists (myself amongst them) because it is important for the problem that we are considering (and also for petroleum exploration). Many equations have been proposed for a calculation of the transformation rate.

In essence, the rate depends on the proportion of smectite to illite, how much potassium is available and the temperature. Figure 6 illustrates what will be happening in the vicinity of the canister. I have calculated the proportion of smectite transformed at several distances from the canister as time progresses. For this, I have assumed that the temperature is con-

Fig. 5. A bentonite quarry in Almería, Spain. The red material is of volcanic origin. The white material is the bentonite, which is formed by chemical alteration mediated by water of the volcanic material.

Fig. 6. Assessment of the proportion of smectite transformed into illite in the vicinity of a canister containing nuclear waste. The orange sector represents the smectite surrounding the canister (about 90 cm from the canister to the outer side). The rate of the transformation decreases as we move away from the canister because the temperature is lower, up to the point where there is no transformation. The shape of the curves is such because the transformation slows down as the proportion of smectite decreases.
constant at each point, and decreases as we move away from the canister. The concentration of available potassium is also assumed to be constant and to correspond to that typical of granitic interstitial water. The calculations are not intended to be rigorous, they simply illustrate two points. First, that the velocity of transformation decreases with distance from the canister, due to the decreasing temperature. A large volume of the smectite layer is not affected by the reaction because the temperature is too low. Second, that the transformation rate decreases rapidly as less smectite is left to react, with the practical result that the reaction is not completed. From the assessment in Fig. 6 it is possible to see that after 100 000 years—a period in which the radioactivity level will reach that of natural uranium ore—the clay is still composed mainly of smectite and will preserve its good sealing properties.

At this point it is necessary to emphasize that the chemical stability of smectite versus illite is only one among many processes that need to be tested and modelled before a specific concept of nuclear waste repository is considered safe. Other such processes are both physical and chemical in nature. For example, studies have also been carried out concerning possible reactions between smectite and alkaline fluids generated from the interaction of interstitial water with concrete plugs in the excavated galleries, and between smectite and the metal canisters. These chemical processes are mainly controlled by the presence of water that may act as a mediator in the reaction and transport the reactive species, thus, impermeable barriers should minimize them and render them negligible. All these physical and chemical processes are integrated into studies for the feasibility of the repositories. There are, also, other considerations, not included in this article, that may alter the decision about the suitability of a specific repository design and the materials used. To give an example, one of them is the retrievability of the waste, which might become advisable because technology has progressed to the point in which the waste can be used again or for other reasons.

**Conclusion**

Studies carried out on the sealing properties and chemical stability of smectite in the conditions foreseen of a nuclear waste repository are providing satisfactory results and indicate that it is possible to use this material as a safe and stable barrier against leaching and transport. Smectite clay does the trick by its very messy character: cations that replace each other rather capriciously, extremely small crystals, interlayer space that takes up water and dissolved cations, layers that can separate and come back close to each other in response to environmental conditions. This is an example of how the combination of a few chemical and structural characteristics in a mineral result in physical and chemical properties that are quite unexpected. Now, these characteristics will have to be finely tuned. Only a trained scientist can differentiate between smectite and illite, so similar they are in their crystal structure and composition, but smectite has the right properties and illite does not. From this perspective, clay provides inspiration for the creation of manmade materials. Little 'tweaks' are all important.

**Suggestions for further reading**


