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(54) **Title**: PRODUCTION OF FIRED CERAMIC ARTICLES

(57) **Abstract**: A method of producing a fired ceramic article comprises the steps of: (i) preparing a clay composition by adding a zeolite and preferably also a sodium compound to a clay and admixing the clay, the zeolite and (if used) the sodium compound to produce said composition; (ii) forming the composition produced in step (i) into a preform of a predetermined shape corresponding to that of the article; (iii) drying the preform; and (iv) firing the preform to produce the ceramic article. The method reduces the firing temperature required to produce the ceramic article and inclusion of the sodium compound provides the advantage of reducing, minimising or eliminating the amount of water required during the blending step (i.e. step (i)). The method also reduces fluoride emissions during the firing step (i.e. step (iv)).

PRODUCTION OF FIRED CERAMIC ARTICLES

The present invention relates to the production of fired ceramic articles and more particularly to the production of such articles by drying and firing a preform comprised of a clay composition. The invention has particular application to the production of bricks, blocks and the like as used for the construction of buildings and has further application in the production of drainage pipes and roofing tiles.

Bricks, blocks and the like for use in construction of buildings have been produced for centuries by the firing of a preform comprised of a clay composition.

Very briefly, clay dug from the ground is worked together usually with a number of additives such as sand, chamotte and colouring agents (e.g. iron or manganese) with, if necessary, the addition of steam and/or water to form a clay composition of appropriate plasticity (usually measured by the "Pfefferkorn Index"). The clay composition is then shaped into a preform corresponding to the shape of the final ceramic article. The preform is then dried by heating to remove "free" water and fired, at elevated temperature, for a period of time to produce the final article. Although the technology is, to say the least, "mature" it is not without its disadvantages in the modern day environment. Two such disadvantages may be mentioned in the context of the present invention.

The first is that a considerable amount of energy is required to provide both the heat required for drying and the elevated temperatures for the firing process. There is also a link between the structural feature of the compressive strength required for the final article and the firing temperature such that generally speaking the higher the firing temperature the higher the compressive strength. Incremental increases of temperature at the upper end of the temperature range are much more expensive than the same incremental increase at a lower temperature. Consequently there is a desire to reduce the firing temperatures for the ceramic articles while still allowing the desired compressive strength to be achieved. Furthermore, the colour of a fired ceramic article may depend on the firing temperature (as well as other factors such as the clay composition and/or kiln atmosphere conditions (which may be oxidizing or reducing). In some instances it may be the case that a firing temperature required to achieve a particular compressive strength for the fired ceramic article will produce an undesired colouration for the final article. In such circumstances, the article may need to be fired at a temperature which still provides the required colour but not necessarily the optimum compressive strength.

The other disadvantage that may be mentioned is fluoride emissions from the clay during the firing process. It is known that clays include fluorides and the firing process results in fluoride emissions (e.g. in the form of hydrogen fluoride) during the firing process. Such fluoride emissions are an environmental problem and whilst they can be removed by appropriate "scrubbers" the latter add considerably to the capital cost of the plant for producing the ceramic articles and specific difficulties in retro-fitting suitable "scrubbers" to existing facilities. Additionally such scrubbers also produce toxic waste which is environmentally undesirable and expensive to dispose of.

It is an object of the present invention to obviate or mitigate the above mentioned disadvantages.

According to the present invention there is provided a method of producing a fired ceramic article comprising the steps of:

(i) preparing a clay composition by adding a zeolite and preferably also a sodium compound to a clay and admixing the clay, the zeolite and (if used) the sodium compound to produce said composition;

(ii) forming the composition produced in step (i) into a preform of a predetermined shape corresponding to that of the article;

(iii) drying the preform ; and

(i) firing the preform to produce the ceramic article.

Incorporation of a zeolite, which is preferably a synthetic zeolite, into the clay has unexpectedly been found to provide two advantages in a process for producing ceramic articles by the firing of clay preforms. The first, all other things being equal, there is a reduction in firing temperature achieved by the incorporation of zeolite to produce an article of a particular compressive strength as compared to the firing temperature required for the production of the same article without zeolite. Thus this feature of the invention allows a reduction in firing temperatures with a consequential saving of energy costs while achieving the required or enhanced compressive strength. This may also provide an additional level of control of finished product colouration. In other words, the invention can allow (for a particular clay composition) the attainment of a particular compressive strength in the final article by using a lower firing temperature at which there is no undesired colouration as compared to the higher temperature that would otherwise be required and at which such discolouration may occur. The second advantage achieved by the present invention is a reduction in fluoride emissions during the firing process. Thus the method of the invention allows production of ceramic articles without the need to scrub gasses from the process, or at the very least a much lower degree of scrubbing than would otherwise be the case.

In a highly preferred embodiment of the invention, a sodium compound is admixed with the clay and zeolite (preferably a synthetic zeolite) in step (i) of the method. Depending on circumstances, the incorporation of the sodium compound helps to reduce, minimise or eliminate the amount of water or steam required at the blending stage of the method (i.e. step (i)) whilst achieving the required plasticity for the clay composition to be moulded or otherwise formed into the preform in step (ii). This may particularly be the case where the clay has been dug and stored outside during relatively dry weather conditions, in which case some modification of plasticity may be required by the addition of water or steam. In fact, in the context of brick making in Northern Europe, there is only a relatively short period of time (during the “wet season”) during which the water content of the stored clay is sufficient to meet the required plasticity without addition of further water.

Reductions in water content of the clay composition (required to achieve a particularly plasticity) are advantageous because they reduce the energy input required at the drying stage which is required before the chemical transition phase which occurs during firing (typically at about 1000°C). Drying may be effected to achieve a water content of less than 1% prior to the firing step. Typically drying will be effected in an oven at a start temperature of about 40°C which is subsequently elevated to 80°C and then 110-120°C to achieve the desired, pre-firing water content in the preform. However the use of an oven is not essential since in hot climates simply leaving the clay to bake in the sun will generally achieve the required water reduction. Irrespective of whatever method is used, drying is important since if too much water remains in the preform the articles being fired may crack or blow apart as water is released in the form of steam.

The invention is applicable particularly to the production of bricks, blocks and the like for use in constructing buildings, for which purposes the preforms will generally be cuboid. It may however also be applied to other ceramic articles obtained by firing clay composition, e.g. drainage pipes, roofing tiles.

No particular modification of the basic manufacturing process for producing a ceramic article is required by the method of the invention – the only difference being the incorporation of the zeolite and (if used) the sodium compound which may be admixed with the clay using entirely standard techniques accompanied by the addition of water or steam as necessary to achieve a required plasticity. Thus the method of the present invention may be carried out using standard mixing apparatus, drying ovens and firing kilns (all as well known in the industry) and the method does not add to the capital cost of the plant for producing the articles.

In step (i) of the method of the invention, the clay, zeolite and (if used) the sodium compound are admixed. Conventional solid additives (e.g. sand, chamotte and/or colouring agents) may also be added at this stage although they may have been pre-mixed with the clay before step (i) of the method. For convenience in what follows, that part of the clay composition comprised of the clay and any solid additives (other than the zeolite and (if used) sodium compound) may be considered to be a "base composition" in which the zeolite and (if used) sodium compound are incorporated. Generally the total amount of the conventional additives (if present) will be up to 20% by weight of the combined dry weight of the clay and any solid additives (but excluding the amount of zeolite and (if used) sodium compound added). The "dry weight" is determined by drying to constant weight in an oven at 105°C.

Water and/or steam may be introduced in step (i) in accordance with conventional practice to provide a final clay composition of the required plasticity for step (ii) in which the preform is formed from the composition. Such forming may, for example, be by extrusion or pressing.

Any clay as conventionally employed in the manufacture of fired ceramic articles may be used in the present invention. Thus the clay may be a sedimentary, e.g. a river or other deposited clay. Thus, for example, clays used in The Netherlands for brick making include Maasclay and Waalclay (both river clays) as well as Westerwalder clay (a sedimentary clay). The skilled person will be well aware of additional clays used in The Netherlands and in other countries.

Irrespective of its source, the clay will generally have the following properties:

Specific Surface	52-96 $m^2 g^{-1}$
< 10 µm	31-56 % by weight
CaO content	0.18-6.2 % by weight
Fe_2O_3 content	0.55-4.9 % by weight
SiO_2 content	67.4-79.5 % by weight

Generally the amount of zeolite added to the base composition will be 0.01 to 10% by weight based on the dry weight of the base composition (i.e. the combined dry weight of the clay and any additives (but excluding amounts of zeolite and sodium compound added). More preferably, the amount of zeolite added to the clay is in the range 0.01 to 5% by weight (on the same basis as above), even more preferably 0.01 to 1% by weight, and most preferably 0.01 to 0.6% by weight.

Examples of zeolites that may be used in accordance with the invention include those classified as LTA, FAU, GIS, MFI, MOR, BEA, FFR, LTL, MTT, ANA, TON, AEL, MWW, CHA, PHI, MER, CLI, NAT, and EMI.

It is generally preferred that the mean particle size of the zeolite is similar to, and more preferably less than, that of the clay.

Particularly suitable zeolites are fine granular materials and particularly those containing at least 90% by weight of particles with a size less than 100 µm. In other words, the d_{90} value is less than 100 µm. More preferably the d_{90} value of the zeolite is less than 10 µm. Preferably the zeolite has a d_{50} value in the range 1-5 µm.

Good results have been achieved using PQ Zeolite A (standard detergent grade), an LTA type zeolite available from Philadelphia Quartz.

As indicated above, a preferred embodiment of the invention utilises a sodium compound in combination with the zeolite. The sodium compound has advantages in that it reduces, minimises or eliminates the amount of water or steam that would otherwise be required to be mixed with the clay to obtain a clay composition of the required plasticity for moulding or otherwise forming into the preform. The sodium compound may also assist in reduction of the firing temperature that would otherwise be required to produce a ceramic article with a particular compressive strength.

The amount of the sodium compound used may be in the range of 0.001% to 10% by weight based on the dry weight of the base composition. More preferably, the sodium compound is added in an amount of 0.001% to 1% and even more preferably in the range 0.1 to 0.5% on the same basis.

The sodium compound is preferably a salt (although other sodium compounds may be used, e.g. alkaline compounds such as sodium hydroxide).

It is envisaged that a wide range of sodium salts may be used and examples include sodium carbonate and other members of the "sodium carbonate family", e.g. sodium sesquicarbonate, trona and sodium bicarbonate. Examples of further salts that may be used include, sodium acetate, sodium phosphate and sodium tripolyphosphate (STPP). Particularly preferred sodium salts are the "sodium carbonate family".

The most preferable sodium salt is sodium carbonate which may, for example, be provided in the form of light ash or heavy ash.

Admixtures of the zeolite and sodium compound are particularly suitable for use in the invention. Generally such an admixture will comprise 0.5 to 99.5% of sodium compound (based on the total weight of the admixture) and 99.5 to 0.5% of zeolite. Conveniently the manufacturer of the ceramic article may be supplied with different blends of the zeolite and sodium compound, these blends differing in their relative amounts of the sodium compound. In this way, one blend may be used when it is desired to achieve a particular plasticity modification and another blend used for a different plasticity modification. In all cases however the blends will be effective to reduce firing temperature and fluoride emissions, as discussed earlier.

The invention is illustrated by the following non-limiting Examples and accompanying drawings, in which:

Fig 1 illustrates the results of Example 1 demonstrating reduction in water content obtained by use of additive compositions (constant relative composition) in accordance with the invention to achieve specified plasticities for various clay masses;

Fig 2 illustrates the results of Example 2 demonstrating reduction in water content obtained by use of additive compositions (varying relative composition) in accordance with the invention to achieve specified plasticities;

Fig 3 is a graph of firing temperature *vs* compressive strength representing the results obtained in Example 3;

Fig 4 shows graphs of firing temperature *vs* compressive strength representing the results obtained in Example 4; and

Fig 5 shows graphs of amount of additive (constant relative composition) *vs* compressive strength representing the results obtained in Example 5.

In the following Examples, Pfefferkorn Index (Pk) values are expressed as a dimensionless quantity in accordance with standard industry practice but it will be appreciated that (strictly speaking) the unit for Pk is mm (as it is the residual height of the sample after the test has been preformed).

Example 1

This Example demonstrates use of an additive composition in accordance with the invention to improve the workability of various clay masses, and more particularly to reduce the water content to achieve a given Pfefferkorn Index (Pk) as compared to that required for the clay without the composition. In this respect, reduction of water content to achieve a given Pk value is important because less heat is required in the drying step (to remove "free" water) of a process for producing fired ceramic articles.

The composition of the invention employed for the purposes of this Example, comprised, by weight, 98% sodium carbonate (light ash) and 2% zeolite (PQ Zeolite A standard detergent grade).

The clay masses tested individually comprised at least 80% by weight of clays 1-6 (identified below) and contained conventional additives such as sand, chammote *and/or colouring agents.*

Table 1

	Spec. surface m^2/g	**% < 10 µm**	**CaO %**	**Fe_20_3 %**	**$Si0_2$ %**
Clay 1	66	-	-	-	-
Clay 2	96	-	-	-	-
Clay 3	78	-	-	-	-
Clay 4	75	40	0.4	1.8	71
Clay 5	71	31	6.2	3.7	67.4
Clay 6	79	47.1	2.2	4.9	70.4

Initially, individual samples of each clay mass were mixed with steam/water (using standard techniques) to provide, for each clay mass, control samples having a Pfefferkorn Index (Pk) of 15 and 20. Each sample was then analysed to determine the total water content of the clay mass as required to achieve the Pk value of 15 or 20 (as the case may be). The values obtained are shown in Table 2 below.

Table 2

Clay No.	Total Water Content at Pk = 15	Total Water Cotent at Pk = 20
1	18.2%	17.0%
2	19.9%	18.8%
3	19.9%	18.8%
4	18.6%	17.5%
5)	18.5%	17.5%
6	16.9%	15.9%

The above procedures were repeated using separate samples of the clay masses and with the addition of amounts of 0.2, 0.3, 0.4 and 0.5% by weight of the additive composition of the invention expressed as a percentage of the total "dry" clay mass (as obtained by drying to contstant weight at 105°C). Once the required Pk values had been obtained (i.e. 15 or 20) the samples were analysed to determine their total water content. In all cases, this was less than the amount required to achieve the same Pk value with the same clay mass (but without the addition of the additive).

For each of the samples prepared with the additive composition of the invention, the reduction in the amount of water required to achieve the same Pk value (i.e. for the same clay mass without additive addition) was calculated as a percentage of the corresponding value shown in Table 2 above.

The results are plotted in the graphs of Fig 1. By way of explanation, there are two graphs for each clay type, one graph in relation to the Pk value of 15 and the other for the Pk value of 20. For any one graph, the percentage water reduction achieved using the additive composition of the invention is represented by the *y*–axis and the percentage additive addition is represented by the *x*–axis, it being understood that the values at the origin represent the control samples (i.e. without the additive composition of the invention).

Most of the results in Fig 1 cover up to 0.5% by weight addition of additive although in the case of Clay 6 the tests were taken up to 1% by weight addition to demonstrate the likely position of the optimum additive amount.

The majority of the graphs clearly show there is an optimum addition rate with only Clay 4 failing to show an optimised level up to 0.5% implying that the optimum addition rate for this particular clay is in excess of 0.5%. The results also clearly show that optimised additions ranging from 0.35% to 0.5% depending on the type of clay. The other observed fact is that the percentage water reduction is also variable depending on the clay type with results ranging from 13% to 18%.

The results of this example clearly demonstrate that the additive composition of the invention allows a significant reduction required in water content required for a particular clay to achieve a specified Pk value. Thus with the reduced water content, less energy is required to effect water removal in the production of a fired ceramic articles such as bricks.

Example 2

This Example demonstrates the effect on the percentage water reduction required to achieve a particular Pk value by varying the relative amounts of sodium carbonate and zeolite in an additive composition.

This Example was carried out on the Clay 2, Clay 4 and Clay 5 masses using 0.3% by weight (based on the "dry" weight of the clay) of additive compositions containing varying relative amounts of sodium carbonate and zeolite. More particularly, the additives compositions tested comprised 100% zeolite (i.e. no sodium carbonate) as well as additive mixtures comprising 30% to 90% sodium carbonate (in increments of 10%), with the balance being zeolite, as well as an additive composition comprising 98% sodium carbonate and 2% zeolite.

The percentage water reduction was determined for each additive composition to achieve Pk values of 15 and 20 in the case of Clays 2 and 4 and a Pk value of 15 in the case of Clay 5.

The results are plotted in the graphs of Fig 2. Each of the graphs is presented with best fit curves.

Although there is a some variability in the results, there is an overall trend in that the higher the relative amount of sodium carbonate higher the percentage water reduction. Optimum compositions were generally in the range of 80 to 98% sodium carbonate (i.e. 20 to 2% zeolite).

Example 3

This Example demonstrates the improvements in compressive strength obtained in accordance with the present invention.

PQ Zeolite A was blended with the Clay 1 mass using conventional techniques such that the resulting admixture comprised 0.3% by weight of the zeolite based on the weight of the clay. Preforms having a cylindrical shape with a diameter of 57 mm and height between 25 and 30 mm were produced from the resulting composition.

For comparative purposes, similar preforms were prepared which comprised either only the clay mass or with 0.3% addition of sodium carbonate thereto.

The various preforms were fired at a range of temperatures and the compressive strengths of the resultant articles measured.

The results are shown in Fig 3 for which it will be seen that the articles containing zeolite (upper line of the graph) had a higher compressive strength for a particular firing temperature than either the preforms with no additives or those containing sodium carbonate.

More particularly, it will be noted from Fig 3 that the article produced from the "blank" preform (no additive) had a compressive strength of about 22 N/mm^2 when prepared at a firing temperature of 1095°C whereas articles produced in accordance with the invention had a compressive strength of about 24 N/mm^2 when the preform was fired at a temperature of about 1015-1017°C. Intermediate results were obtained in relation to the articles produced using sodium carbonate as an additive.

Example 4

This Example demonstrates the effect on compressive strength of fired ceramic articles produced from the Clay 2, Clay 4 and Clay 5 masses using additive compositions containing different relative amounts of sodium carbonate and zeolite. For the Clay 2 mass, the Example also demonstrates effect of firing temperature.

For the purposes of this Example, individual samples of the clay masses were produced containing a total amount of 0.3% percent of additive compositions containing 30 to 90% by weight of sodium carbonate and correspondingly 70% to 30% by weight of zeolite (in increments of 10% by weight). Additionally tested was an additive comprising 98% sodium carbonate and 2% zeolite and also an additive comprising 100% zeolite. For the purposes of comparison, a blank sample of the clay mass was tested (i.e. no zeolite or carbonate additive addition).

Cylindrical preforms were prepared from the samples with sizes as described in Example 3.

The samples were dried by heating and subsequently fired to produce ceramic articles. In the case of the Clay 2 mass, the samples were fired at temperatures of 960°C, 1000°C and 1040°C. The firing temperature in the case of the Clay 4 and Clay 5 masses was 1095°C.

The results are shown in the graphs of Fig 4 which link the compositions of the additive with the impact on the compressive strength of products produced expressed as N/mm^2 and also in the case of the Clay 2 mass compare the compressive strengths at different firing temperatures.

The results indicate that optimum compressive strength appears using additive compositions containing from 80 to 90% sodium carbonate (and correspondingly 20% to 10% by weight zeolite).

In the case of the Clay 2 mass, the results indicate that the additive compositions can give increased compressive strength even at reduced firing temperatures. It can be reasonably deduced that compressive strengths similar to the

Blank (i.e. the industry standard) could be achieved at reduced temperatures thus driving a reduction of energy in the firing stage as well as giving more control over the colour of the bricks. Similar but more pronounced results are observed with the Clay 4 mass with the compressive strength peaking between 80 and 90 % sodium carbonate content (20 to 10% zeolite content) again added at the 0.3% level. See also Figure 3 for the variation of compressive strength with temperature.

Example 5

This Example demonstrates the effect on compressive strength of fired ceramic articles produced from the Clay 5 mass using different amounts of an additive in accordance with the invention containing 98% light ash and 2% PQ Zeolite A. The firing temperature was constant at 1035°C.

The amounts of the additive used were 0.2%, 0.3%, 0.4% and 0.5%. Additionally tested was a "blank" of the clay mass (i.e. no additive addition).

Cylindrical preforms were prepared as described in Example 3 and tested for compressive strength subsequent to firing at 1035°C.

The results are shown in Fig 5 and show increased compressive strength (compared to the blank) at additive additions of 0.2%, 0.3% and 0.4%, although with some loss of compressive strength using 0.5% additive.

Example 6

This Example demonstrates reduction in fluoride emissions achieved by the method of the invention.

Preforms were prepared from Clay 6 mass both with and without various additives as detailed in the following Table 3:

Table 3

Preform No.	Additive	Amount (based on weight of clay)
1	-	-
2	Na_2CO_3/Zeolite (98/2)	0.3%
3	MgO	1.0%
4	Zeolite	1%

The zeolite used for Preforms Nos. 2 and 4 was PQ Zeolite A.

The preforms were fired and the resulting ceramic articles analysed for fluoride content using a pyrohydrolytic technique with a detection limit of 0.01%. Thus the higher the fluoride amount in the final article, the less fluoride emission during firing. The results are shown in Table 4 below:

Table 4

Preform No.	Firing Temperature	Fluoride Content of Ceramic Article (by weight)
1	1090°C	<0.01%
2	960°C	0.04%
3	1040°C	<0.01%
4	1040°C	0.04%

The unfired clay mass was analysed separately and was found to have a fluoride content of 0.05% by weight on a dry basis.

It can be seen from the results presented in Table 3 that ceramic articles produced in accordance with the invention (i.e. from Preforms Nos. 2 and 4) had significantly higher residual fluoride contents than the other two preforms. More specifically, ceramic articles produced in accordance with the invention retained about 80% of the original fluoride content of the clay. This is to be contrasted with the comparative examples (Preforms Nos. 1 and 3) for which the fired samples contained less than 0.01% by weight of fluoride (i.e. below the detection limit of the analytical technique) indicating that substantially all of the fluoride was lost during firing.

Example 7

This Example provides a comparison of properties of fired bricks produced in a commercial furnace from a particular clay mass both with and without an additive composition in accordance with the invention.

The Example was carried out using Clay 1 mass and an additive composition comprising 98% by weight sodium carbonate and correspondingly 2% zeolite.

A sample of the clay mass was mixed with steam/water to provide a Pk value of 4 to 5 mm. It was found that the total water content of this ("control") sample was 23.4%.

A further sample of the clay mass was mixed with 0.3% by weight (based on the "dry" weight of the clay mass) of the additive composition and sufficient water/steam to provide a Pk value of 4 to 5 mm. It was found that the total water content of this sample was 21.7%, i.e. a reduction of about 8% compared to the water content of the control sample.

Bricks were produced from the two clay samples using standard techniques and a firing temperature of 1095°C. There was no visual difference in the bricks produced from the two samples.

The following Table 5 provides a comparison of properties of the bricks produced.

Table 5

	Control	**With 0.3% addition**	**Difference**
length (mm)	210.8	210.0	-0.4%
width (mm)	98.1	97.4	-0.7%
Density (kg/m3)	1783	1803	+1.1%
Water absorption (%m/m)	9.2	9.1	-1.1%

Water absorption (%V/V)	16.4	16.3	-0.7%
Compressive strength (N/mm2)	12.8	14.3	+11.7%

CLAIMS

1. A method of producing a fired ceramic article comprising the steps of:

(i) preparing a clay composition by adding a zeolite and preferably also a sodium compound to a clay and admixing the clay, the zeolite and (if used) the sodium compound to produce said composition;

(ii) forming the composition produced in step (i) into a preform of a predetermined shape corresponding to that of the article;

(iii) drying the preform ; and

(iv) firing the preform to produce the ceramic article.

2. A method as claimed in claim 1 wherein the zeolite is an LTA, FAU, GIS, MFI, MOR, BEA, FFR, LTL, MTT, ANA, TON, AEL, MWW, CHA, PHI, MER, CLI, NAT and/or EMI zeolite.

3. A method as claimed in claim 1 or 2 wherein the zeolite is a synthetic zeolite.

4. A method as claimed in any one of claims 1 to 3 wherein the zeolite is a granular material.

5. A method as claimed in claim 4 wherein the zeolite has a d_{90} value of at most 100μm.

6. A method as claimed in claim 5 wherein the zeolite has a d_{90} value of at most 10μm.

7. A method as claimed in claim 6 wherein the zeolite has a d_{50} value of 1-5μm.

8. A method as claimed in any one of claims 1 to 7 wherein the amount of the zeolite added is 0.01 to 10% by weight based on the dry weight of the base composition (as herein defined).

9. A method as claimed in claim 8 wherein the amount of the zeolite added is 0.01 to 1% by weight based on the dry weight of the base composition.

10. A method as claimed in claim 1 or 9 wherein the zeolite is a granular material.

11. A method as claimed in any one of claims 1 to 10 wherein the sodium compound is added to the clay.

12. A method as claimed in claim 11 wherein the amount of the sodium compound incorporated in the clay composition is in the range of 0.001% to 10% by weight based on the dry weight of the base composition.

13. A method as claimed in claim 12 wherein the amount of the sodium compound incorporated in the clay composition is in the range of 0.001% to 1% by weight based on the dry weight of the base composition.

14. A method as claimed in claim 7 wherein the amount of the sodium compound incorporated in the clay composition is in the range of 0.1% to 0.6% by weight based on the dry weight of the base composition.

15. A method as claimed in any one of claims 1 to 14 wherein the sodium compound is a sodium salt.

16. A method as claimed in claim 15 wherein the sodium compound is selected from sodium carbonate, sodium sesquicarbonate, trona, sodium bicarbonate, sodium acetate, sodium phosphate sodium and sodium tripolyphosphate (STPP).

17. A method as claimed in claim 16 wherein the sodium compound is sodium carbonate.

18. A method as claimed in claim 17 wherein the sodium carbonate is provided in the form of light ash or heavy ash.

19. A method as claimed in any one of claims 11 to 18 wherein the sodium compound and the zeolite are added to the clay in the form of an admixture.

20. A method as claimed in any one of claims 1 to 19 wherein the preform is a cuboid.

21. A method as claimed in claim 20 wherein the ceramic article is a brick or block for building.

22. The use of a zeolite, preferably a synthetic zeolite in the manufacture of a ceramic article produced by firing a clay preform for reducing fluoride emission during the firing process.

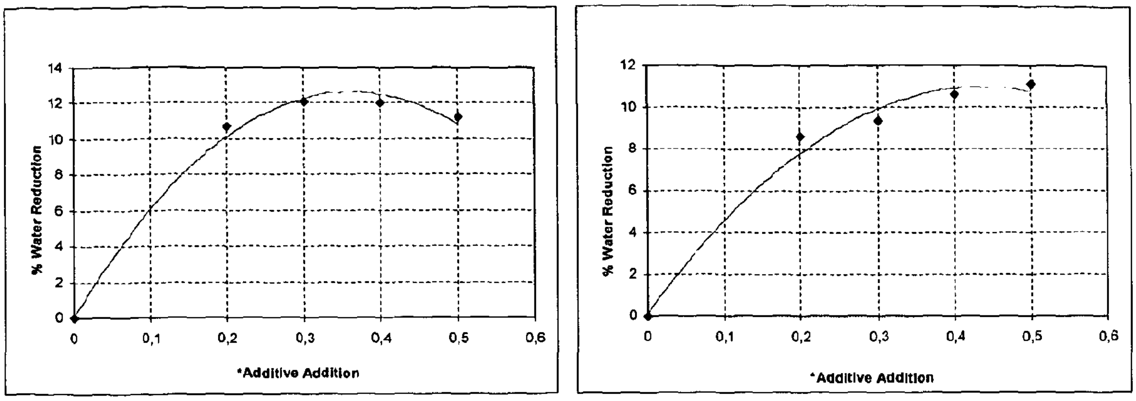
23. The use of a zeolite, preferably a synthetic zeolite, in the manufacture of a ceramic article produced by firing a clay preform for reducing the firing temperature.

24. An admixture of a sodium compound and a zeolite for use in producing fired ceramic articles.

25. An admixture as claimed in claim 24 comprising 0.5 to 99.5% of the sodium compound and 99.5 to 0.5% of the zeolite, the percentages being based on the weight of the admixture.

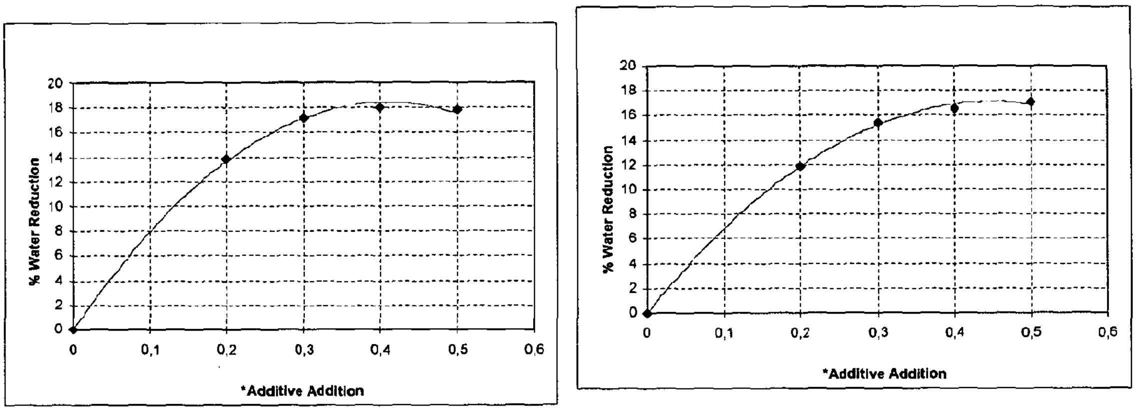
Pfefferkorn 15: **Pfefferkorn 20:**

Clay 1



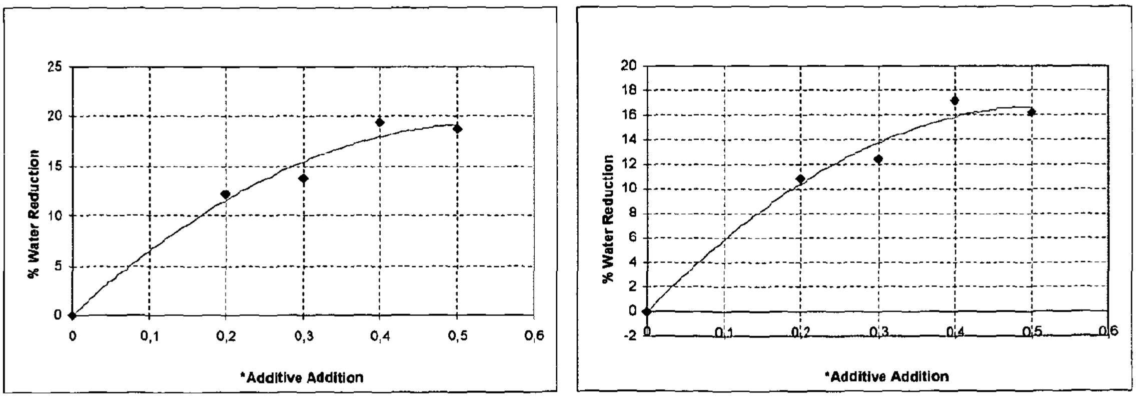
Water Content Control: 18.2% 17.0%

Clay 2



Water Content Control: 19.9% 18.8%

Clay 3

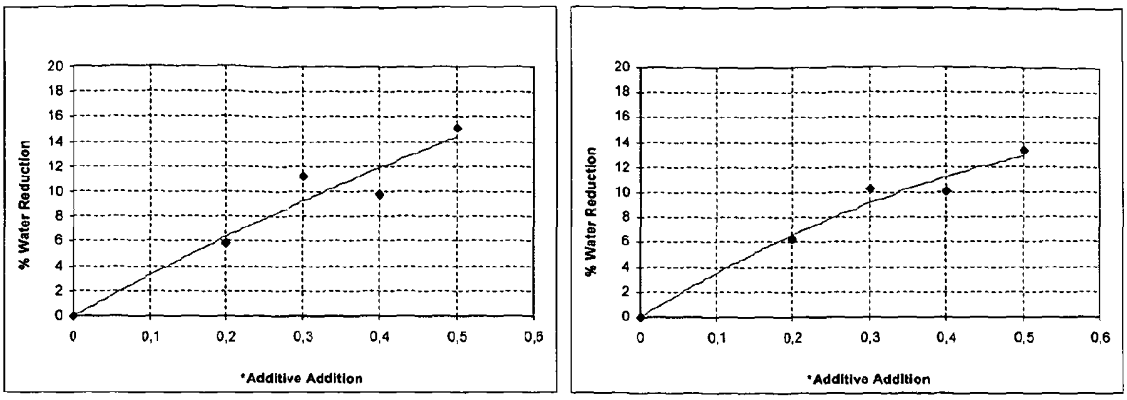


Water Content Control: 19.9% 18.8%

**** Additive addition rate as a % of total clay mass***

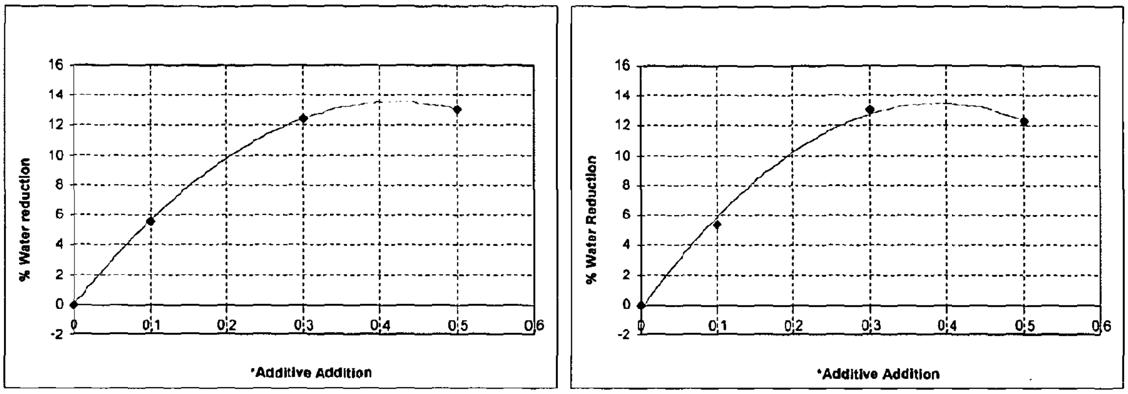
Fig 1

Clay 4



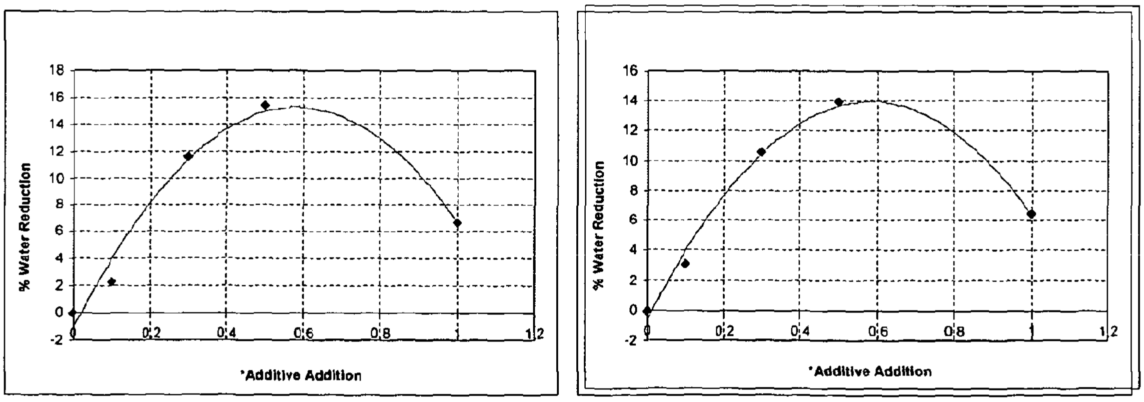
Water Content Control: 18.6% 17.5%

Clay 5



Water Content Control: 18.5% 17.5%

Clay 6



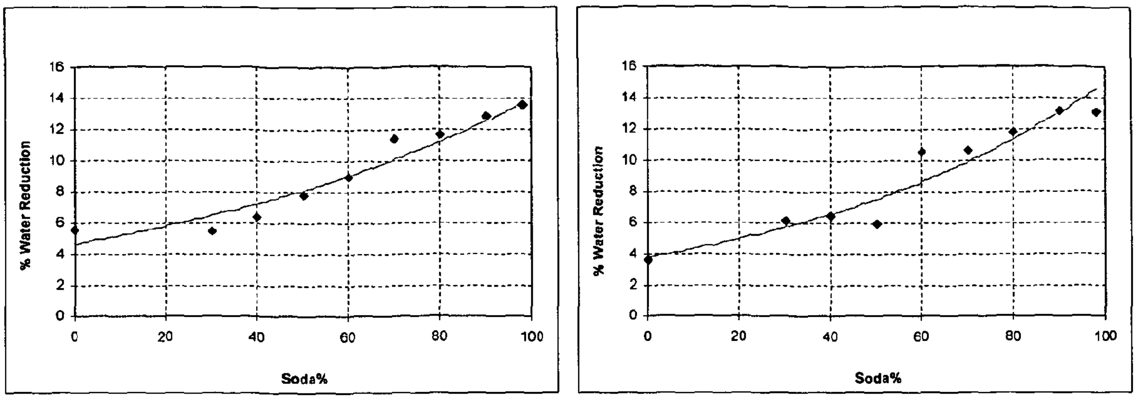
Water Content Control: 16.9% 15.9%

**** Additive addition rate as a % of total clay mass***

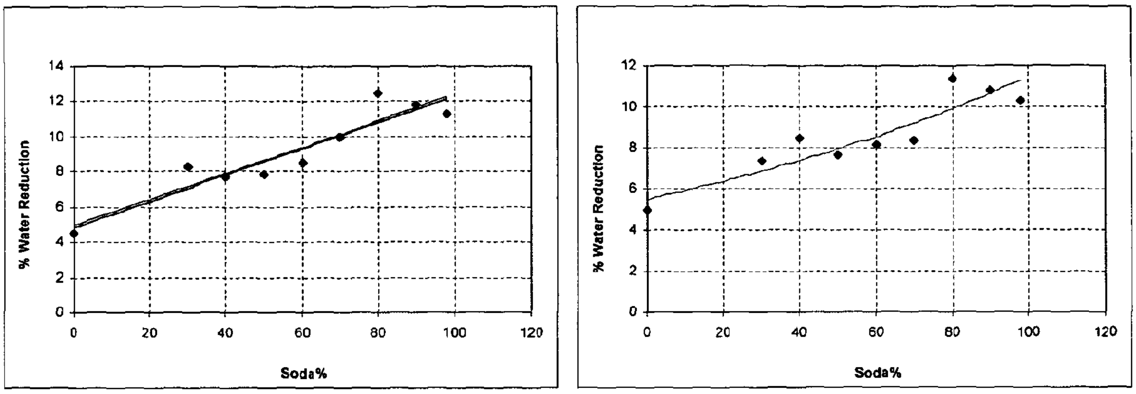
<u>**Fig 1 (Cont'd)**</u>

Pfefferkorn 15: **Pfefferkorn 20:**

Clay 2



Clay 4



Clay 5

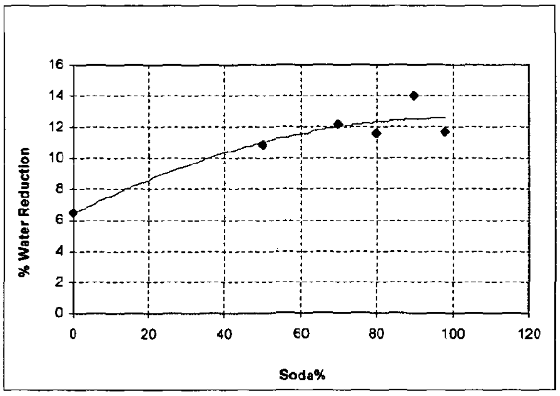


Fig 2

Clay 3

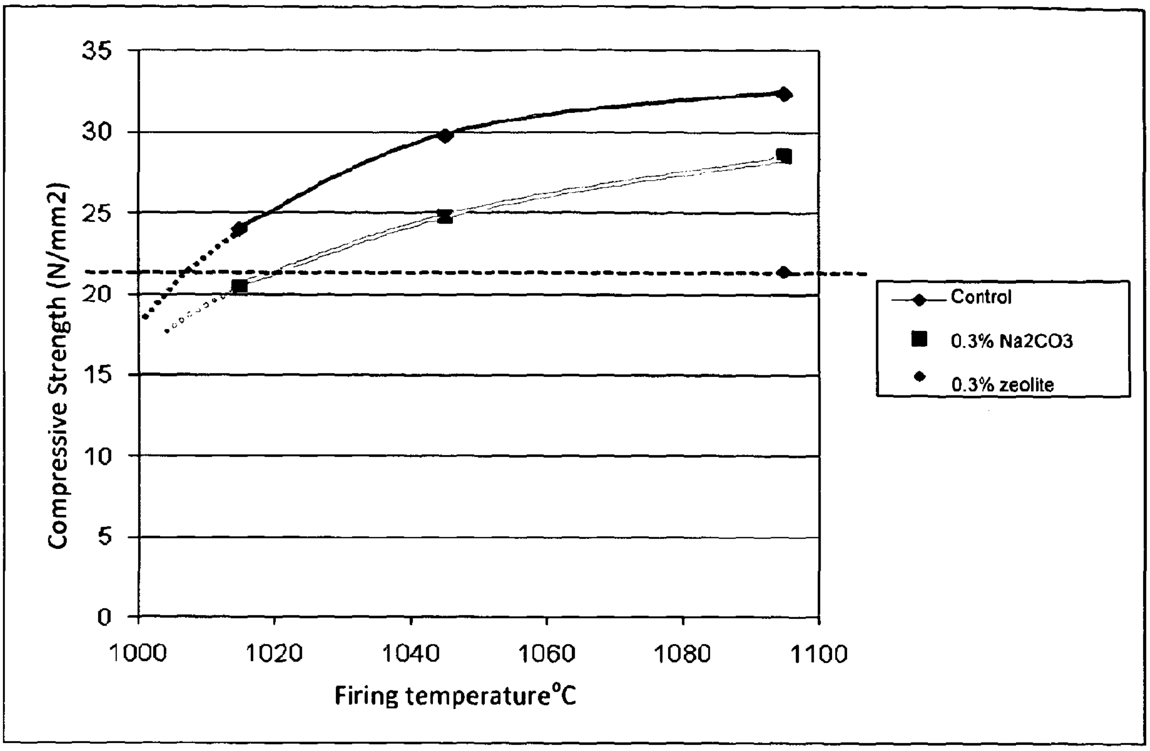
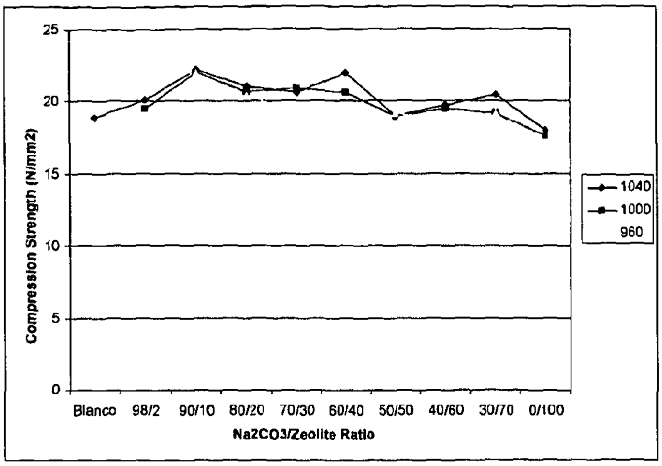
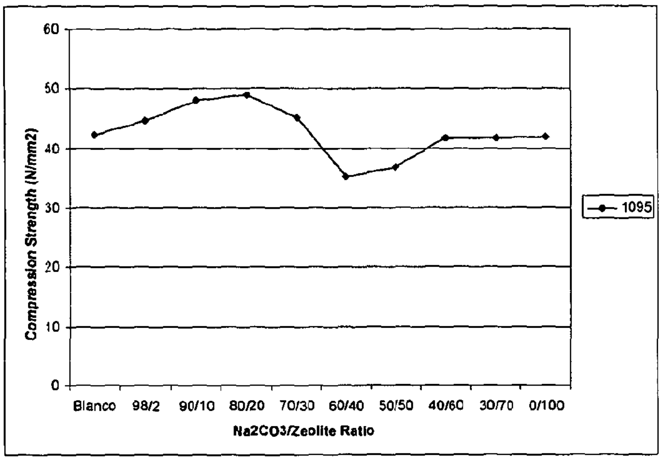

Compressive Strength (N/mm2)
35
30
25
20
15
10
5
0
1000
1020
1040
1060
1080
1100
Firing temperature°C
Control
0.3% Na2CO3
0.3% zeolite

Fig. 3

Clay 2



Clay 4



Clay 5

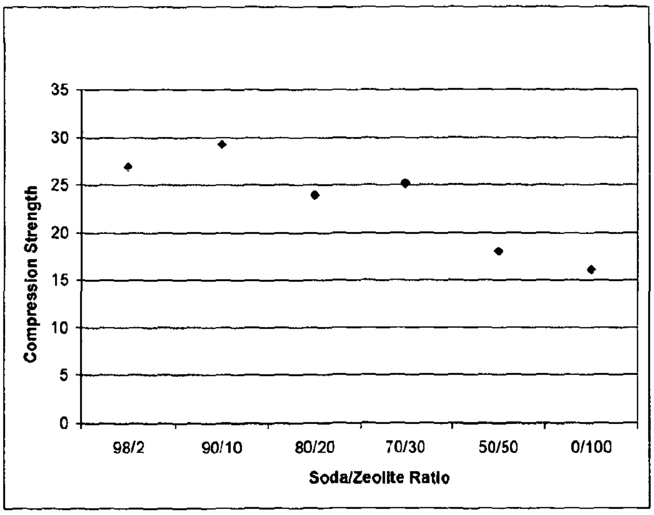
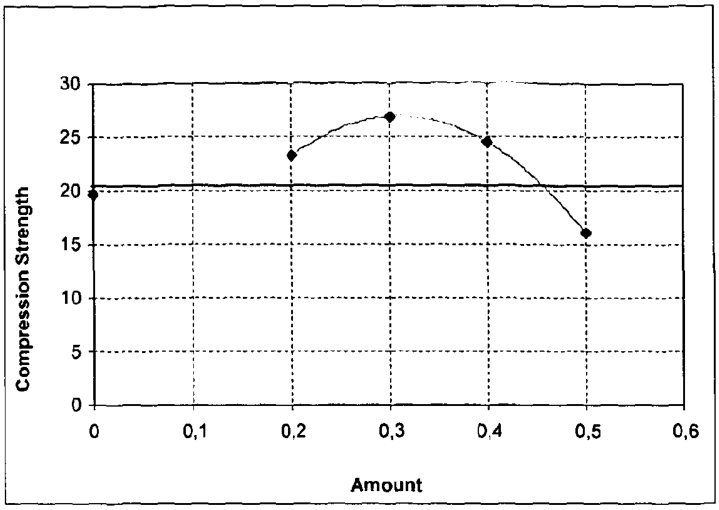


Fig 4



Firing temperature: 1035°C

Fig 5