Clay/water mixture by use of nano-sized water droplets “dry-water”

Mélange argile/eau à l'aide de gouttelettes d'eau de taille nanométrique "eau sèche”

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ABSTRACT: Dense clay can be used for sealing of boreholes and isolation of waste containers. Expansion of the clay to fill the space between containers and confining rock takes place by uptake of water of the clay, which thereby provides effective isolation. The issue is to prepare clay inserts with properly selected water content. The paper describes preparation of clay seals by mixing air-dry clay powder with nanoparticles of water droplets coated with very thin shells of a hydrophobic silicious substance (“dry water”). It behaves as dry powder and is easily mixed with dry clay. On compaction to the desired density the shells break into microscopic fragments while water becomes homogeneously distributed in the mass. Laboratory tests verify that the properties of clay prepared in this way are the same, or better, than of commonly saturated clay.

RÉSUMÉ : On peut utiliser de l'argile dense pour sceller les forages et isoler les conteneurs de déchets. L'expansion de l'argile pour remplir l'espace entre les récipients et la roche confinant a lieu par absorption d'eau de l'argile, ce qui fournit ainsi un isolement efficace. La question est de préparer des inserts d'argile avec une teneur en eau correctement sélectionnée. L'article décrit la préparation de joints d'argile en mélangeant de la poudre d'argile séchée à l'air avec des nanoparticules de gouttelettes d'eau revêtues de coquilles très minces d'une substance siliceuse hydrophobe ("eau sèche"). Il se comporte comme une poudre sèche et se mélange facilement avec de l'argile sèche. Lors du compactage à la densité souhaitée, les coquilles se cassent en fragments microscopiques tandis que l'eau se répartit de manière homogène dans la masse. Des essais en laboratoire vérifient que les propriétés de l'argile préparée de cette façon sont les mêmes, ou mieux, que les argiles couramment saturées.

KEYWORDS: dry-water, nano-particles, clay/water mixing, water saturated clay.

1 INTRODUCTION

In experimental soil mechanics and a number of applied powder technologies it is desired to prepare material samples with a defined, homogeneous degree of water saturation. This is the case in applied food technology and for concepts for sealing of boreholes and sites for disposal of hazardous waste making use of dense smectite-rich clay (Yong et al, 2010). The seals can be placed in the form of precompacted expandable clay objects with specified geometry, dry density and water content (Ting, 2015). The most common way to saturate artificial clay samples in soil meachanical laboratories for testing and for preparing borehole seals is to confine them in oedometer-type cells with filters at the ends and let water be taken up by suction through the filters, but this is a tedious diffusion-type process. The slowness is exemplified by the about one week long time required for saturation of a 2 cm thick sample of dense smectite-rich clay taking up water from two ends, and the 16 weeks required for a 4 cm thick sample, and the 2 year long time needed for saturating a sample with 10 cm thickness. For preparing a 20 cm thick clay block for borehole sealing saturation takes about 20 years. We describe here a novel, quick procedure for preparing clay blocks of any size with homogenously distributed porewater by mixing air-dry clay powder or granulate with “dry water” (DW) consisting of droplets of water coated with very thin shells of a silicious substance (Forny, 2008). On compaction to the required density the shells break into fragments that are smaller than silt grains. The released water becomes uniformly distributed in the mixture. The new presented method for preparing clay samples, like borehole seals, is based on the principle that compaction of homogeneously fine, air-dry clay granules mixed with uniformly distributed dry-water droplets under a pressure of at least 20-40 kPa crushes the latter, by which the expelled water is quickly distributed among neighboring clay particle aggregates. The research presented in this paper is based on work by Bomhard, 2011 and followed up by manufacturing DW-wetted clay seals for full-scale borehole sealing projects. Pre-saturated blocks of dense clay, serving as isolation of containers with heat-producing high-level radioactive waste in repositories, minimize the temperature of the seals and containers and thereby reduce their corrosivity. An essential question, dealt with in the present paper, is if the remainders of the crushed silicious shells of the droplets are big enough to significantly make the physical properties of the DW clay deviate from those of conventionally saturated clay.

2 MATERIALS

2.1 “Dry water”

“Dry water” consists of water droplets contained in spherical, very thin shells of hydrophobic, fumed silica particles (Forny, 2009, Bomhard, 2011). The powder is dry and lyophobic, and has a water content by weight of about 90%. It flows like flour when poured into laboratory cells or large containers for compaction to the desired dry density. The angle of internal friction is reported to be at least 44º (Bomhard, 2011).

The silica coating repels water and prevents the water droplets from combining at ordinary temperature. The material is produced on an industrial scale by exposing volatile chlorosilanes to high temperature by flame hydrolysis and reaction with methyl chlorosilanes after cooling. Its primary use is as filling agent for plastics and as additive in food production (Lankes, 2006; Bomhard, 2011). It is available on the market by different suppliers. Wacker Chemie AG delivered DW in the present study. The size distribution was 1-10 μm and the specific surface area 20 to 35 % of that of smectite clay. The residual silanol content of the hydrophilic silica is 25 % and the carbon content about 2.8 % of the solid part of the DW.

2.2 *Clay seals*

The tightening component of a borehole seal is dense expandable clay (smectite) that sorbs water from the confining rock or soil by its potential to bind water between the 1 nm thick Si/O and Al/Mg/OH lamellae (Pusch, 2015). It is tightly contained in a perforated metal tube that is fitted into the hole to be sealed, see Figure1. The clay expands through the perforation and embeds the tube at a rate that depends on the density and degree of water saturation, Figure 1. The expansion, which can be up to about 3 times, is caused by establishment of one, two or three water molecules thick intraparticle hydration layers. The expansion is uniquely controlled by the dry density and access to water.

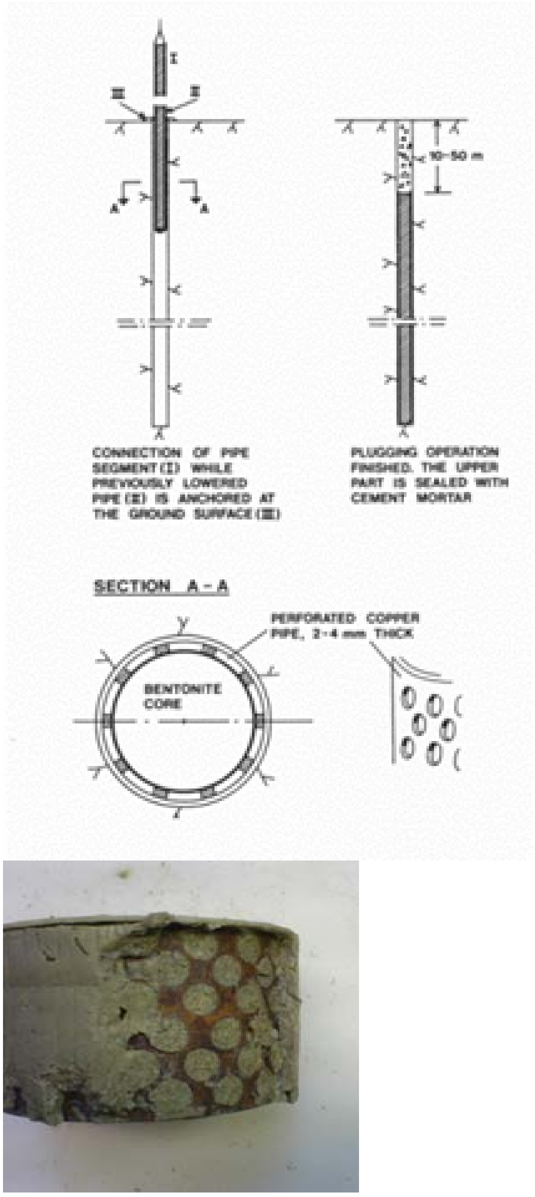

Figure.1. Borehole sealing by use of dense smectite clay. Top: Sealing stages. Lower: 24 h plug of clay migrated from the dense clay core in the perforated tube to fill the narrow space between tube and rock (Pusch, 2015).

2.3 *Interaction of clay and DW*

Figures 2 and 3 show schematically how DW droplets are linked in the microstructure of smectite clay after mixing dry clay powder and DW. The strongly hydrophilic clay considered in this paper will suck up water given off from crushed DWs that are uniformly distributed in the DW/clay mixture.

Compression of clay with DW droplets makes them break at a pressure of 40-80 kPa and cause subsequent uniform wetting of the clay. The obtained degree of water saturation can be 100 % or lower, depending on the needs; the required amount of water is calculated and the corresponding amount of DW added by mixing. Pre-saturated blocks of dense clay for borehole sealing and isolation of waste canisters in a repository perform differently depending on the ultimate degree of water saturation. An important question dealt with in the present paper, is whether the remainders of the crushed silicious shells of the droplets can significantly affect the physical properties of the DW clay and make them deviate from those of conventionally saturated clay.

Figure 2. Microstructural voids with DW droplets between 3-7 nm thick stacks of smectite lamellae in uncompacted air-dry smectite clay (Pusch, 2015).

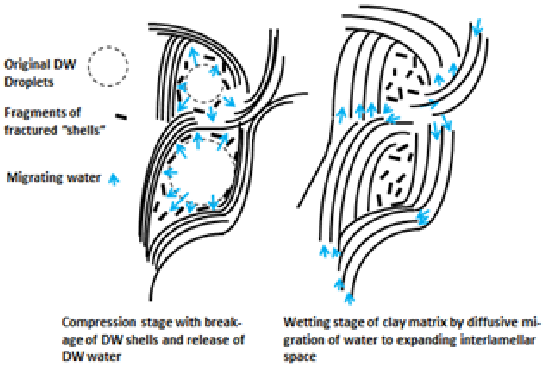

Figure 3. Redistribution of DW water at compaction (left), and subsequent maturation of the clay matrix (right).

3 EXPERIMENTAL

3.1 Clay and DW material

The clay used in the study was a mixed-layer (illite/smectite "Holmehus") clay belonging to a Paleocene formation of Tertiary age with 55 % expandable minerals, mainly montmorillonite (Yang, 2015). Quartz content is about 15 % including cristobalite and amorphous silica and feldspars, pyrite and mica make up about 7 %. The content of residual silanol and carbon makes up less than one weight percent.

The DW material was prepared by adding 50 g pyrogenic silica powder (Whacker HDK2000) to 500 g of distilled water in a mixer and agitating it for about 2 minutes. By running the mixer at 20,000 rpm for 2 minutes the DW appeared as light, dry powder for being mixed with clay. Figure 4 illustrates the size of the droplets and the thickness of their coatings ("shells") of hydrophobic silica. Since the surface of DW particles is entirely covered by hydrophobic material the material is felt dry and performs as dry powder of sugar or flour.

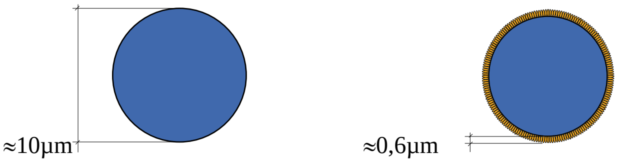

Figure 4. Silicious DW droplet with coating ("shell").

The hydration energy of DW droplets is mirrored by the release and evaporation of water from them in different environments. Left in air the confined water diffuses slowly through the coatings of the droplets, a process that successively releases the water contained in them. In practice, only freshly prepared DW should be used.

3.3 Mixed clay and DW

DW material was prepared for reaching complete saturation of clay after compaction in oedometers. Samples with the dry densities, 1370, 1800 and 1900 kg/m3, were made for determining the hydraulic conductivity and expandability. The conductivity was determined by applying a hydraulic gradient of 67 m/m (meter water pressure difference per meter flow length) at percolation with distilled water. The filters confining the samples at each end were connected to burettes and the pressure was adjusted to maintain constant clay volume. The oedometer cells were mounted in a compression apparatus for recording the expandability in the form of swelling pressure.

3.4 Results

3.4.1 Chemical constitution

EDX analysis of dried DW-clay indicating presence of iron, calcium, sulphur, silica and aluminum. The latter element represents clay particles and silica shells of DW. Fe was present both as sorbed exchangeable ion in and on the clay minerals, in shell fragments, and in precipitated complexes in the natural clay. The atomic spectrum of the remainders of crushed droplet shows Si and Fe to be important cationic components. The role of chlorine from the pyrogenic substance, if still present, is unimportant because of its coupling to the silicious component and because it makes up a very small fraction of the solid mass.

3.4.2 Microstructural constitution

Figure 5 illustrates the typical microstructural appearance of DW clay without visible residual shell fragments. The photo reveals the strong variation in mineral composition (quartz grains are white, feldspars brown and clay minerals greenish). The row of small black dots are organic remainders. Open voids cannot have been larger than 20 µm. The micrograph was taken of the surface of a section exposed by layerwise tape peeling.

Figure 5. Holmehus clay microstructure. Optical micrograph of moist DW-saturated clay with 1570 kg/m^3 wet density (magnification 250x).

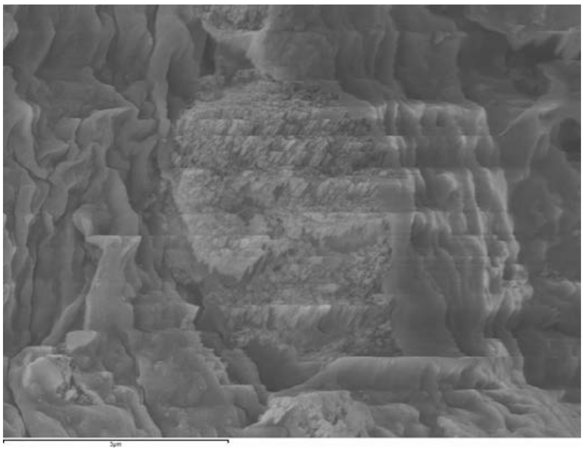

Figure 6. SEM micrograph showing remnants of a crushed DW particle with a size of about 2 µm.

3.4.3 Geotechnical data

The hydraulic conductivity of i/DW-saturated clay and ii/clay conventionally water saturated is given in Table 1.

Table 1. Comparison of hydraulic conductivity (K, m/s) and swelling pressure (ps) for tests of DW-saturated Holmehus clay and samples prepared by conventional wetting, i.e. by suction of air-dry clay powder compressed and confined in oedometer cells for saturation and percolation with distilled water (RW).

Wetting type	Dry density (kg/m^3)	Saturated density (kg/m^3)	K (m/s)	P_s, (MPa)
DW	1430	1900	1E-13	3.2
DW	1270	1800	7E-13	2.2
DW	980	1570	1E-10	0.3
RW (1)	1430	1900	2E-12	2.7
RW (1)	1270	1800	2E-11	1.3
RW (2)	1065	1670	1E-10	0.3

(1)Ting, 2015; (2) Equivalent clay with slightly higher montmorillonite content

The DW-saturated clay was consistently somewhat less conductive than the conventionally wetted clay, presumably by more uniform distribution of water and more homogeneous microstructural constitution. The swelling pressure exhibited a similar pattern: the values are higher for the DW samples than for the conventionally saturated clay. As for the conductivity, this is believed to be caused by a more uniform distribution of water and a more homogeneous microstructural constitution of the DW-clay. The higher values for DW clay proved that the very fine fragments of silicious shells did not hinder the smectite stacks to hydrate and expand. They were confined in small voids in the clay.

4 DISCUSSION

The essential matters to be discussed and further investigated are:

- Were the expectations fulfilled?
- Is there any scale effect or limitations respecting the homogeneity of DW-wetted smectite clay objects like borehole seals?
- Is there any “after-effects” in the form of syneresis and spontaneous fissuring of DW-wetted smectite clay?
- Does the porewater of DW clay behave as in ordinarily saturated clay?

The response to the first questions is that the microstructural models forming the basis for predicting the water saturation process apply and confirm that the performance of conventionally wetted clay and clay saturated by DW are similar. Scale-dependence has not been investigated but handling of differently sized DW-wetted clay samples shows no differences and preliminary tests indicate that the technique can be applied for preparing seals for large-diameter boreholes. The matter of physical processes related to long-term storage needs further study but for clay seals exposed to external water pressure in practice, no desiccation or phase separation are expected. Nuclear magnetic resonance for revealing differences in association of clay minerals and porewater are planned.

5 CONCLUSIONS

The major conclusions from the study are:

- DW saturation of clay made by adding this apparently dry substance to air-dry clay material by thorough mixing and subsequent compaction causes instant uniform wetting and quick homogenization. The very thin silicious coatings of DW droplets break on compaction under less than 100 kPa pressure and create numerous silicious fragments smaller than 1 µm, which assemble in small clay voids without reducing the expansion potential of the clay but causing slight reduction of the hydraulic conductivity by clogging.
- The expandability and swelling pressure of DW-saturated clay is higher than of ordinarily wetted smectite clay since expansion and loss in density of clay particles by expansion into microstructural voids is hindered by such fillings.
- DW wetting gives immediate saturation since it takes place in conjunction with the compaction of the clay. The advantage of the method is that the samples instantly reach a state of uniform distribution of porewater at any desired degree of water saturation. The technique is economically and practically feasible, especially for preparation of big blocks for which conventional ways of saturation require many years or decades.
- Further research is desired for investigation of matters listed under DISCUSSION and of the role of economics related to the time and cost for preparing prewetted and compacted DW-wetted clay objects of both small and large size. Another option is to investigate the possibility of manufacturing suitably wetted concrete in containers from which it can be extruded and compacted in boreholes for serving as seals or supports.

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7 REFERENCES

Bomhard, J,. (2011). Dry Water. Master of Sci. Thesis. Luleå University of Technology, Dept. Civ., Environmental and Nat. Res. Engineering, Sweden.

Forny, L., (2009). Influence of mixing characteristics for water encapsulation by self-assembling hydrophobicsilica nanoparticles. Powder Technology, Vol. 189, No2, (p.263).

Lankes, H., (2006). Liquid absorption capacity of carriers in the food technology. Powder Technology, Vol.134, No 3, (pp.201-209).

Pusch, R., (2015). Bentonite Clay. Taylor and Francis Group. (ISBN-13;978-1-4822-4343-7).

Pusch, R., 1983. Borehole sealing for underground waste storage. ASCE Proc. J. Geotechnical Engineering. Vol. 109, No.1 (113-119)

Pusch, R., Yong, R.N., (2010). Stiffening of smectite buffer clay by hydrothermal effects. Engineered Geology, Vol. 116, (pp.211-31).

Xiaodong, L., Prikryl, R., Pusch, R., (2011). THMC-testing of three expandable clays of potential use in HLW repositories. Applied Clay Science, Vol.52 (pp.419-427).

Yang, T., (2015). Borehole sealing with expandable buffer clays in HLW disposal; Lab-scale performance. Licentiate thesis, Division of Geotechnical Engineering, Luleå University of Technology, Sweden. ISBN: 978-91-7583-474-0, (80 pp)

Yong, R.N., Pusch, R., Nakano, M., (2010). Containment of High-Level Radioactive and Hazardous Solid Wastes with Clay Barriers. Taylor & Francis, Spon Press, London (468 pp).