# Consequences of using additives for reducing the amount of mixing water needed in the heavy clay ceramic industry

Considerations related to energy savings and technical production aspects

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TCKI is structured as a foundation and serves about 75 participating companies, primarily in the Netherlands and Belgium. The participants are comprised primarily of companies producing masonry bricks, clay pavers, roofing tiles, wall and floor tiles, sanitary ware, sewage pipes, windowsills, crest tiles, refractory and earthenware products. TCKI has a consultancy and measurement department, a drawing office and extensive laboratory facilities for providing the participants with the necessary services.

**Summary**

At the request of the 'Koninklijk Verbond van Nederlandse Baksteenfabrikanten' (KNB = Royal Association of Dutch Brick Manufacturers) and SenterNovem, an investigation was carried out into the technical production aspects, the energy related aspects and the economic aspects of adding additives to reduce the amount of mixing water needed in clay formulations. The objective was to reduce the amount of energy needed for the drying process. To that end, the (theoretical) modus operandi of most such agents was described and an investigation was carried out into the use of three selected additives (in a dosage of several tenths of a percent).

In particular, the effect was investigated on the concentration of organic carbon, the amount of mixing water needed, the consistency stability, the moisture transport, the green product strength, the physical and mechanical characteristics of the fired product, and the leaching behavior of the fired products.

The conclusion was that, in reality, there are insurmountable obstacles with regard to moisture conductivity. This is negatively impacted to such an extent that crack-free drying within an acceptable time frame is no longer possible. The only way to ensure that the reduction in moisture transport is acceptable is to limit the reduction in the amount of mixing water needed to a very slight reduction. As a result, an analysis of the energy related aspects and the economic aspects was not carried out.
The only possible aspect that deserves further consideration is the addition of such additives to products that are extruded at the shrinkage limit (very stiff extrusion) or the use of the additive, Textrol EA, a lecithin which can be expected to itself act as a lubricating agent, which in the case of extrusion processes could possibly result in an improved operational process and a lower amount of required mixing water.

**Introduction**
Energy-saving in relation to the production processes in the ceramic industry is increasingly becoming a topic of discussion. In the first place, there is increasing political pressure to reduce the consumption of energy, in particular energy derived from fossil fuels. In the second place, the energy used for production is becoming an increasingly large cost item.
Generally speaking, most of the energy used is needed to ensure evaporation of water from the products before they can be fired. In addition, a great deal of energy is also needed for firing the products in the kilns.

There are various ways of trying to further reduce the consumption of energy within a company. One possible way is to reduce the amount of water in the wet shaped product. It may then be possible to reduce the amount of energy needed to dry it. Important aspects in this regard are that the production process itself does not become too difficult, that the appearance of the product does not change significantly, and that the physical and mechanical characteristics of the product are retained. Many of the products involved are also sold on the basis of an attractive exterior.

It is possible to reduce the amount of mixing water needed by reducing the amount of clay minerals in the clay recipe. An investigation into such an approach was carried out and published in KGK no. 2: 2007. The conclusion was that reducing the very fine particle percentage by mixing in sand (the cheapest additive in this regard) could have significant consequences for the technical production aspects of the process. However, in particular for the production of pressed masonry bricks, such an approach could result in justified energy and cost savings. In absolute terms, the amount of mixing water required can be reduced by 5% if the absolute loam percentage ( particles <10 µm) were to be reduced by 10% abs.

Another way to reduce the amount of mixing water required for shaping the products is the addition of small quantities of specific additives to the clay recipe. The additives involved fall under the category of *plastifiers*.
The possibilities created by the addition of such plastifiers have been investigated in the past inside as well as outside the Netherlands. In many cases, the reduction of the amount of mixing water required remained limited to a maximum of one or just a few percent in absolute terms. In very many cases, the technical consequences for the production process were not, or hardly, investigated.

At the request of the Koninklijk Verbond van Nederlandse Baksteenfabrikanten (KNB), TCKI carried out an investigation with the aim of obtaining additional insight into the types of additives, their effects, and the consequences for the product and the technical production processes. SenterNovem subsidized this investigation.

The following section provides an overview of the general aspects with regard to how plastifiers work and the results of an investigation into the addition of three selected additives.

**How do plastifiers work?**

The addition of a chemical additive with the aim of reducing the amount of mixing water needed to achieve the same shaping consistency usually also influences the rheological behaviour (flow behaviour) of the clay body.

This influence is often related to the fact that the use of various organic or inorganic additives impacts the thickness of the exchange layer of the clay minerals in which the exchangeable adsorbed cations are present on the surface. This adsorption of cations (positively charged particles) to the plate shaped clay minerals compensates for the shortage of electrical charge in the clay minerals. This linkage of compensating cations is not rigid and can be realized at a larger distance from the surface of a clay mineral (the linkage takes place in a so-called defuse exchange layer).

An exchange can take place, whereby a linkage also exists to any change in the concentration and type of cations available in the free pore water. Clay minerals will preferentially adsorb cations with a large electrical charge and/or cations with a concentrated charge present. In this regard, the preferred order will be as follows:

$H^+$, $Al^{3+}$, $Ba^{2+}$, $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$, $K^+$, $Na^+$, $Li^+$.

This preferential order is also influenced by the extent to which the hydration water surrounding the cations reduces the charge concentration of these cations.

An additional influence can be expected from organic or inorganic anions which enter into a precipitation reaction with cations that are exchanged with newly available cations. Such exchanges will progress further in this situation.

An equilibrium always develops between cations absorbed onto the clay minerals and cations which can move freely in the surrounding pore water. The extent to which the clay will behave in a more or less plastic fashion will depend on where this equilibrium lies and which cations are adsorbed to which clay minerals and to what degree.

This is related to the thickness of the exchange layer. This layer becomes thinner if the compensating cations are stronger and therefore bound more closely to the surface of the clay minerals, and the layer becomes thicker if this bond is less strong and therefore more diffuse (refer to preferential order). The thickness of the exchange layer can also be influenced by adsorption (also in this layer) of large anions, for example large negatively charged organic particles.

If the exchange layer is thin, the clay minerals will be able to approach each other quite closely, and mass-attraction forces will result in the formation of a rigid overall structure (similar to a house of cards) of clay minerals linked to each other. This results in a loss of plasticity, of the kind resulting from clay minerals sliding along against each other. In the case of a thick exchange layer, the clay minerals will approach each other less closely and no such overall structure will be formed. The result is a behavior characterized by maximum plasticity (see figure 1). The house of cards structure contains more water than a structure in which clay minerals are all oriented in one direction and can move alongside each other.

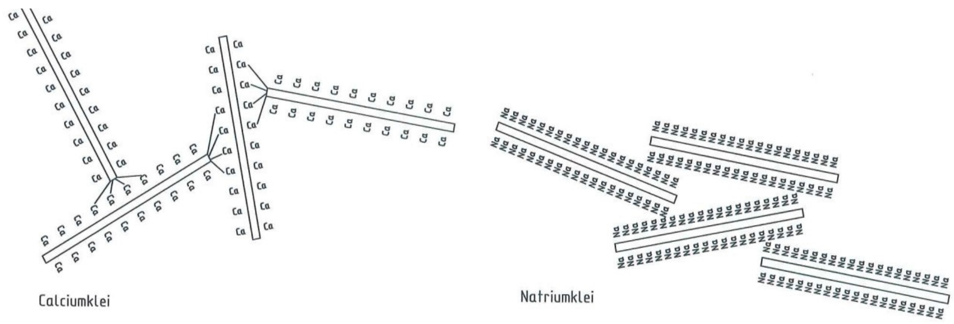


Figure 1: Clay minerals with calcium occupation (left) and clay minerals with sodium occupation (right)

In advance, the following aspects can be identified as deserving further attention in relation to the addition of such plastifiers:

- the basic recipe should contain such a small quantity of moisture that, after the addition of such a plastifier, the consistency of the clay remains adequate and there is no risk of deformation of the wet shaped products;
- it should be possible to add the additives at such an early stage in the clay preparation that the additive will be completely homogenized in the mixture and that there will be enough time remaining to ensure that the necessary exchange reactions on the surface of the clay minerals can take place;
- the addition of such plastifiers can have an influence on the sintering behaviour of the clay;
- the addition of such plastifiers can have a negative impact on the concentration of water-soluble salts in the clay, thereby increasing the risk of product discolorations;
- the addition of such plastifiers can have a negative impact on the moisture transport during the first drying phase of the bricks (the phase in which evaporation is still taking place at the surface of the product and in which evaporation is accompanied by shrinkage).

**The investigation**

The investigation focused in particular on the production of handmade and pressed bricks. However, the results are also applicable to the production of wire-cut products in the heavy clay ceramic industry (bricks, ceramic roof tiles, and possibly also drainage and sewer pipes).

The investigation into the addition of additives was carried out using recipes based on three different types of basic clays: a red-firing Maas clay, a yellow-firing “löss”loam and a white-firing Westerwald clay. These recipes cover a broad range of formulations as used in the Netherlands and Belgium.

With regard to the additives, the following three substances were used:

- Disal®: a “super” plastifier used in the concrete industry;
- KP 1131: a plastifier recommended by the supplier Zschimmer & Schwartz with exceptional abilities with regard to reducing the amount of mixing water needed;
- Textrol-EA: Lecithin: a product from the soya processing industry supplied by the Barentz company; it works more as a lubricating agent rather than on the basis of ion exchange on the surface of clay minerals.

For each clay ingredient, three different recipes were tried out per additive: a control (i.e. with no additive) and two dosage levels of the additive concerned. The dosage levels were chosen on the basis of the experience already acquired by TCKI and/or in coordination with the supplier. A low basic dosage level was used as well as a dosage at four times the basic level in order to obtain a good idea of the effects of the additive. For Disal® and for KP 1131, the dosages used were 0.1% and 0.4% in terms of mass, and for Textrol, 0.05% and 0.2% in terms of mass.

For each recipe, the following analyses were carried out: particle size distribution, specific surface area, concentration of organic carbon, and concentration of water-soluble components.

For the recipes with the highest dosage of additive and for the controls, the following additional analyses were carried out: the amount of mixing water needed to achieve a Pfefferkorn value of 15 mm (small measuring apparatus, height of drop = 100 mm, weight of object dropped = 780 g), consistency stability, and moisture conductivity behaviour.

For each recipe investigated, trial bricks were formed by hand (see figure 2). These trial bricks were then first dried in the laboratory area and then in a drying oven set to 40°C. After drying and before firing, the trial bricks were analyzed to determine the green strength (three

bricks per recipe). The products made using Maas clay and “löss”loam were fired at a top temperature of 1070°C. The products made with Westerwald clay were fired at a top temperature of 1200°C.
The fired products (three bricks per recipe) were analyzed for the following: net dry density, initial rate of water absorption, free water absorption, compressive strength, and leaching behaviour with respect to the critical opponents for the ceramic industry ($SO_4$, F, As, Mo, Cr and V).



Figure 2: Forming trial bricks by hand

**Results**
The addition of 0.4% Disal® leads to an increase in the concentration of organic carbon by circa 0.15%. Addition of 0.2% Textrol leads to an increase in the concentration of organic carbon by circa 0.10%. The addition of KP 1131 leads to only a very small increase in the concentration of organic carbon. These additions did not significantly affect particle size distribution and specific surface area.
The results of the investigation into the water-soluble components in the clay recipes are presented in Table 1.

Table 1: Water-soluble components.

| Recipe | Water-soluble components | | | | | Conductivity |
|---|---|---|---|---|---|---|
| | Ca | Na | K | Mg | S | |
| | % CaO | % $Na_2O$ | % $K_2O$ | % MgO | % $SO_4$ | mS/m |
| 100 % Maas | < 0.011 | 0.002 | 0.0013 | 0.0010 | 0.005 | 4 |
| Maas/ 0.4 % DISAL | < 0.011 | 0.028 | 0.0013 | 0.0010 | 0.062 | 10 |
| Maas/ 0.4 % KP 1131 | < 0.011 | 0.046 | 0.0012 | 0.0008 | 0.008 | 15 |
| Maas/ 0.2 % Textrol | 0.015 | 0.003 | 0.0010 | 0.0010 | 0.005 | 7 |
| 100 % löss | 0.026 | 0.005 | 0.0040 | 0.0011 | 0.012 | 13 |
| Löss/ 0.4 % DISAL | 0.027 | 0.041 | 0.0037 | 0.0018 | 0.089 | 20 |
| Löss/ 0.4 % KP 1131 | < 0.011 | 0.070 | 0.0023 | 0.0020 | 0.013 | 27 |
| Löss/ 0.2 % Textrol | 0.044 | 0.005 | 0.0036 | 0.0017 | 0.010 | 14 |
| 100 % Westerwald | < 0.011 | 0.002 | 0.0024 | 0.0017 | 0.004 | 5 |
| Westerwald/ 0.4 % DISAL | < 0.011 | 0.034 | 0.0073 | 0.0035 | 0.098 | 13 |
| Westerwald/ 0.4 % KP 1131 | < 0.011 | 0.069 | 0.0040 | 0.0060 | 0.009 | 24 |
| Westerwald/ 0.2 % Textrol | 0.012 | 0.002 | 0.0040 | 0.0030 | 0.004 | 8 |

The addition of additives to the clay always results in a larger or smaller increase in the concentration of water-soluble salts in the clay. This increase was greatest for the addition of KP1131 and DISAL and the sodium component. In these materials, sodium is also the effective agent when it comes to reducing the amount of mixing water needed. However, if this component is transported to the surface during the drying process and accumulates there, it could lead to an undesirable divergent surface colour as well as 'stickiness' in the product. The addition of DISAL leads to an increase in the concentration of water-soluble sulphate. If this compound is transported to the surface during the drying process, it can lead to a white discoloration on the surface, which would be particularly visible on those parts of red-coloured and dark coloured products especially parts not treated with sand. The addition of Textrol has only a limited effect on the quantity of water-soluble calcium.
The results with regard to water retention, consistency stability, and moisture conductivity coefficient are presented in Table 2.

Table 2: Water retention, consistency stability and moisture conductivity coefficient.

| Recipe | Moisture content at a Pfefferkorn residual height of 15 mm | Consistency stability | Moisture conductivity coefficient |
|---|---|---|---|
| | % | % moisture per mm residual height | $m^2/s$ |
| 100 % Maas | 25.7 | 0.35 | $8.1 \times 10^{-8}$ |
| Maas/ 0.4 % DISAL | 24.3 | 0.28 | $3.8 \times 10^{-8}$ |
| Maas/ 0.4 % KP 1131 | 20.0 | 0.12 | $3.0 \times 10^{-8}$ |
| Maas/ 0.2 % Textrol | 24.6 | 0.33 | $6.6 \times 10^{-8}$ |
| 100 % löss | 22.3 | 0.35 | $11.8 \times 10^{-8}$ |
| Löss/ 0.4 % DISAL | 22.8 | 0.27 | $5.1 \times 10^{-8}$ |
| Löss/ 0.4 % KP 1131 | 21.6 | 0.12 | $3.1 \times 10^{-8}$ |
| Löss/ 0.2 % Textrol | 22.4 | 0.30 | $9.4 \times 10^{-8}$ |
| 100 % Westerwald | 22.4 | 0.31 | $7.5 \times 10^{-8}$ |
| Westerwald/ 0.4 % DISAL | 21.5 | 0.27 | $5.0 \times 10^{-8}$ |
| Westerwald/ 0.4 % KP 1131 | 16.8[1)] | 0.05[1)] | $3.3 \times 10^{-8}$ |
| Westerwald/ 0.2 % Textrol | 23.8 | 0.37 | $7.7 \times 10^{-8}$ |

1) If the analysis is carried out on a clay sample which has had a great deal of time to allow the moisture to penetrate, higher values are found for the consistency stability and the moisture content at a Pfefferkorn value of 15 mm.

The results presented above make it clear that the addition of the three additives intended to reduce the amount of mixing water needed accomplishes the desired effect to a greater or lesser degree. DISAL and Textrol have only a limited effect roughly speaking (up to circa 1% in absolute terms), whereas KP1131 has a much greater effect (up to circa 5 % in absolute terms).

With the exception of the recipe involving the addition of KP 1131, the consistency stability of the recipes with the various additives remains fairly good. The clay recipe involving the addition of KP 1131 leads to an extremely low consistency stability. It should be noted that the use of this additive results in a clay that is very sticky and not at all workable in the case of lower Pfefferkorn values. It also becomes quite stiff over time.
The results presented also make it clear that in all cases the use of additives to lower the amount of mixing water needed negatively impacts the water transport characteristics. This deterioration is very striking for the addition of KP 1131. The reduction in water transport caused by the addition of Textrol is perhaps acceptable, but all the other additives lead to a significantly poorer or much poorer drying behaviour as well as drying curves that are clearly

(much) longer. This was also made clear by the brick drying trials in the laboratory, in which case the highest dosage of product KP 1131 led to clear cases of cracks appearing (see figure 3).
The only problem caused by the addition of Textrol (besides a slight decrease in the moisture conductivity coefficient) is that the amount of mixing water needed is not - or hardly - reduced at all.

Figure 3: Crack formation in products made with the addition of 0.4 % KP 1131

The use of Disal® and - to a certain extent - also of KP 1131 leads to an increase in the strength of the green products in those recipes whereby the control bricks demonstrate a somewhat lower green strength. These additives therefore cause of the products to 'stick together' more effectively.

The use of additives did not affect the color of the product and its technical characteristics, such as net volumetric mass, initial water absorption, passive water absorption and compressive strength.
The addition of Disal® and - to a lesser extent - of KP 1131, led to a significant increase in the leaching of sulphate, particularly in the products made with the calcium rich “löss”loam. For the products made with the calcium rich “loss”loam, the addition of Disal® also led to an increase in the leaching of chromium and molybdenum.

**Conclusions**
1. The search for and investigation into the use of specific additives for clay recipes with the objective of lowering the amount of mixing water needed in the clay recipe without negatively impacting the technical characteristics of the product was not successful. In other words, it will not be possible to realize energy savings within the framework of the ceramic production process in this way via the addition of the additives investigated (and probably of practically all types of additives intended to lower the water concentration). All known and investigative additives either have little or no effect (no reduction of water content) or have unavoidable negative side effects.
2. The most striking negative side effect is the (sometimes very great) deterioration in the moisture conductivity, which will necessitate longer drying times and lead to an increase instead of decrease in the amount of energy used.
3. It was also determined that the use of additives leads to an increase in the concentration of water soluble components in the clay. The fact that this did not result in any product discolorations may be related to the very slow drying process of the products in the laboratory area.

4. Additional side effects caused by some additives, in particular when used with calcium rich clay types, are that the leaching rates and the risk that minerals will collect on the surface increase for the components chromium and sulphate.
5. The addition of the additives investigated does not significantly affect the colour and physical/mechanical characteristics of the product.
6. The only potential useful application seen here is the addition of Textrol for the production of wire-cut products. This (lecithin) soya derivative might be used as a 'lubricant' with relatively dry clay types, which would perhaps make it possible to further decrease the already low moisture content. This might be feasible without excessively reducing the water transport characteristics of the clay recipe. However, one would then have to take into consideration an increase in the concentration of organic matter and a possible increase in the flue gass emission of specific volatile organic components. Finally, it may be possible to use additives for decreasing the amount of mixing water in clay recipes which are extruded in a very stiff state and no longer exhibit any drying shrinkage.
7. The only feasible way of reducing the water content in the clay recipe (and thereby realizing energy savings) consists, for a limited number of product types (in particular pressed masonry bricks), of further reducing the concentration of loam particles (< 10 μm) in the basic recipe (also see document KGK 2007, no. 2).