Consequences of using additives for reducing the firing temperature 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 clay recipes for the purpose of lowering the temperature. The objective of doing so is to reduce the amount of energy consumed during the firing process.
In the course of the investigation, the (theoretical) effect of such additives was described and the effect was investigated of two selected additives, namely glazing waste and ground monitor screen glass in a dosage of up to 4%.
In particular, the influence was investigated of such additives on the thermal behaviour of the clay recipe and on the physical and mechanical characteristics of the fired product as well as the leaching behaviour of the product at various temperature intervals.

It was concluded that, in particular for the red-firing Maas clay and the white-firing Westerwald clay, there are real possibilities for realizing a significant lowering of the sintering temperature (40°C to 60°C) and for achieving energy savings. The possible energy-saving was estimated at between 0.7 and 3.4 m^3 of natural gas per ton product.

For yellow-firing products based on a calcium rich clay, it would be difficult to implement these steps, as it is not possible to retain the yellow product colour if the top temperature is lowered.
For products based on Maas clay, a possible additional benefit is that the leaching of arsenic can be reduced in this fashion.

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 by modifying the ingredients/recipe used. One possible way is to reduce the amount of water in the wet shaped product. This method was investigated and reported on in publication KGK no. 2, 2007 and in KGK no. 1, 2008.

Another method is the use of an additive that causes the clay to sinter effectively at a lower top temperature. Additives that lower the sintering temperature are natural or synthetic compounds containing chemical elements that already exhibit a flow-type or sintering type of behaviour at a lower temperature. The sintering behaviour of a clay mass is determined by the presence of basic oxides which are able, at higher temperatures, to break into the rigid and stable network structures of silicon (and aluminium) oxides, thereby causing the formation of amorphous and glasslike structures.
The extent to which this occurs or has an effect depends not only on the chemical composition but also on the size of the individual particles containing these elements and on the temperature.

For the production of technical ceramic ware and, in some cases, fine ceramic ware - when mass powders are ground - it is possible to adjust the fineness of the ground material used. However, for the production of heavy clay ceramics, this does not play a role.
Chemical elements which have the potential of lowering the top temperature include alkali and alkali earth compounds such as sodium, potassium, calcium, barium and magnesium. Various metal oxides, such as the oxides of manganese, lead and divalent iron as well as borates, can also lead to a decrease in the required top temperature.

Various of these elements are bound to clay minerals or present in clay in some other form. On the basis of practical experience, it is also known that the higher the concentration of very fine particles present in a clay (i.e. the higher the concentration of clay minerals present), the lower the required top temperature will be. When fired at this lower top temperature, the fired colour of the iron present in the clay becomes more orange-red. In order to achieve the desired quality and at the same time retain this colour, one must use a clay recipe with a higher concentration of very fine particles.
However, due to the extra water retention in a clay with a higher concentration of very fine particles, the energy consumption in the dryer will increase. As a result, the addition of a clay with a higher concentration of very fine particles to the recipe is not a realistic option when it comes to reducing the consumption of energy.

If one does not want the energy consumption in the dryer to increase, then the elements mentioned above must be added in a non-water-binding form.

It is already clear beforehand that the following aspects deserve further attention:

- If the additive used to lower the sintering temperature contains water soluble components, consideration must be given to the risk that these components will collect on the outer surface of the product during the first drying phase and result in a discoloration of the surface after the firing process or else cause the products to melt together during the firing process;
- The additive must be dosed early enough in the clay preparation process that it becomes completely homogenized. A lack of homogeneity will result in undesirable quality variations;
- If the additive is present in the form of particles, the particles should be fine enough to ensure that no melting spots occur;
- Many additives contribute their own colour;
- A lower top temperature may result in a different product colour;
- The addition of additives to lower the sintering temperature can lead to greater differences in density and therefore differences in size and colour, if the firing process in a particular installation is subject to a certain degree of temperature inhomogeneity. In addition, products may more readily become subject to deformation and packages in the kiln may become unstable more readily;
- The price of an additive and the quantity that needs to be dosed should be such that the energy-saving achieved is not overshadowed by the increase in cost of the ingredients needed for the recipe.

The investigation

The investigation into the addition of additives to lower the sintering temperature was carried out using recipes based on three different types of basic clays: a red-firing Maas clay, a yellow-firing, calcium rich “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 two substances were chosen:

- ground monitor screen glass from SIMS/MIREC (100 µm finely ground);
- glazing waste from the fine ceramic industry.

Originally, the intention was to include a third material, “Borax”, in the investigation, but this material turned out to be unavailable at the time of the investigation.

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. The low dosage level used involved a concentration of 1% in terms of mass and the higher dosage was 4% in terms of mass. This was done in order to get a good idea of the effects of the additive.

The chemical composition was determined for each component as well as the three basic clays used. For every recipe, the particle size distribution and the specific surface area were determined. For the recipe with the highest dosage of an additive and for each control, the thermal behaviour was determined with the help of a so-called dilatometer curve.

For each recipe, trial bricks were formed by hand (see figure 1). These trial bricks were first dried in the laboratory area and then in a drying oven set to 40°C. The products made from Maas clay and from lössleem (4 bricks per recipe) were fired at a top temperature of 1070°C. The products made from Westerwald clay were fired at a top temperature of 1200°C. In addition, products from all the recipes were fired at lower top temperatures in order to determine the lowest temperature at which it was still possible to produce products with identical product characteristics. The lower top temperatures used were 1050°C and 1030°C for the Maas clay and lössleem recipes, and 1170°C and 1140°C for the recipes based on Westerwald clay.
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 (one brick) for critical components in the (Dutch) ceramic industry (SO_4, F, As, Mo, Cr and V) as well as components specifically present in the additives (Ba, Pb and Zn).

Figure 2: Forming trial bricks by hand.

Results

The chemical composition of the basic clays used and the additives is presented in table 1.

Table 1: Chemical composition and sulphur concentration for basic clays and additives used to lower the sintering temperature (elemental oxides and loss on ignition in %).

Element (oxide)	Maas clay	“Löss”loam	Westerwald clay	Monitor screen glass [1)]	Glazing waste
SiO_2	77.3	67.4	79.5	59.5	54.0
Al_2O_3	9.1	6.2	11.4	2.8	7.9
CaO	0.49	6.2	0.18	1.7	4.9
MgO	0.67	1.0	0.16	0.90	0,83
Fe_2O_3	4.3	2.5	0.55	0.08	0.21
Na_2O	0.55	0.77	0.15	7.5	5.1
K_2O	2.0	1.4	1.2	7.2	1.5
Mn_3O_4	0.14	0.06	0.01	-	0.05
TiO_2	0.63	0.57	1.0	0.24	0.06
PbO	< 0.01	< 0.01	< 0.01	7.0	0.14
ZnO	< 0.01	< 0.01	< 0.01	0.19	0.98
Cr_2O_3	0.02	0.01	0,02	-	0.07
BaO	0.03	0.02	0.13	7.2	0.06
ZrO_2	0.06	0.07	0.06	0.90	7.9
Ignition loss	3.5	9.6	4.1	-	1.3
S	0.006	0.018	0.041	-	< 0.005

1) Analyses provided by the supplier

The differences in chemical composition between the various clay types are clear. The “löss”loam has a low concentration of aluminium (contains few clay minerals) but is rich in calcium. The Westerwald clay has a higher concentration of aluminium (contains more kaolin clay minerals). The Maas clay clearly contains iron.

In particular, the glazing waste has high concentrations of sodium, zinc and zircon. The monitor screen glass has high concentrations of sodium, potassium, lead and barium. In both of the additives used to lower the sintering temperature, elements have been identified as being present which could cause this type of sintering behaviour.
The additives used do not significantly affect the specific surface area.
Figures 2, 3 and 4 present the dilatometer curves.

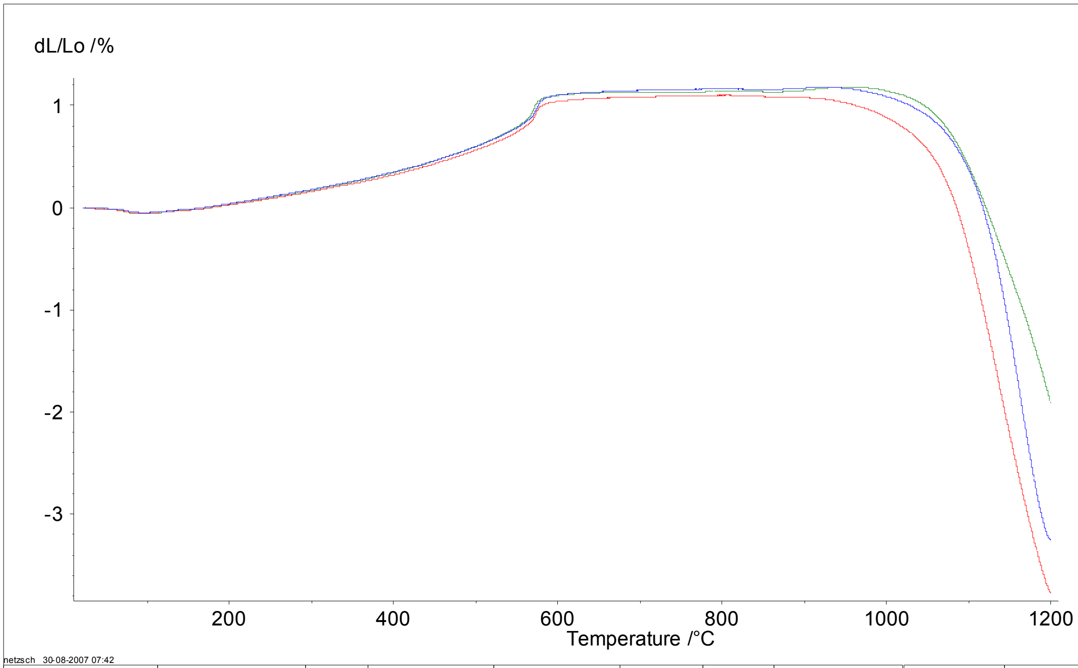

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Figure 2: Dilatometer curves for Maas clay (green = without additive, red is glazing waste 4 % and blue is monitor screen glass 4 %)

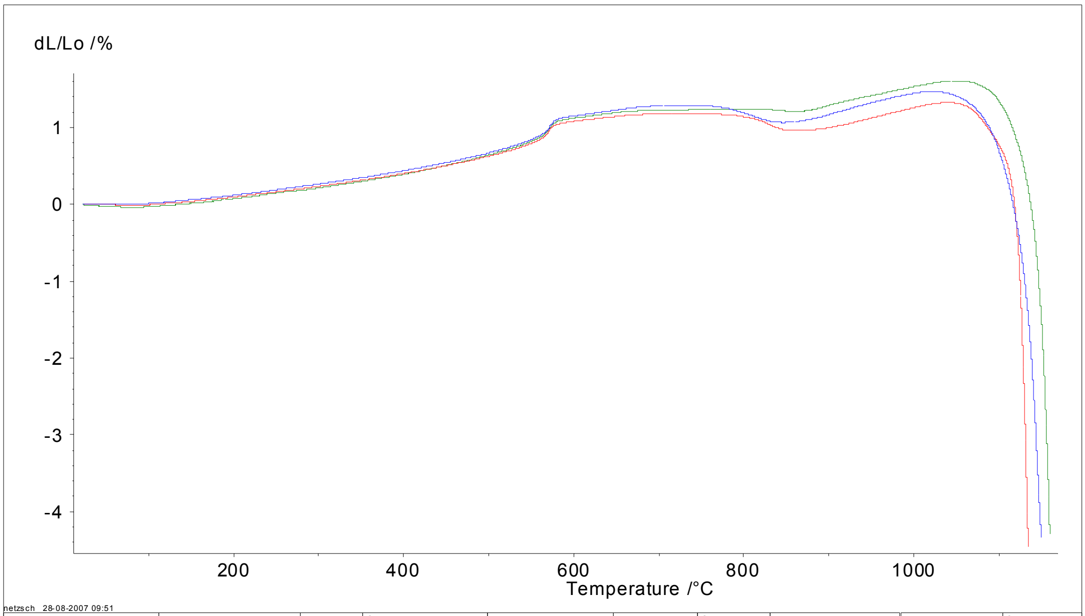

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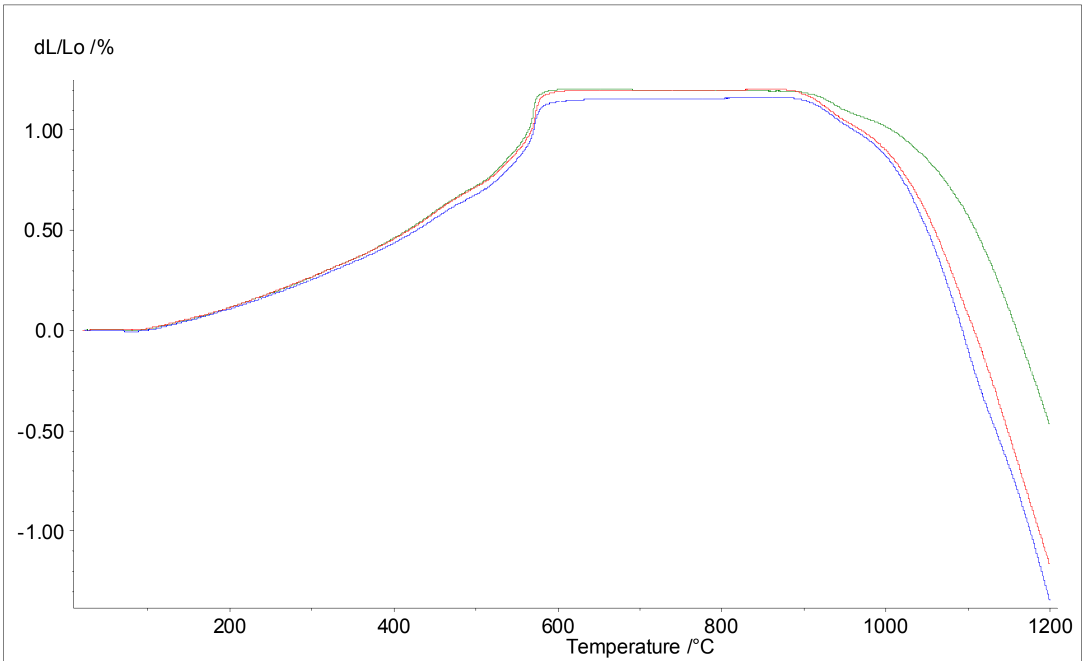
Figure 3: Dilatometer curves for “löss”loam (green = without additive, red is glazing waste 4 % and blue is monitor screen glass 4 %)



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[3] NETZSCH DIL 402EP	I-904063 ww_bbglas.d...	KNB	WW/beeldbuisglas	25-7-2007 12:22:41	24.380 mm	1/1	25/1.00(K/min)/1200	---/--- / ---/---	021

Figure 4: Dilatometer curves for Westerwald clay (green = control, red is glazing waste 4 % and blue is monitor screen glass 4%)

It is clear that addition of the two additives leads to the realization of a certain degree of firing shrinkage at a lower temperature and that the sintering curves for the different recipes are very different. If sintering takes place at a lower temperature, the interval during which organic material is burned may be shortened. If the sintering curve slopes steeply downwards, it may be an indication that the risk of thermal deformation of the products is greater.

The photographs of the products fired at the various top temperatures are presented in figure 5. Tables 2 through 5 provide an overview of the physical and mechanical characteristics of the various products.

Figure 5: Photographs of fired products made with the use of additives intended to lower the sintering temperature (from top to bottom: Maas clay, “Löss”loam and Westerwald clay)

Table 2: Net dry density of trial bricks fired at various top temperatures.

Recipe	Net dry density (kg/m^3)		
	Top temperature 1 1070^{o}C (Maas/Löss), 1200^{o}C (Westerwald)	Top temperature 2 1050^{o}C (Maas/Löss), 1170^{o}C (Westerwald)	Top temperature 3 1030^{o}C (Maas/Löss), 1140^{o}C (Westerwald)
100 % Maas	1941	1913	1871
Maas/ 4 % monitor screen glass	2010	1947	1901
Maas/ 4 % glazing waste	2026	1972	1919
100 % löss	1646	1647	1645
Löss/ 4 % monitor screen glass	1717	1679	1664
Löss/ 4 % glazing waste	1690	1656	1642
100 % Westerwald	2053	2032	1998
Westerwald/ 4 % monitor screen glass	2080	2068	2040
Westerwald/ 4 % glazing waste	2075	2060	2055

Table 3: Initial rate of water absorption of trial bricks fired at various top temperatures.

Recipe	Initial rate of water absorption (kg/m^2.minute)		
	Top temperature 1 1070^{o}C (Maas/Löss), 1200^{o}C (Westerwald)	Top temperature 2 1050^{o}C (Maas/Löss), 1170^{o}C (Westerwald)	Top temperature 3 1030^{o}C (Maas/Löss), 1140^{o}C (Westerwald)
100 % Maas	3.0	3.3	3.6
Maas/ 4 % monitor screen glass	2.0	3.0	3.3
Maas/ 4 % glazing waste	1.6	2.4	2.8
100 % löss	2.0	2.2	2.1
Löss/ 4 % monitor screen glass	1.7	2.2	1.9
Löss/ 4 % glazing waste	4.7	4.6	2.9
100 % Westerwald	0.4	0.5	0.7
Westerwald/ 4 % monitor screen glass	0.3	0.3	0.4
Westerwald/ 4 % glazing waste	0.0	0.0	0.3

Table 4: Free water absorption of trial bricks fired at various top temperatures.

Recipe	Free water absorption (mass %)		
	Top temperature 1 1070^{o}C (Maas/Löss), 1200^{o}C (Westerwald)	Top temperature 2 1050^{o}C (Maas/Löss), 1170^{o}C (Westerwald)	Top temperature 3 1030^{o}C (Maas/Löss), 1140^{o}C (Westerwald)
100 % Maas	8.1	9.2	10.5
Maas/ 4 % monitor screen glass	6.5	8.2	9.4
Maas/ 4 % glazing waste	5.6	6.8	8.4
100 % löss	13.6	13.6	14.1
Löss/ 4 % monitor screen glass	11.1	11.8	13.0
Löss/ 4 % glazing waste	11.5	12.8	13.7
100 % Westerwald	4.3	5.0	6.1

Westerwald/ 4 % monitor screen glass	2.8	3.2	4.0
Westerwald/ 4 % glazing waste	2.9	3.3	4.0

Table 5: Compressive strength of trial bricks fired at various top temperatures

Recipe	Compressive strength (N/mm^2, normalized according to EN 772-1)		
	Top temperature 1 1070^{O}C (Maas/Löss), 1200^{O}C (Westerwald)	Top temperature 2 1050^{O}C (Maas/Löss), 1170^{O}C (Westerwald)	Top temperature 3 1030^{O}C (Maas/Löss), 1140^{O}C (Westerwald)
100 % Maas	48.4	38.9	28.9
Maas/ 4 % monitor screen glass	64.4	51.9	42.7
Maas/ 4 % glazing waste	82.6	61.3	51.9
100 % löss	40.1	32.4	25.9
Löss/ 4 % monitor screen glass	55.5	43.9	40.7
Löss/ 4 % glazing waste	66.9	58.5	41.6
100 % Westerwald	85.9	88.0	76.6
Westerwald/ 4 % monitor screen glass	110.3	89.2	89.2
Westerwald/ 4 % glazing waste	110.8	102.7	100.0

Conclusions

1. For certain clay types, it is feasible to use additives to lower the sintering temperature and thereby realize energy savings.
2. For the production of masonry bricks from Maas clay, the addition of 4 % (100 µm finely ground) monitor screen glass or of 4 % glazing waste can reduce the top temperature required from 1070°C to 1030°C without a significant deterioration in product colour and/or physical/mechanical characteristics.
3. For the production of masonry bricks from a white-firing Westerwald clay, a reduction in top temperature was realized from 1200°C to 1140°C, whereby the same effects were realized as for Maas clay.
4. For the production of yellow-firing masonry bricks (from calcium rich clay such as the “löss”loam used in this investigation), the issues involved are more complex. Here also it is possible to use the additives mentioned to reduce the top temperature from 1070°C to 1030°C while at the same time maintaining the physical and mechanical product

characteristics. However, the problem is that at this lower top temperature, it is not possible to maintain the yellow colour of the product. As a result, the use of additives to lower the sintering temperature for yellow-firing products based on calcium would not seem to be a realistic option. This might also be true for bronze-firing products and product colours other than the red and white products investigated until now in this study.

5. For products based on calcium rich clay, the lower top temperature also leads to a large increase in the quantity of leachable chrome and sulphate. The latter would increase the risk of efflorescence.
6. No extra leaching was detected in this investigation with regard to the components specifically added to the recipes in the form of additives used to lower the sintering temperature (e.g. barium, zinc and lead). However, the risk of extra flue gass emissions for these components may increase.
7. In addition to lowering the top temperature, the addition of glazing waste in particular leads to a reduction in the quantity of leachable arsenic, molybdenum and vanadium. This may be related to a change in the oxidation state of these components, which could reduce their mobility.
8. With regard to the production process in practice (at lower firing temperatures as well), the following aspects will also have to be taken into account: increased thermal instability of the products and a more limited timeframe for the combustion of organic compounds due to the fact that the products will already become dense at a lower temperature. The components must also be ground finely enough and homogeneously distributed throughout the entire mass of clay in order to prevent excessive stickiness and melting spots.
9. The energy savings realized by lowering the top temperature is estimated at between 1.2 and 5.6 m^3 of natural gas gross per kind of fired product, depending on the top temperature and the reduction achieved. However, due to the lower energy content of the products cooling down, there will be less heat available for the drying process. As a result, the net energy savings are estimated at from 0.7 to 3.4 m^3 of natural gas per ton product.
10. As energy is also needed for grinding monitor screen glass down to a fraction < 100 µm , the actual energy savings realized by adding this material will be somewhat less. The amount of energy needed for grinding the material has not been quantified.