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SWELLING INHIBITORS FOR CLAY MATERIALS: COMPARISON OF INDUSTRIAL AND NATURAL SURFACTANTS

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Abstract

Humidity variations due to the climate of Western Europe induce many problems in clay-rich building material. Indeed, the repetition of wet/dry cycles leads to swelling and shrinkage phenomena. Thus, cracks and material loss may appear. A solution to limit the volume change of bulk material consists of using surfactants. This study focused on the behavior of swelling montmorillonitic clay mixed with a series of 9 surfactants: 3 diaminoalkanes with different carbon chain lengths, polyethylenimine and triton X-100 (industrial surfactants) were compared to natural products (bio-inspired/bio-sourced) such as lawsone, pork gelatin, saponin and dopamine.

The swelling at the clay sheet scale before and after treatment was observed on powders using X-ray diffraction analyses after conditioning at low and high relative humidity, while the swelling deformation at macroscopic scale was assessed on specimens submitted to imposed hygric conditions via the continuous measurement of axial deformation. In complement, the microstructure was investigated by mercury intrusion porosimetry. Diaminoalkanes appeared to be the more efficient swelling inhibitors for the crystalline swelling, in particu-

lar, those with long carbon chains. Nevertheless, some of natural additives also showed a high capacity to reduce swelling at both macroscopic and microscopic scales which would suggest the possible use of less toxic additives/natural as swelling reducer.

Introduction

Clay minerals belonging to the smectite family are able to swell when they are in contact with water (vapor or liquid). When the relative humidity (RH) in the air becomes low, the clay minerals reach a new equilibrium inducing a contraction of their volume. The repetition of swelling/shrinkage cycles at clay minerals microstructure scale is then responsible for pathologies (Doehne et Price 2010) like cracks, shedding or flaking. A solution to avoid these phenomena consists of using surfactants as swelling inhibitors.

Surfactants are amphiphilic chemical molecules with a hydrophilic head and a hydrophobic body. The head may be either cationic (positive charge), anionic (negative charge), amphoteric (one positive and one negative charge depending on the pH of the environment) or non-ionic (no charge).

Swelling inhibition may occur by cationic exchange between the interlayer cations of the clay minerals and the cationic surfactants (Wangler et Scherer 2009; Bourgès et Simon 2018) or by pore blocking (Li et al. 2018) with non-ionic surfactants, especially.

The aim of this study is to compare the efficiency on the crystalline and macroscopic swelling of industrial surfactants (α - ω -diaminoalkanes (Wangler et Scherer 2009; Bourgès et Simon 2018), polyethylenimine (Guancheng et al. 2016), triton X100 (Ahmed Muherai, Junin, et Badr Binmerdhah 2009)) and natural products (pork gelatin (Li et al. 2018), saponin (Moslemizadeh et al. 2017), betaine, dopamine (Xuan et al. 2013) and lawsone (Moslemizadeh, Reza Shadizadeh, et Moomenie 2015)). Experiments were conducted on clay powders as well as on compacted clay/sand/surfactant specimens.

Materials and methods

1 – Materials

Clay: the tested clay was a montmorillonitic clay from Sardaigne (from ABM company) with a CEC = 102.1 ± 6.1 meq/100 g (Norme NF EN ISO 23470 2018). It contains more than 95 % of montmorillonite with small amount of kaolinite, quartz and illite/muscovite.

Sand: siliceous sand from a quarry near Paris with

a granulometry 0/1 mm was used to manufacture compacted clay/sand(/surfactant) mixture.

Surfactants: various surfactants (from Sigma-Aldrich) were used: diaminoalkanes with a 2, 3, and 8 carbons chain, dopamine, polyethylenimine, lawsone, pork gelatin, saponin, triton X100 and betaine (see Tab. 1).

2 – Sample preparation

2 – 1) Clay powder treatment: montmorillonite powder was added to a 1.96 wt% aqueous surfactant solution with a solid/liquid ratio of 3 %. After stirring for 24 h and centrifugation, the collected clay mud was dried at ambient humidity and temperature before being grinded to pass through a 63 μ m sieve. The powder was then conditioned at different relative humidities (RH) using desiccators with silica gel for RH \approx 10 % and K₂SO₄ saturated salt solution for RH \approx 95 % at lab temperature.

2 – 2) Clay/sand/surfactant specimen preparation: the reference specimens (without any surfactant) were manufactured by mixing 23.62 wt% of montmorillonite, 55.12 wt% of sand and 21.26 wt% of ultrapure water before a 48 h hours rest for homogenisation. After rest and before the molding, the pastes were kneaded for homogenisation. For the law, sap, bet, DC2, DC3 and DC8-treated specimens (see Tab. 1 for abbreviations), the mass proportions of montmorillonite, sand, ultrapure water and surfactant were 23.35 wt%, 54.47 wt%,

Table 1: List of the tested surfactants. A: amphoteric, CE: cationic exchange, NI: non-ionic; WR: water repellent, HB: hydrogen bonding, EI: electrostatic interaction.

Index	Name	Abbrev.	Formula	Type	Mechanism
(1)	Betaine	Bet	(CH ₃) ₃ N ⁺ -CH ₂ -C(O)O ⁻	A	CE and EI
(2)	Saponin	Sap	Association between a sugar and a steroid or an alkaloid steroid or a triterpene	NI	WR
(3)	Reference	Ref	–	–	–
(4)	Lawsone	Law	(C ₆ H ₄)-C(O)-C(OH)=CH-C(O)	NI	WR and HB
(5)	Triton X-100	TX100	C ₈ H ₁₇ -C ₆ H ₄ -(OCH ₂ CH ₂) _n OH ; n \approx 10	NI	HB
(6)	Pork gelatin	Gel	Mix of several amino-acid: glycine, proline, valine, lysine, alanine, arginine	NI	HB, WR and EI
(7)	Dopamine	Dop	(OH)2(C ₆ H ₃)-(CH ₂) ₂ -NH ₃ ⁺	C	CE and EI
(8)	Polyethylenimine	PEI	{-CH-[(CH ₂) ₂ -NH-] _n -CH-}	C	CE
(9)	1,3-diaminopropane	DC3	*H ₃ N-(CH ₂) ₃ -NH ₃ ⁺	C	CE
(10)	Ethylenediamine	DC2	*H ₃ N-(CH ₂) ₂ -NH ₃ ⁺	C	CE
(11)	1,8-diaminooctane	DC8	*H ₃ N-(CH ₂) ₈ -NH ₃ ⁺	C	CE

21.01 wt% and 1.17 wt%, respectively. In order to have a plastic paste able to be mold, the proportions in PEI and gel treated specimen were fixed to 23.55 wt%, 54.95 wt%, 21.20 wt% and 0.30 wt% respectively. 22 mm diameter and 45 mm height cylindrical specimens were molded under a soft static compacting charge until a constraint of 0.15 MPa was reached. After molding and demolding, the specimens were dried at 23 °C at 50 % RH for at least 5 days before testing.

3 – Analytical methods

3 – 1) *X-ray diffraction (XRD)*: a D8 Advance from Brüker, Co Ka anode ($E = 40\text{ kV}$, $I = 35\text{ mA}$) was used. Conditioned powders were mounted by front loading on sample holder and a kapton film ($7.5\text{ }\mu\text{m}$ thin) was used to prevent hygric variation during analysis.

3 – 2) *Mercury intrusion porosimetry (MIP)*: for the specimens pore network investigation, MIP analysis with an Autopore™ IV 9500 (from Micromeritics) were realized. After drying under air, samples were freeze-dried before analysis at low and high pressure using a 10 and 30 s stabilization time, respectively. The pressure applied to mercury was ranged from 3,6 kPa to 413 MPa.

3 – 3) *Linear swelling measurement*: the linear deformation of the specimens under hygric condition (30 and 90 % RH at 23 °C in climatic chamber) was continuously measured using Linear Variable Differential Transformer (LVDT) axial displacement sensors.

Results and discussion

1 – Impact of surfactants on crystalline swelling

The surfactant effect on the crystalline swelling, namely the change of interlayer spacing d (in Å) was measured with XRD on clay powders conditioned at low and high humidity, respectively 10% RH and 95% RH (Fig. 1). The difference between interlayer spacing at low and high humidity (Dd) was calculated (Fig. 2).

The Figure. 1 shows that surfactants had various effects on the d -value when the reference (n°3)

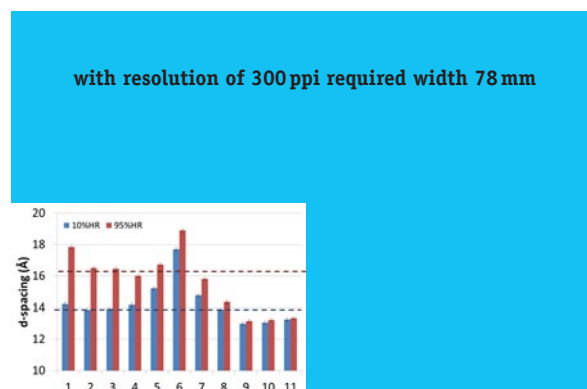


Figure 1: Interlayer spacing of the montmorillonitic clay at low (blue lines) and high (red lines) relative humidity. (products in X-axis are given in table 1).

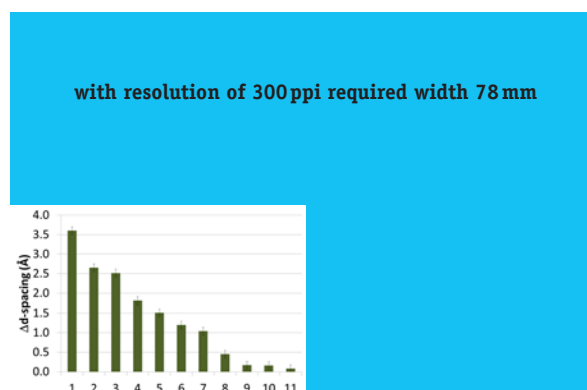


Figure 2: Treated montmorillonite powder Dd spacing corresponding to $d(95\%RH) - d(10\%RH)$ (products in X-axis are given in table 1).

corresponding to the clay without treatment was compared to other samples. The gelatin-treated and DC3-treated powders (n°6 and n°9, respectively) presented a $d = 17.7 \pm 0.1\text{ Å}$ and $d = 13.0 \pm 0.1\text{ Å}$ at $RH = 10\%$, which is in good agreement with previous studies (Li et al. 2018; Wangler et Scherer 2009). The reference (n°3) presented a $d = 14.0 \pm 0.1\text{ Å}$. All the other tested samples showed a d -value within that range. The difference in behavior (either increasing or decreasing the d -value compared to the reference) may be a consequence of the size of the surfactants molecules and/or the clay/surfactant interaction. Indeed, gelatin consists of very large molecules, comparable to a polymer. Once in suspension with clay, the clay sheets enlarge (due to the presence of liquid water), allowing the gelatin molecules to enter the interlayer space. Thus, the d -value in-

crease would be linked to steric forces and not to water uptake. When the gelatin-treated clay was submitted to low RH, the heavy gelatin molecule prevented the collapse of the interlayer space. By contrast, whatever the relative humidity, the DCX ($X = 2, 3, 8$) decreased the interlayer spacing compared to the reference. We assume that the tested diaminoalkanes molecules had two $-\text{NH}_3^+$ groups on both side of the carbon chain (at pH value below 12). Such protonated groups are able to make electrostatical bonds with the negative charge on the basal surface of clay sheets, whose stacking creates interlayer spaces. Then, neighbouring clay sheets could be attached together by strong electrostatic forces, which decreases the interlamellar space and prevents its change in presence of water. In this case, the diaminoalkane molecules play a role of cation exchangers with a strong affinity for the clay surface. Furthermore, the length of the carbon chain does not seem to influence the d-value, as it is observed with the alkylammonium chains ($[(\text{CH}_3)_3\text{N}-\text{C}_n\text{H}_{n+2}]^+$) (Ipek Nakas et Kaynak 2009). Additionally, the Dd-spacing of the montmorillonite powders in Figure 2 varied too with or without treatment. The untreated montmorillonite showed a Dd equal to 2.5 \AA . Betaine and saponin treatments induced larger Dd-spacing than the one in the reference sample (an 43% and an 6% increase were observed, respectively). The increase observed for betaine surfactant is probably due to the high capability of betaine molecules to adsorb itself water molecules. As a proof, a dynamic vapor sorption (DVS) analysis realized on this product showed more than 500% water uptake of its initial weight at 90% RH. In the case of saponin, a visible biocolonization at high RH producing filaments may lead to the higher swelling compared to the reference. Indeed, saponin is a plant-derived compound (based on sugar) and its bio-origin makes it an environmental friendly surfactant, but it is still submitted to biodegradation. In conclusion, the most efficient surfactants for reducing the crystalline swelling were the cationic ones, especially the diaminoalkanes as well as dopamine and polyethylenimine to a lesser extent.

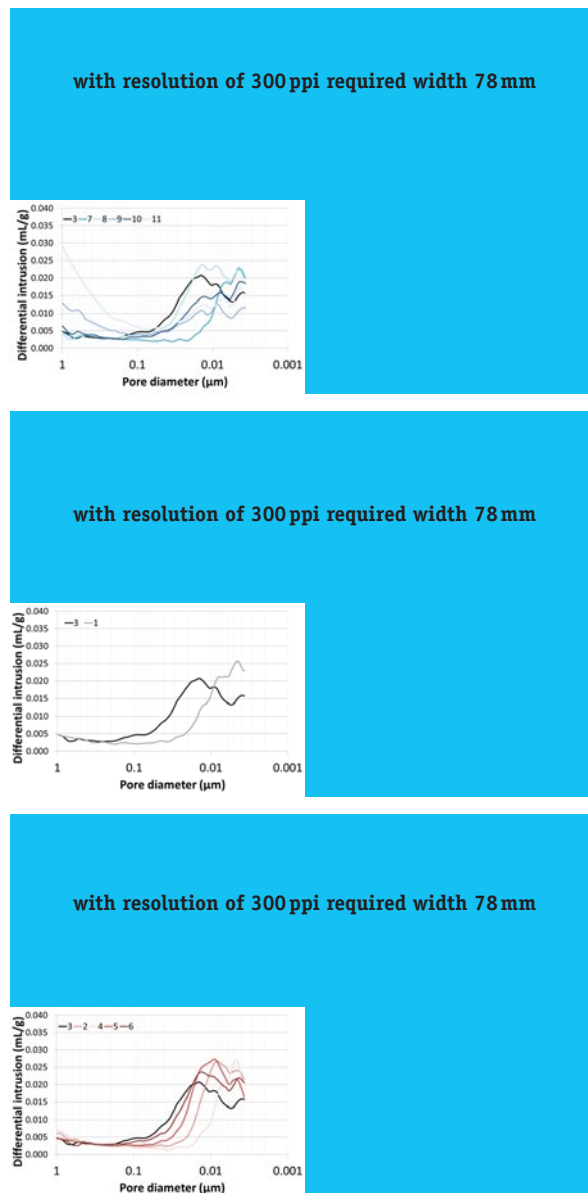


Figure 3: Nanopore size distribution measured on specimens. (a) cationics surfactants ; (b) amphoteric surfactant ; (c) non-ionic surfactant.

2 – Pore size distribution

For assessing the impact of the treatment on the microstructure of the specimens, mercury intrusion porosimetry was applied. The pore distributions are given by the differential cumulative mercury intrusion ($dV/d\log(d)$ in $\text{mL}/\text{nm}/\text{g}$ with $d = \text{pore diameter}$). Each treated specimen presents similar curve profiles, namely two families of pore size with macropores ($d = 2\text{--}400 \mu\text{m}$) and nanopores ($d = 0.003\text{--}0.1 \mu\text{m}$).

Figure 3 and Figure 4 show the nanopore and macropore size distribution on untreated and treated

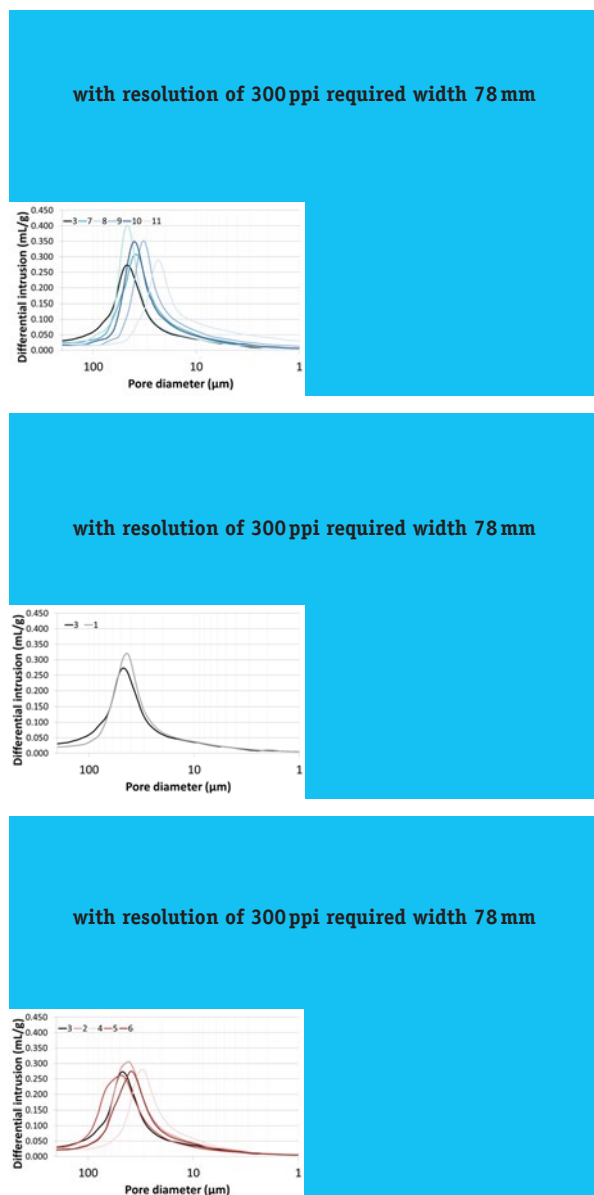


Figure 4: Macropore size distribution measured on specimens. (a) cationics surfactants ; (b) amphoteric surfactant ; (c) non-ionic surfactant.

specimens. The capillary pores around $2\mu\text{m}$ were almost absent in such microstructure governed by the particle size distribution of 0/1mm sand and the low fraction of montmorillonite (30%). The total porosity of samples and their volumetric mass (ρ , air dried at 25°C) are summarized in Table 2.

The total open porosity measured by MIP was comprised between 29.0% (law) and 33.3% (DC8). The lawsonite (as used) was a fine powder product, partially undissolved in water. Thus, particles may fill the porosity, that become unaccessible for mercury.

Table 2: Total porosity (determined by MIP measure) and volumetric mass of the specimens.

Product	Bet	Sap	Ref	Law	TX100	Gel
n (%)	29,7	32,3	30,5	29,0	32,0	30,7
ρ (g/cm ³)	1,75	1,75	1,76	1,79	1,65	1,76
Product	Dop	PEI	DC3	DC2	DC8	
n (%)	31,6	32,0	31,4	31,2	33,3	
ρ (g/cm ³)	1,75	1,77	1,73	1,74	1,70	

Furthermore, a tendency for the 3 diaminoalkanes is visible: DC2, 3 and 8-treated specimens had a 31.2%, 31.4% and 33.3% total porosity, respectively. Thus, the longer the carbon chain was, the higher the total porosity was.

The macropore size distribution also appeared to depend on the surfactant treatment. Indeed, the mean pore diameter fluctuated between $24\mu\text{m}$ (for DC8, n°11) and $48\mu\text{m}$ (for PEI, n°8). These differences may be due to the compaction rate during the manufacturing of the specimens. Indeed, specimens were molded at the same water content. Consequently, the consistence of the clay/sand/surfactant pastes varied a little with the type of added surfactant. For example, the DC8-treated paste was more fluid (with water migration/drainage during the compaction) than the paste with PEI, which was less plastic than the untreated paste. So the compaction rate to reach the 0,15 MPa compressive stress (taken as the target to stop the compaction) varied from one specimen to another.

Some products seemed to decrease the nanopores amount, especially for law (n°4) and dop (n°7)-treated specimens which had smaller pores than the reference untreated specimen. The DCX (n°9, 10 and 11) and the PEI (n°8) were characterized by three nanopore size distribution located on Figure 4 with the dash lines at $d = 12\text{--}14\text{ nm}$, $d = 7\text{--}8.8\text{ nm}$ and $d = 3,9\text{--}4.5\text{ nm}$. The same tendency appeared on PEI-treated specimens even if the PEI is a bigger molecule compared to the diaminoalkanes, but both have $-\text{NH}_3^+$ groups in common. Further results (repeatability of the measure for example) are required to better understand such fine microstructure at clay aggregates scale.

3 – Macroscopic swelling

The Figure 5 shows the $D_{\text{dilatation}}$ (difference between the maximal dilatation at 90% RH and the minimal dilatation at 30% RH) measured specimens. As for the crystalline swelling, the bet-treated specimens (n°1) showed a higher swelling rate, probably due to the hydration of the product. Furthermore, the swelling deformation at macroscale was reduced by 27% with the DC2 (n°10), by 46% with the DC3 (n°9) and by 63% with the DC8 (n°11) compared to the reference. Thus, the longer the carbon chain of diaminoalkanes was, the more the swelling was reduced. This phenomenon is not visible on crystalline swelling with a total swelling inhibition with the three products. Note that TX100 (non-ionic surfactant) is as efficient as the cationic surfactants on the macroscopic swelling inhibition.

Conclusions

Except for the treatment with betaine and saponin, the tested surfactants showed good swelling inhibition properties. In particular, we observed a total inhibition of the crystalline swelling with the diaminoalkanes. The non-ionic products (except saponin) showed an intermediate effect (28 to 52% of decrease) compared to the cationic products. At the macroscopic scale, the most efficient product was the triton X-100 with a 61% swelling decrease compared to the untreated reference. After comparison, cationic surfactants decreased the swelling with an efficiency of only 27% for DC2 or 44% for dopamine. In this study the surfactants were used in excess but Bourgès et Simon (2018) showed that an excess of surfactant leads to a decrease of mechanical properties. So a compromise between the quantity of product, the dilatation rate and the mechanical properties still need to be realized.

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