

# **Clay: a natural and surprising nanomaterial**

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Clays are a family of materials that are omnipresent in our daily lives and in our environment. Dry, they seem as solid as rocks, muddy, they flow like oils. They are now used in the construction of very large structures and often form the subsoil of urban areas. How do civil engineering technicians manage to overcome the difficulties they pose?

## 1. A universal material



*Figure 1. Bisons from the cave of the Tuc d'Audoubert [4] [Source: Leroi-Gourhan Arlette, 1984: L'Art des cavernes : Atlas des grottes ornées paléolithiques françaises (CC BY-SA 4.0)]* 

If there is one material that is confused with the history of humanity, it is clay. It is mentioned in chapter 1 of the *Book of Genesis* in the Bible. According to the translations, the words **clay, clay, silt or earth** are used: "*Then the Lord God shaped man with the clay of the ground, breathed into his nostrils a breath of life and man became a living being*" [1].

Clay is undoubtedly one of the materials that contributed to the **birth of art**: the bison in the prehistoric cave of the Tuc d'Audoubert (Ariège) were made from wet clay. Without any firing, the models have been able to keep wet for 15,000 years (Magdalenian period) in the cave discovered by Begouën [2] in 1912. The relative humidity of 100% [3] allowed this conservation (with some cracks) (Figure 1, [4]).

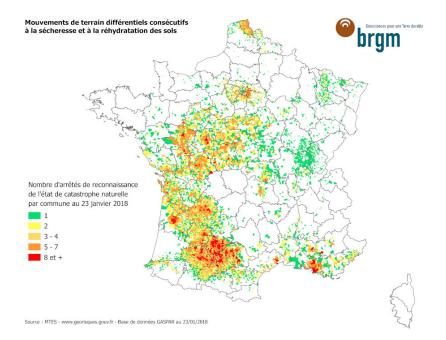
It is also through clay that **writing** developed **in Mesopotamia** at the time of Ur and Sumer more than 3000 years BC [5]. The clay tablets, engraved with styli by the scribes in cuneiform writing, are the first written traces of the history of humanity. In particular, the epic of Gilgamesh tells the story of the king of Uruk in 12 clay tablets written more than 2000 years before Christ (Figure 2, Tablet XI, The Flood).



Figure 2. Epic of Gilgamesh, Tablet XI (2000-1500 BC) [Source: British Museum (CC0)]

**The firing of clay** for pottery and cooking utensils dates back to the Neolithic and appeared in Asia and the Fertile Crescent. The control of the mixture of clay and water, drying, shrinkage without cracking and firing has accompanied the development of humanity in all settlement areas. And the resistance of the fired clay gives archaeologists a reading of history through the shards of pottery of various civilizations.

Clay is also a wonderful product that has been used since the dawn of humanity in **pharmacopoeia and cosmetics**: for example, the body paintings of the Amazonian Indians, beauty masks with clay, such as the green clay of organic shops or the mud baths of spa resorts. More prosaic are the "terre de Sommières" used as a natural stain remover or the basic component of the anti-diarrheal drug "Smecta®". Clay is also used in toothpaste, in the paper industry, as a filler in paints. Clay is everywhere in our environment and has always been used extensively.



*Figure 3. Map of communes that have been declared as natural disasters due to drought (January 23, 2018), see ref. [7] [Source:* © *BRGM].* 

Finally, clay is a **building material** and is the support for many buildings. Earthen constructions, be they adobe, cob or mud bricks, are widespread throughout the world and at all latitudes. Important constructions such as the **ziggurats of Iraq**, included reinforcements in reed straw (see <u>Soil reinforcement: techniques that have become essential</u>). But as a construction support, clay poses many problems. Depending on climatic or hydraulic conditions, its volume can vary by absorbing water or by shrinking during drying: this is called **shrinkage and swelling**. In France, drought episodes since 2003 have caused enormous damage to single-family homes and other buildings: more than **8,500 municipalities have been recognised as being in a state of natural disaster**, opening up the possibility for owners to receive compensation through insurance. These damages are neither spectacular nor "media", they do not cause accidents to anyone but only major **cracks** compromising the safety of the building. The overall cost over the last few years is significant: it is in the order of 8.5 billion euros over the period 1990-2013 [6]. The map in Figure 3 shows the municipalities concerned where more than **23,000 natural disaster orders** have been published [7]. And current global warming will not improve this effect: according to climate change models by 2100, the cost of withdrawal-swelling could be between 50 and 100 billion euros for the period 2020-2100.

### 2. A natural nanomaterial

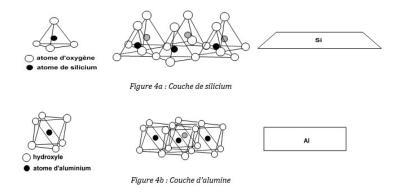


Figure 4. Top (a) : Silicium layer ; Below (b) Alumine layer [Source: Philippe REIFFSTECK].

The clays come from the physicochemical alteration of siliceous rocks, especially granitic rocks. During their decomposition by climatic agents, these rocks produce very fine particles of clays of different kinds. These can then be washed and transported before being deposited by sedimentation. The clays are made of **Si silicon, aluminium Al and OH hydroxyl** organized in layers that are stacked in **sheets**. In Figure 4a, the SiO4 tetrahedrons are assembled in a layer represented by a trapezoid. Octahedrons are formed by an aluminium atom surrounded by six OH hydroxyl atoms and are associated in a layer symbolized by a rectangle (Figure 4b) [8].

Two or three of these base units form an elementary sheet (Figure 5). **Kaolin** (used in porcelain) is the stacking of an Si layer and an Al layer while **smectites** have an Al layer between two Si layers.

Different cation substitutions can also occur, leading to different clay minerals.

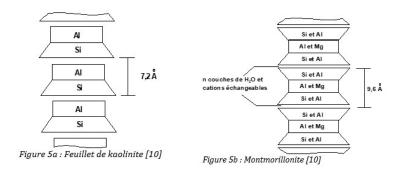


Figure 5. Top (a) : Kaolinite ; Below (b) : Montmorillonite [Source: Philippe REIFFSTECK]

Thus Mg<sup>+++</sup>, K<sup>+</sup>, Fe<sup>++</sup> cations can replace Al<sup>+++</sup> cations depending on weathering conditions or during sedimentary transport of clay particles and form clay minerals such as montmorillonite.

These sheets, of **nanometric** size (10 Å = 1nm =  $10^{-9}$ m), are stacked to give clay aggregates and the clay structure is either dispersed or flocculated with face-face or edge-face bonds. Stacks can consist of 1 to 100 elementary sheets. On the surface of the sheets and between the sheets, water particles can be adsorbed by electrochemical effect, depending on the nature of the clays. This is particularly the case for smectites where the bonds between sheets are weaker: these electrochemical properties generate the **major role of water** in the behaviour of clays, particularly **shrinkage and swelling**: water adsorption leads to a spacing of the sheets and swelling.

This interaction between water and clay finds its source in the specific surface of the clay particles: if we deployed the surface of all the elementary leaves of one gram [9] of montmorillonite, we would obtain 600 m<sup>2</sup> (and 50 m<sup>2</sup> for a kaolinite) !

The water content of a clay is defined as follows: it is the ratio between the water mass and the clay mass after drying at  $105^{\circ}$ C. It varies from 0% for a dry powder to values of more than 300 or 500% for montmorillonites. The clay deposits on which Mexico City is built [10] have a water content of more than 300% (varying from 150 to 600%).

Depending on its water content, a **clay's consistency** varies, which leads to the definition of "state limits" or Atterberg limits [11] : **liquidity limit and plasticity limit**. They depend on the mineralogical nature and are used to characterize clays in geotechnical engineering. Above the liquidity limit, clay behaves like a highly viscous liquid (see <u>How matter deforms: fluids</u> and solids) while below the plasticity limit, clay cannot be shaped without cracking. These variations in water content are accompanied by variations in volume.

Natural alluvial soils consist of a mixture of sand, silt and clay particles. The clay content of a soil is defined as the percentage by weight of particles less than 0.002 mm.

### 3. Clay and permeability

Clay and clay materials are widely used in civil engineering works. One of the most interesting properties of clays is their low permeability, up to one million times lower than that of sands (see <u>Diffusion and percolation in soils</u>)). Waste storage centres use **compacted clay** layers to provide a seal that isolates deposits from the outside environment. Some products associate a centimetre layer of bentonite [13] with a geomembrane. Another application is for dams and dikes. Large backfill dams (e. g. Serre-Ponçon and Grand'Maison; see <u>Soils for engineer</u>) are made up of different zones and the sealing function is provided by a compacted clay core or a material containing sufficient clay particles. Dykes, small agricultural dams, hillside water reservoirs and other reservoirs are often made of compacted clay earthen embankments.

The storage of nuclear waste is planned in a thick layer of **clay** in eastern France: it is a highly consolidated clay more than 500 metres deep, whose impermeability will ensure the containment of radioelements [13].

### 4. Consolidation and settlement



*Figure 6. Grape press: in this case, the fluid is expelled radially: this is called radial consolidation. [Source: © Etienne Flavigny]* 

Many cities and megacities have developed in valleys, estuaries, lakeside or seafront areas. The subsoil of these areas is made up of alluvial materials, silts, clays and mud. These materials are often of high water content and have **consolidated** under the weight of sedimentary layers deposited successively during the geological eras. This consolidation corresponds to **the expulsion of pore water** under the effect of stress (see <u>How matter deforms: fluids and solids</u>) applied by the upper layers.

Any surface construction adds additional stress and then causes an additional **settling**, on the scale of the building constructed, of a backfill or an urban area. An analogy that can be made of this process is that of a fruit press (Figure 6) where the juice is expelled under the effect of the stress applied [14] by the screw acting on the tray.

Due to the low permeability of clays, settlement develops over time ranging from a **few days to several centuries**. Several examples are famous. **Mexico City Cathedral** was built in 1560 and covers some of the Aztec temples demolished for its construction. The settlements reach more than 2.5 m with differential settlements [15] of 1.25 m between the West and East towers. Several preservation works have been undertaken, including those of **under-excavation**: they consist in excavating from wells to create a settlement on the side where the settlement is less (Figure 7)



Figure 7. View of Mexico City Cathedral [21] [Source : Arian Zwegers, (CC BY 2.0), via Flickr]

This technique has also been successfully used to reduce the differential settlement of the Leaning Tower of Pisa : Burland *et al.* [16] have thus been able to "rejuvenate" the inclination: it has returned to the value it had 300 years ago.



Figure 8. Osaka Airport Platform [24] [Source Thorfinn Stainforth (CC BY-SA 3.0), via Wikimedia commons]

A current example is the Osaka Airport Platform [17] (Kansai International Airport). This is an artificial island 1.25 x 4 km built at a water depth of 18 m. The **expected settlements were about 11 m** and allowed a finished level of 4 m above sea level. The observed settlements were stronger than expected (about 14.3 m) and led to major work to raise the peripheral wave protection walls and also to work on the buildings.

Another cause of subsoil compaction in large metropolitan areas is the lowering of groundwater tables: water needs require pumping into the subsoil. The induced effect is to lower the level of the slicks. The soil layers that were subjected to Archimedes' thrust are no longer subjected to Archimedes' thrust and their apparent weight increases. This creates an overload and therefore a settlement developing over the entire area. We then talk about the **subsidence of the site**. This phenomenon affects Bangkok [18], Shanghai and Venice in particular. This decline is in addition to sea-level rise, making these metropolitan areas vulnerable to flooding.

In geotechnical engineering, the evaluation of construction settlements is an important part of the project: by how much will the building settle and in how long will it be reached?

### 5. The resistance of clays

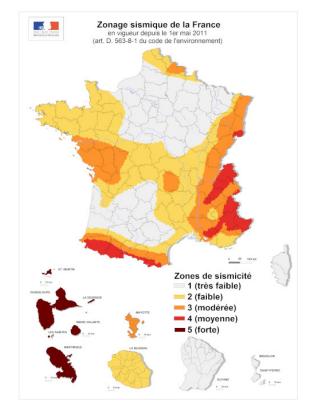


Figure 9. Seismic zoning of France. See ref. [20] [Source BRGM]

Another aspect of geotechnical engineering is to protect against failure. To do this, it is necessary to know the resistance of the clays. These are materials that have a **cohesion and an angle of friction** (see <u>How matter deforms: fluids and solids</u>) Their cohesion, a phenomenon similar to a kind of glue between the elementary sheets, depends on the water content and history of the clayey deposits, while the angle of friction is related to mineralogy. These two parameters are used in the **stability calculations of the foundations of structures**, dams, dikes and excavations. When the applied loads become stronger than the strength of the clay, there is a rupture. This rupture can occur in the short term, especially at the end of construction, or in the long term. Landslides provide an example where clay resistance is the important parameter controlling the stability of a slope, whether natural or anthropogenic (see <u>Landslides</u>).Building on clay soils of poor quality or insufficient strength has led to the development of soil improvement techniques (see <u>Soil reinforcement: techniques that have become essential</u>). to increase resistance and also reduce settling.

For cities with clayey alluvial layers in their subsoil, earthquakes can have considerable induced effects: we speak of a **''site effect''**[19]. Seismic waves can be trapped in clay layers and are **amplified**. An example is the destructive earthquake that struck Mexico City in 1985: although the epicentre of this earthquake is distant, seismic stresses have been amplified in central Mexico City, a city built on clayey deposits with very high water content and low cohesion. The consideration of this phenomenon has been integrated into the seismic zoning of France; the Geneva-Annecy-Grenoble-Valencia Alpine Trench area is in Seismicity Zone 4, the strongest in the metropolitan territory [20] (Figure 9): the presence of significant thicknesses of fine clayey alluvium explains this zoning.

### 6. Messages to remember

Clays are found everywhere in nature.

They are at the crossroads of many sciences and technologies.

Their properties are derived from their sheet structure.

Present in the subsoil of alluvial sites, their behaviour generates difficulties for civil engineering structures

#### Notes and references

Cover image. Leaning Tower of Pisa. [Source: Kistel1 (CC BY-SA 4.0)]

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