TNO
Institute of Applied Physics

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Utilisation of Waste Materials

TNO

TNO-report

TNO Institute of Applied Physics

UTILISATION OF WASTE MATERIALS

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1. Introduction

Do You Have a Moment for Khaminal and Yuy? The time? The 3rd Century after Christ. The place? The Mayan city of Teotihuanc, a well-known metropolis comprising about 100,000 inhabitants, buzzing with activity. A small and somewhat temperate party is being thrown at the Institute for Classical Mayan Ceramics (CMC), a branch of the Academy of Chronological Science and Temporal Philosophy (ACSTP).

Khaminal and Yuy, two young researchers, have succeeded in developing a completely new method for making earthen cooking pots. The principle is simple, as with all good ideas. The clay is first pressed over a pot-shaped mould; the rough form is then placed on a potter's wheel where it is perfected and given the finishing touch. The advantages of this technique are a greater rate of production and high dimensional stability. The latter was a special requirement of the principal, the prestigious Guild of National Decorators (GND). Dimensional stability will at last provide this leading cultural interest-group the opportunity of raising the quality of the geometrical figures produced to meet international standards. Much is expected of exports to the North.

Virtually overnight, the mysterious Mayas changed the methods used to produce their everyday pottery. That is a fact. However, this magnificently organised people certainly had better things to do than while away the days dreaming up fancy abbreviations and acronyms.

TNO-TPD *

Curious letter combinations such as TPD-TNO are the result of our own staccato era. An era however where we still are preoccupied with classical ceramics, one of the oldest products in the world.

Our work consists of finding innovative solutions for a wide variety of clients, national as well as international, and, in so doing, we collaborate successfully with several universities.

Key words : Industrial wastes,Chrome sludge, Coal ash, Fly ash, Building materials

TNO
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A solution for the problem of waste materials.

To reduce the problem of waste materials dumping, it is imperative that fwaste materials should be utilised in an environmentally safe manner either as a raw material for other products or for some other beneficial purposes. While such large quantities of waste materials get accumulated facing very serious problems of safe disposal, the building material industry is on the verge of diversification and it could be possible with the help of the industry to sensibly put to use such waste products into very useful, interesting and cost effective items. The idea of "No Waste" that is accepted and followed in developed countries can be transferred to our situation. However, although there are industrially feasible methods that have been developed and practised abroad effectively, it is not sensible to exactly imitate those technologies. For example, fly ash is a "Scarce Material" in the Netherlands to the extend they import from other countries. However, the quality of the fly ash differs mainly concerning residual carbon and other fluxes and hence it becomes very difficult to follow same processes for utilisation. Hence the situation calls for a definite way of our own thinking to prove the possibilities of an integrated approach for the fly ash and clay based building materials.

This report describes a few examples of work that has been carried out by the TNO Ceramic Department. Work that has been carried on the utilisation waste materials as alternate for the use of raw materials for building products.

TNO is the Netherlands Organization for Applied Scientific Research. TNO's primary tasks are to support industry, the authorities and other groups of the community in technological innovation, and to assist clients in solving problems.

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2. The Netherlands Organisation for applied scientific research (TNO)

TNO is the Netherlands Organization for Applied Scientific Research. TNO's primary tasks are to support industry, the authorities and other groups of the community in technological innovation, and to assist clients in solving problems. TNO does this by rendering services and translating technologies into practical applications, either for individual companies or for research associations. TNO is a fully independent R&D organization with a staff of about 4600 and a total turnover of more than 350 million ECU a year. TNO's R&D takes place at fifteen institutes and laboratories, spread throughout the Netherlands.

Dutch industry and ministries are important clients of TNO. Not only does TNO work for individual companies; groups of companies or a whole branch of industry also regularly call upon the services of TNO. A large number of industrial clients belong to the small and medium-sized enterprises (SME's) In addition, TNO works for an increasing number of companies and establishments abroad. At present TNO derives about 25 per cent of its market turnover from contract R&D for the foreign private sector and international organizations. R&D conducted by TNO is largely directed at answering questions of practical importance. However, TNO maintains close contacts with basic research institutions, both at home and abroad, in order to translate the most up-to-date technologies and insights into practical applications. TNO's major activities are R&D, the transfer of know-how, and the application of technologies in products and processes.

TNO is a member of the European Association of Contract Research Organizations the European Materials Research Consortium (EMARC) and the European Industrial Research Management Association (EIRMA).

TNO Institute of Applied Physics (TPD)

The TNO Institute of Applied Physics operates within TNO. The TPD has a staff of 350 and a gross turnover of DFL. 65 million. Its major activities are Instrumentation, Optics, Acoustics, Process Physics, Computer Sciences and Inorganic Material Research. The Materials Department is subdivided into Technical Ceramics, Traditional Ceramics , Glass Research and Inorganic Material Chemistry . The Inorganic Material Research Department is located on the grounds of the Eindhoven University of Technology, close to the faculty of Chemical Engineering. The department has a staff of 50 and a gross turnover of DFL. 12 million.

TNO-TPD Department of traditional Ceramics

The TNO group of Traditional Ceramics is an independent research institute. Today it forms part of the TNO Institute of Applied Physics. The group of Traditional Ceramics has a staff of 12 and a gross turnover of DFL. 2.2 million.

Traditional ceramics is one of the many interest areas of the TPD-TNO Institute of Applied Physics, a contract research organisation with more than 50 years of experience. Interdisciplinary projects on the verge of physics, chemical technology and mechanical engineering are our specialty when it comes to materials research. Next to traditional ceramics also technical ceramics and glass are researched in TPD's domicile near the Eindhoven University of Technology. TPD's head offices are situated in Delft, the city where it was founded shortly before the Second World War under the auspices of the Delft University of Technology. We were simultaneously incorporated into the TNO Organisation, which is now with a 4,500-strong staff the largest contract research organisation in the Netherlands. With approximately 380 staff members, TPD serves a clientele which varies from small high-tech companies to large multi-nationals. About 80% of our work stems from industrial assignments.

Centre of expertise

TPD's Traditional ceramics research concentrates on exploratory and applied research into tile, whiteware, sanitary ware and building ceramics, as well as the industrial production of refractories. Apart from research, we also offer a wide array of knowledge-based products, of which workshops for companies are an example. Activities take place on the grounds of the Eindhoven
University of Technology, because of the cooperation between this University and our institute. This, combined with the relationship with the Delft University of Technology, as well as the broad scientific and technological base of TNO, makes the Materials Section in Eindhoven a international centre of expertise in the field of traditional ceramics.

Next to industrial assignments, traditional ceramics research is also carried out for the national government and the European Community. Nowadays about 30% of our workload is coming from beyond the national borders. Since our government is a staunch supporter of our exploratory research activities, we are able to provide industry's questions about tomorrow - and the day after that - with an answer today.

Research

In recent years demand has concentrated to researching ways of saving energy and reducing noxious emissions. Because of this, our understanding of clay mixtures and of energy and gaseous emissions (fluoride) is increasing enormously. We are learning more and more about the characteristics and influence of raw materials, product and kiln atmosphere. Working in close cooperation with industry, we have studied possible uses for lower quality clays. We are always busy translating our knowledge in this field to practical and technological solutions.
Our research and development activities include the following areas:
- manufacture and processing of ceramics and refractory materials
- ceramic products: materials science, product properties and product development
- recycling of inorganic waste materials
- energy and environment in the ceramics industry
- standardisation and certification
- consultancy and knowledge transfer to industry

This is What You Can Expect

Our work for the ceramic industry is naturally aimed at lowering their (production) costs by improvement of the company processes. Sometimes through translation of state-of-the-art technology to the specifications of the ceramic industry, sometimes through complete new finding.
To be more specific: in recent years our projects covered a whole range of traditional ceramics technology fields, such as:
- optimising industrial drying plants by means of physical and mathematical modelling, experiments and on-site measurements and improvement; new design concepts of dryers.
- optimising the firing process by physical modelling and experiments related to the need for better firing control and faster firing times; new design concepts for kilns.
- research into the formation of fluoride during the firing process, and possibilities for "process-integrated measures" to limit the emission of fluorides in the tile and brick production,
- research into emissions, flue gases and cleaning installations
- theoretical and experimental studies into reduction firing of roofing tiles and bricks,
- energy-efficiency, proces-integration, energy-scans, energy and environmental surveys, etc.

- raw materials, including the prediction of raw material behaviour in the production and process applications for calcinated clay , waste, harbour sludge, chrome-containing sludge from the leather industry, etc.
- research and development of refractory materials
- research into the dry pressing of wall tiles and, more recently, roofing tiles and bricks
- CAD/CAM for pottery and tile companies
- pressing of hand-shaped and moulded bricks
- characterization and improvement of glazes
- modelling the mechanical characteristics of floor tiles
- developing methods and tests for slip resistance of tiles
- application of radiant tube burners

CERLABS

Of course we can not do this alone. That's why we are founding member of a European consortium of ceramic laboratories: CERLABS. This group's goal is to create a platform for all European ceramic laboratories to discuss and exchange information at an international level. Institutions outside Europe have shown an interest in this form of collaboration, and several are presently members of CERLABS.

How can we work with you?

TPD-TNO has a very enthousiast team with experts working for years for the ceramic industry. People who know how to plan a project and how to listen carefully to a client's needs. And that is very important when you are talking about research... We carry out small, medium- sized and large projects for a wide clientele, Dutch as well as international. Collective projects involving several different industries, EC projects and industrial consultancy are all possible. If you would like us to research areas other than ceramics, we can quickly assemble a multidisciplinary project group. The various areas in which the TPD is active, and the diverse specialisations of other TNO institutes offer interesting prospects of achieving quick results. Please don't hesitate to contact us if you have a question that needs to be answered.

The Building Ceramics Group and waste materials

Has proven experience in developing various building materials to commercial production levels based on the wholistic approach of waste utilisation and pollution abatement. Presently a CSIR-TNO linked project is under progress in which RRL(T) and the Building Ceramics Group of TNO at Eindhoven are actively participating. They also develop consolidated fly ash in various ways for a variety of possible end users. Ceramic flux binding of fly ash is a controlled way of creating a thin glass layer around the fly ash particles making use of the fluxing constituents already present. Cold bonded fly ash is a low temperature organic/inorganic binder system to react and bond fly ash particles to high strengths.
In both institutes is a wide range of expertise from the TNO Netherlands and RRL(T) to develop fly ash based building materials. The TNO building group has a experience of applied science and practical technology for over 50 years. They are also willing to set up a plant that can produce new and usable building materials based on fly ash.

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3. Utilisation of chrome-containing sludges

Introduction

The underlying paper describes in short the most relevant results of the entire project: "Utilisation of chrome-containing sludges", as part of the TNO-CLRI programme: "Institutional strengthening of the Indian leather sector in the field of environmental technology".
Moreover it deals in detail with the outcome of the more recent brick making experiments at laboratory- and technical scale and the underlying study of the high temperature chemistry of chromium to ensure a safe production and product.
The research dealing with the finding of a safe process ensuring acceptable mechanical brick properties with acceptable low contents of hexavalent chromium was executed by: two CSIR Institutions:

- the Regional Research Laboratory in Trivandrum (RRL-T)
- the Central Leather Research Institute in Madras (CLRI)

and the TNO Institute of Applied Physics Eindhoven, Department of Traditional Ceramics (TNO-E)

The Indian leather industry produces yearly about 150.000 ton of chrome-containing sludge which is classified among hazardous wastes. This is one of the toughest environmental problems of leather making for which hardly any practicable solution was available at the start of the TNO-CLRI programme. Even stringent introduction of the newest in-tannery environmental technology will nor reduce the magnitude of this problem in India. In this decade the scheduled doubling of the Indian leather production together with strongly reduced emissions of chome, resulting from the introduction at large of new environmental technology, will lead to a nearly constant amount of sludge. However these sludges which will originate mainly from biological treatment systems will contain substantially lower quantities of chromium.

The project was started with three options of sludge applications:

- in bricks
- in refractories
- in pigments.

However, the low purity of tannery sludges made only one option, the application in bricks in principle viable. To become at short notice acquainted with problems related to admixture of chorme sludges in brickmaking a technical scale experiment was executed in Quilon, India. Although the sludge quality was very poor due to presence of large quantities of foreign material, the bricks obtained had acceptable mechacical strengths but the content of leachable Cr(VI) after firing was about 20 times higher than te maximum allowable level according to the Dutch standard NEN 7341.
The large differences found in levels of leachable chrome between the different laboratories induced the start of setting up well defined (NEN 7341) leachability test systems at RRL-T and CLRI and a critital review of the prevailing conditions in the laboratory kilns at TNO-E and RRL-T. It turned out that the firing process in the semi-closed RRL-T furnace proceeds more or less under reducing conditions and at elevated carbon dioxide pressuresx. The TNO-E furnace, however, approaches closely the situation of a usual technical kiln: mostly a rather well-ventilated system in which the firing process is oxidative and proceeds at low carbon dioxide pressure.
It thus became evident that in the RRL-T furnace the presence of carbon dioxide induced less pyrolysis of calcium carbonate and thus less alkalinity in the brick sample obtained, this together with the lack of oxygen revealed samples with a low Cr(VI) content.

Evidently the conditions in the TNO-E furnace and to a lesser extent in the industrial Quilon kiln lead to high alkalinities and extractable Cr(VI): the pH of aqueous extraction reached maxima of up to 11 and the conversion of chrome(III) added into chrome (VI) of up to 90 % !
These findings were very fruitful in defining the conclusive experiments to elucidate the essentials of the high temperature behaviour of trivalent chromium in klins and to find practical ways to circumvent the presence of too high Cr(VI) content in the bricks obtained.

It turned out that firing under exclusion of oxygen and increased carbondioxide pressure is not feasible in the usual practice.

The important breakthrough was reductive cooling after conventional firing till 900 ^{o}C and soaking, followed by closing the kiln as far as possible. When cooling, by injection of water and reductors like kerosene, till about 100 ^{o}C the Cr(VI) content can be reduced till levels below 40 mg/kg. This laboratory finding was confirmed by an experiment on technical scale at M/s. Raja Tiles in Trichur, Kerala.

Brick making under reduced cooling conditions is practiced in the Netherlands but new to the Indian industry. During a workshop with the Indian brick making industry the typical black color of the bricks (and roofing tiles), as well as the substantial reduction of firing energy (up to 20%) and a possibility of a general upgrading of process quality when introducing this technology were considered to be attractive industrial features.

The total emission of waste streams in Indian leather industry amounts approximately 150.000 tons of solid wastes containing 5000 tons of Cr.
In view of the magnitude of the Indian brick production (approx. 40.000 - 45.000 mln pieces in 1992) processing yearly 90 - 1000 million tons of clay, the application of 150.000 of chrome sludge must be considered as well feasable.

For the leather industry the safe processing of chrome sludges in brick making is a great relief which fits nicely in an integral approach to the solution of its environmental problems.

Based on the laboratory experiments at RRL, Trivandrum and subsequent confirmation trials at TNO (The Netherlands), the following factors were established, along with the undoubtful inference that the sludge-clay bricks have good strength.

- (1) Tannery sludge upto 30% wt can be mixed in red burning clays although this will range between 10-30% depending on the quality of clays.
- (2) Extrusion and firing are the appropriate steps for making such bricks.
- (3) Firing temperature will be around 800-900°C depending on the quality of clay.
- (4) A reduction firing process devised for such bricks under laboratory condition is the only solution for preventing reoxidation of Cr(III) to Cr (VI) in such bricks. A result of this is that such bricks would be black in colour since iron oxide in clay also gets reduced in the temperature range of 500-550°C.
- (5) A suitable kiln, therefore, has to be identified for the firing of sludge-clay bricks where the kiln has to be fully made air tight and inside maintained reducing during firing. The visit of RRL Scientists to Netherlands provided opportunity to talk to Mr. de Vries of the TNO on this process in detail. They also were able to see the factories where the reduction firing is adopted to produce black roofing tiles.

Identification of the factory at TRICHUR, KERALA, INDIA

For the scale up experiments, a factory in Central Kerala was identified after examing the facilities in many tile and brick factories in Kerala. M/s. Tiles, Trichur is one of the oldest tile factories with progressive thinking and has a spare production line which is used mainly for experiments. These facilities include a pan mill, extruder and shuttle kiln with capacity to fire about 2500 bricks. The fuel used is primarily oil, but wood can also be used as fuel. Basically the kiln is designed for firing under oxidising conditions, but compact enough to modify for reducing atmospheres, essentially by keeping excess pressure inside.

Raw Materials for the sludge-clay mixture

The clay was taken from the stock of the factory and had a reasonably high plasticity. No mixing of different varieties of clay was required since the one available was already mixed and aged sufficiently. The chemical analysis showed (Table I) that the iron oxide content was about 2.3% and under usual oxidising firing conditions a bright brick red colour is observed. The results of physical characterisation test for this clay are presented in Table II. There is an average dry to fired shrinkage of 3.4% at 700°C to 800°C and this was taken as the top firing temperature.

Table I: Chemical analysis of clay

SiO_2	:	62.80
Al_2O_3	:	22.48%
Fe_2O_3	:	2.3 %
CaO	:	0.21%
LOI	:	12.36%

Table II: Physical characterisation of clay

Property	Firing Temperatures °C 700°C	800°C	900°C
Density (g/cm^2)	1.669	1.760	1.760
Porosity (%)	17.820	14.500	22.000
Shrinkage (%)	3.640	5.100	4.096

The sludge was arranged through the CLRI from two main sources representative of the present and future tannery industry in India. They are, low chromium containing sludge (3%) designated as A, high chromium containing sludge (5%) available from common effluent treatment plants (CET) designated in this report as B. Further in order to got a moderate chrome, a 1:1 mixture of the A and B samples were made and was designated as C. Detailed chemical analysis showed that the sludge A has 2.69%, B has 5.75% and C has 4.22% chromium oxide, while all the three samples had loss on ignition (organics) of about 50%.

Clay-sludge mixtures were made in the factory by carefully layering the clay and the sludge such that the composition were:

				Chromium content as analysed %
1.	Mixture 1	-	85% clay - 15% A	0.254
2.	Mixture 2	-	85% clay - 15% B	0.406
3.	Mixture 3	-	90% clay - 10% C	0.227

Accordingly within the limits of large scale mixing efficiency, the following were the actual chromium content in the mixtures 0.254%, 0.406 and 0.227% in mixtures 1, 2 and 3 respectively.

. Fired Properties of Sludge-Clay Mixtures

The physical properties of small tiles of size 50 mm x 50 mm x 10 mm followed by dry pressing the mixtures 1, 2 and 3 fired at 700, 800° and 900°C are presented in Table III(a) and (b). As the temperature is increased, we find a reduction in porosity and increase in shrinkage. However, the particular clay has a reasonable firing temperature of about 800°C. In all the cases, the sludge-clay mixtures has lower densities and slightly higher porosities as expected. The sludge clay mixtures also are identified by the loss on ignition values which are higher than the clay samples. There is only marginal difference in the calculated and experimental values of sludge (taking into account 50% loss on ignition of sludge).

Table III (a) : Loss on ignition of the clay and clay - sludge mixtures

Mixture		
Sludge - Clay I	:	15.398%
Sludge - Clay II	:	16.473%
Sludge - Clay III	:	15.130%
Clay	:	12.368%

Table **III** (b): Fired properties of sludge - clay mixtures

Property	Mixture I 700°C	800°C	900°C	Mixture II 700°C	800°	900°C	Mixture III 700°C	800°C	900°C
Density (g/cm^3)	1.497	1.61	1.623	1.584	1.658	1.72	1.55	1.67	1.68
Porosity (%)	21.95	13.92	20.00	25.00	15.38	25.71	22.2	25.0	17.428
Shrinkage (%)	1.89	2.9	2.1	4.0	4.27	3.27	5.9	4.7	3.76

. The Reduction Experiment

All tile clay bodies when fired under normal oxidising atmoshperes, assume the brick red colour which is due to the presence of Fe_2O_3. By creating a reducing atmosphere during cool-ing of Fe_2O_3 containing clay bodies it has been seen (ref. 1-3) that the $Fe_2)O_3$ can be reduced to Fe; FeO or Fe_3O_4 depending on the extent of reducing the minimum temperature for reduction is conttinued upto 400°C. Since Cr (VI) is more easily reducible chromium could also be reduced under similar circumstances. In fact the earlier studies conducted at TNO/TPD Eindhoven showed that a cooling upto 250°C-300° C is required to prevent the reduced Cr(III) getting reoxidised to Cr (VI).

Selection of Recuction Kiln

Since in India, reduction firing is not followed in tile industry on a regular production line. However, M/s. Raja Tiles, Trichur had an extra facility of an experimental kiln, though of oxiding type. Further, the management was forward looking and agreed for the experiment. . The kiln is one which can be heated by firing of wood there are two fire mouths each on the two sides, a heavy door and two cars which go into the shuttle kiln. The total capacity of the kiln is about 2500 bricks which accounts for about 8 tonnes of clay.

The Reductant

Usually in such cases either H_2/H_2O, or CH_4/H_2O or CH_3OH/H_2O may impart the property as reductant. In the present situation judicious mixtures of kerosene and water are found the most suitable since the industry uses kerosene in the extrusion work. Hence it was discussed and finalised with TNO that for this experiment, known quantities of kerosene and water will be manually added or mechanically controlled such that the reducing situation judicious mixtures of kerosene and water are found the most suitable since the industry uses kerosene in the extrusion work. Hence it was discussed and finalised with TNO that for this experiment, known quantities of kerosene and water will be manually added or mechanically controlled such that the reducing gases are formed by allowing them to react at the point of injection. However, adequate care has to be taken due to the high carbon content and low ignition temperature of kerosene when injected together which may result in enormous volume expansion.

. Experiments on Reduction of Chrome Sludge-Clay Bricks at Trichur

(a) Extrusion of Sludge-clay mixtures to bricks

The three mixtures 1, 2 and 3 containing 15% sludge A, 15% sludge B and 10% C were kept for a week after stacking each composition separately and then cut vertically and extruded into the form of bricks. The moisture content of the extruded mass was about 16%. Homogeneity of the mixtures were evaluated by taking random samples and finding the value of the loss on ignition. The bricks were dried in covered area for about 10 days and then further dried in wood fired smoking chambers.

(b) Modification in the kiln for reduction

The kiln has many small outlets for keeping temperature sensors, peep holes for observing the extent of firing and air gaps at the door as well as the way to the chimney. Further, since the kiln is fired by wood, there are four fire mouths of about 60 cms diameter through which the wood is introduced. All these ultimately should be sealed fully by the time reduction starts.
As a first step, a metal tube of 10 cm dia was introduced through a hole in the top of the kiln with a ceramic portion at the end which projected into the kiln. The other end of the metal tube was extended to about 6-8 meters where two inlets join which carry water and kerosene respectively. The water and kerosene can be separately introduced into the pipe at predetermined proportion and rates. All the openings of the kiln have been closed not to allow inlet of air except the fire mouths and the chimney. After loading the bricks in the kiln, the door also was closed air tight. The thermocouple holes were also sealed, after fixing them. The thermocouples were connected to a side table where a selector switch and millivolt meter/temperature indicator where continuous measu-rement of the temperature from five different points inside the kiln, were done.

(c) Reduction firing Experiment I

After making the preparations in the kiln, two cars were loaded with sludge-clay bricks of about 1250 numbers each and were pushed into the kiln. The door was closed air tight. The firing was started by slowly introducing the fire wood uniformly from all the four fire mouths.
After reaching the top temperature of 780°C and soaking for about 30 minutes, the reduction started with an initial flush of steam to keep a positive pressure inside the kiln, simultaneously closing the fire mouths and the outlet to the chimney. This was followed by the sequence of water + kerosene mixtures as provided in Table VI.

The requirment of kerosene and water mixture was precalculated based on the theoretical basis, taking into account the total weight of bricks being fired and the iron

oxide and chromium oxide content present in clay. However, there was an excess of about 50-755 given towards losses through the kiln due to imperfact sealing.
The practical solution was always to keep a positive pressure maintained inside the kiln. The first experiment was stopped at 400°C in view of its long cooling time and reduce reoxidation of the chromium and iron took place through the passing in of air through the imperfectly sealed holes.

(d) Reduction Firing Experiment II

This has been a repetition of expriment I, excepting that more precautions were taken with respect to sealing the kiln from entering of air during cooling and also the addition of reductants were continued till the temperature was reduced to less than 250°C. In view of the absence of any external cooling system, the rate of cooling below 500°C was extremely slow (0.2 °C/min) which could be seldom controlled by the addition of water + kerosene mixture.
However, all though the cooling range, care was taken to observe a positive pressure inside the kiln.
The whole bricks samples in this experiment were black or black/grey and not red at all. It has thus been possible to conduct reduction experiment successfully in the most convential kiln fully designed earlier for oxidative firing, by judiciously controlling the reduction parameters. The leachability results of chromium from this experiment are presented in Table IV.

Table **IV**: Analysis of leachable chromium (vi) from the various compositions fired in the experiment

	Sample	Leachable chromium (VI) mg/kg
I	(15% sludge A)	NIL (< 5)
II	(15% sludge B)	NIL (< 5)
III	(10% sludge C)	NIL (< 5)

<u>Conclusion</u>

It has been possible by the experiment to show that leachable chromium can be brought to nearly zero levels by cooling the fired sludge-clay bricks under controlled reducing conditions. The first time finding of RRL (T) that partial reducing atmosphere in kiln can bring down leachability of chromium incorporated in sludge clay bricks which was later confirmed by TNO/TPD Eindhoven has thus been applied succesfully at the Trichur Experiment by following the parameters finalised during the visit of RRL (T) scientists to TNO. This finding and similar innovative ideas were also discussed at an Industry - R&D meet organised in Trichur where active participation from the tile and brick industry resulted. In view of this, a future strategy has been suggested to extend the reduction firing technology in a most wider sense to the tile and brick industry in this region, in addition to that being already extended to the tannery industry.

4. Fly ash and coal residues as new raw materials for building products.

4.1 Chemical and physical properties of fly ash

Coal contains inorganic mineral components, which remain as ash after burning. The ash can take two forms:

- Bottom ash
this is the fraction that is collected at the bottom of the incinerator and consists of coarse and heavy particles;

- Fly-ash
this is the lighter fraction which has been carried away with the flue gases.

In powder coal fired electricity plants, 80%-90% of the total ash consists of fly- ash. The fly-ash is almost completely collected in the kiln stack through air filters. The chemical and physical properties of the fly-ash are strongly dependent on the type of coal used, the grain size of the coal and the way the plant is operated.

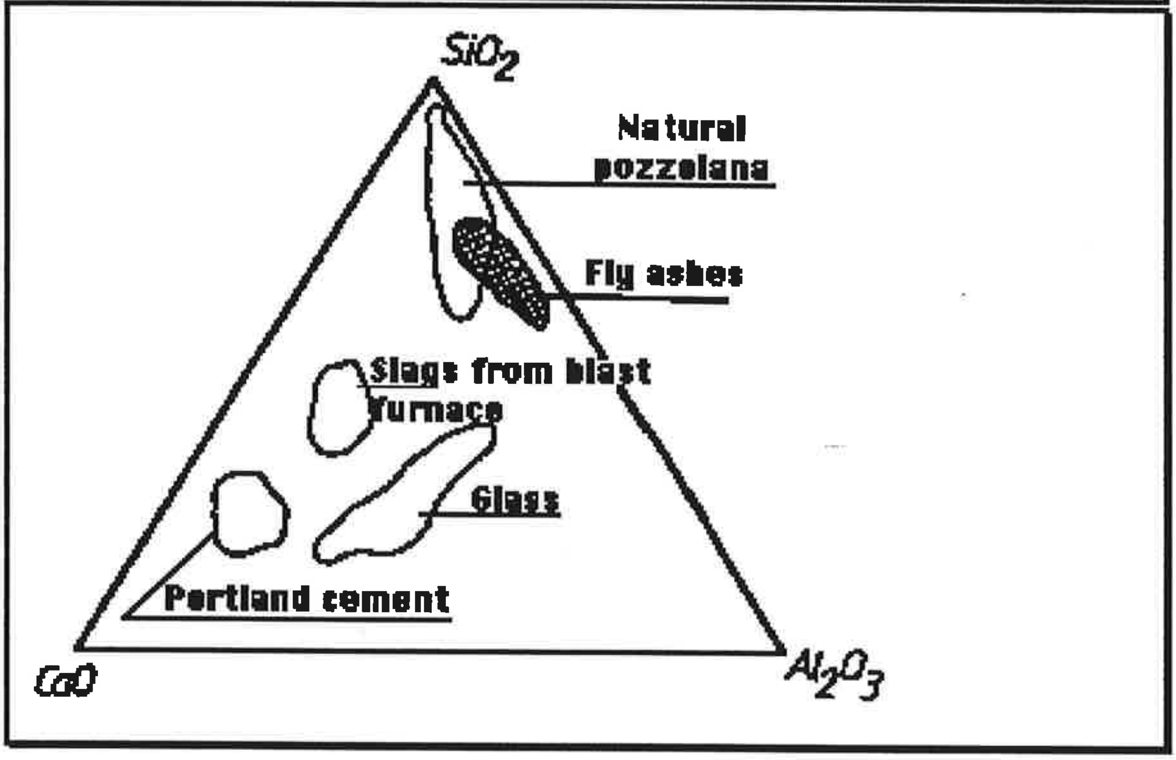
Fly-ash consists mainly of oxides (about ten), of which SiO_2, Al_2O_3 and Fe_2O_3 form more than 80% of the mass. Furthermore, a large number of trace elements are usually analysed, sometimes more than 50, most of which in low (0.1 - 0.01% $^m/_m$) or very low (<0.01% $^m/_m$) concentrations. Usually a certain percentage of unburned coal is also present.
Morphologically, fly-ash consists of round particles with a glassy structure. A small fraction of the minerals occurs in crystalline form, for instance quartz (SiO_2), hematite (Fe_2O_3), mullite ($Al_2O_3.SiO_2$). A separate fraction, 4% - 5% of the fly-ash, consists of so- called floaters, which are hollow glassy particles filled with gas bubbles (N_2 en CO_2), which makes them float on water. Their properties differ somewhat from the other particles.

SOME TYPICAL PHYSICAL CHARACTERISTICS OF FLY ASH

PROPERTY	
Specific density	2000 - 2400 kg/m^3
Powder density	800 - 1000 kg/m^3
Grain size diameter	0,5 - 200 µm
Grain size distribution	85 á 95 % < 75 µm 65 á 83 % < 37 µm
Specific surface	3000 - 4500 cm^2/g
Asphalt number	25 - 60
pH value (general)	8 - 10 min. 5 - max. 12

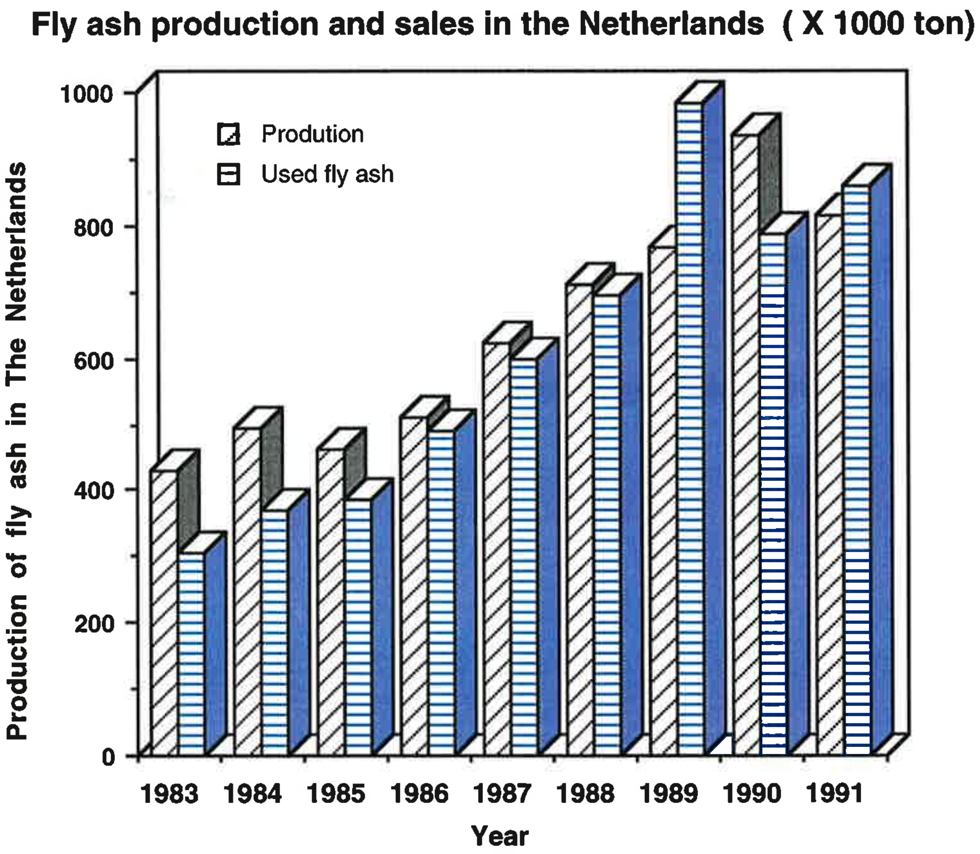
Chemistry of fly ash in comparison with other materials

FLY ASHES IN COMPARISON WITH SOME MATERIALS



4.2 Fly ash and coal residues as new raw materials for building products.

The Netherlands has a well-advanced policy on environmental and energy conservation. The use of coal in the Netherlands demands an integral approach in which logistic as well as technological and environmental problems demand solutions. To address these inter related problems the National Clean Coal Programme (NOK), a ten Years programme, was established. Under funding by the Netherlands government, the Netherlands agency for energy and the environment (Novem) was charged under NOK with responsibility for establishing means of ensuring recovery of desulphurisation residues. These Activities, in this framework, have included research, development, technology demonstration and market introduction. Novem has set up the programmes and projects in co-operate with companies and research organisations such as the TNO organisation. In this program is, concerning the environmental protection, also aimed to the goal of reuse fly ash. Although the use of coal-waste as raw-materials in the cement, ceramic- or lime industry is possible. There are develop several new applications and products. This with respect on the fly ash used in The Netherlands. One of the aims of the National Clean Coal Programme (NOK) is the development of appropriate possibilities for the enormous amounts of waste materials released when coal is massively used for the generation of energy. coal is not acceptable as energy resource if its waste materials cannot be reused. Some coal waste materials can be recycled to new products



The possibilities to development this materials demands on the structure of the available fly ashes.

New Products are:
- Activated-slag-cement
- Polysil-concrete
- Artificial-gravel
- Calcium-silicate-bricks
- Ceramic- bricks
- Ceramic-paving-stones
- Calcined-gypsum-anhydried-products
- Anhydride-self-levelling-floors
- Ceramic- gravel
- Isolation materials

The effective utilisation of the existing as well as expected fly ash resources is more demanding due to the need for finding out alternate raw materials for building materials from ecological point of view.
We will discredited two specific new building materials from fly ash:

Product A	Flux bonded fly ash	To develop high strength, dense, flux bonded fly ash for possible applications as bricks, tiles other building materials.
Product B	Cold bonded fly ash.	High strength, cold bonded fly ash as energy saver.

4.3 TNO ceramics project case on flux bonded fly ash

CFBA-BUILDING PRODUCTS SYSTEM

THE TECHNOLOGY

THE PRODUCTION PROCESS

THE PRODUCTS

THE TECHNOLOGY

The “CFBA-BUILDING PRODUCTS “ technology is an exclusive technology (patented) which allows mixtures, formed out of fly-ash, clay, additives and a binder to be transformed into high quality building products. Such a transformation is carried out in a high temperature tunnel kiln. The thus formed products have the same physical properties as ceramic building products.

“CFBA-BUILDING PRODUCTS“ open new perspectives. They contribute significantly to solving a number of important problems in the field of ashes of coal-fired power stations. Problems related to supply electrical energy, to the environment, to the residues, and to building industry.

“CFBA-BUILDING PRODUCTS “ are innovative products that are patented in India, and developed in collaboration between the **CSIR institute** “RRL-T “ in India and **TNO-TPD** Ceramic Department in The Netherlands.

“CFBA-BUILDING PRODUCTS “ create the possibility to use more than 85% of fly-ash in ceramic building materials. All the other materials are locally available.

CFBA-BUILDING PRODUCTS are products with a future!

THE PRODUCTION PROCESS

Introduction

The process developed by RRL and TNO creates the possibility to use more than 85% of fly-ash in 'ceramic' building materials. The process is based on well mixing of the raw materials, forming by semi dry pressing, drying and sintering of the formed products. The optimum composition of the mixture varies depending on the available materials and the properties required. All raw materials are locally available.

General outline of the production process

The production process can be outlined as follows:

- Storage of individual components
- Mixing
- Storage of mixed body
- Forming
- Glazing (if desired)
- Firing
- Storage of ready product

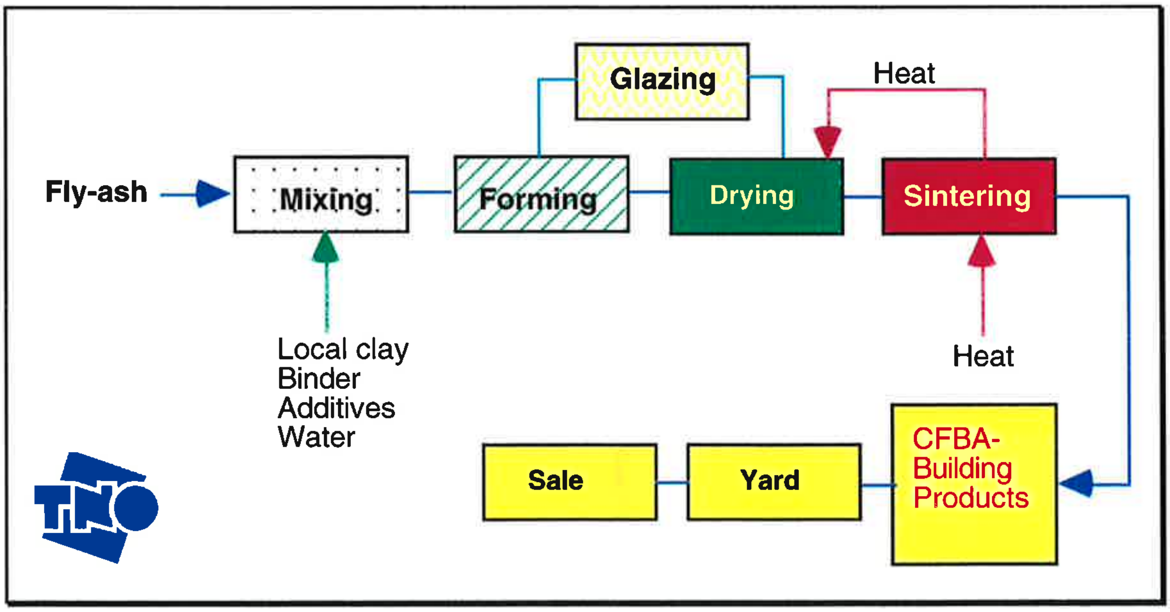


Figure 1 Schematic diagram of the production process of "CFBA-BUILDING PRODUCTS".

THE PRODUCTS

With the “CFBA-BUILDING PRODUCTS” production process a range of different building products can be made.
- Facing bricks
- Paving bricks
- Wall tiles
- Floor tiles
- Hollow blocks
- Separating blocks

All these products can be made in different colours, in different sizes and glazed if necessary.

The potential market:
The question whether there is a good market for the "CFBA-BUILDING PRODUCTS" is fundamental. The size of the potential market is determined by three factors:

- The application range of “CFBA-BUILDING PRODUCTS”.
- The size of the market for each application.
- The competitive position of “CFBA-BUILDING PRODUCTS” in relation to existing products.

The application range of “CFBA-BUILDING PRODUCTS”.
“CFBA-BUILDING PRODUCTS” find their most important application in the replacement of existing building products. Especially in the replacement of heavy clay ceramic products.
The above mentioned list of possible CFBA building products indicates that there is a wide application range. Much of these products have an existing market, such as facing bricks, whilst others, like glazed products in different colours, separating blocks and paving bricks must find their own way in the market.

The size of the market for each application.
Making an estimation of the potential market for “CFBA-BUILDING PRODUCTS” is not easy. The nearby market is the building market in the city Calcutta which is still growing. Also the number of inhabitants is growing from now 14 million people. Calculations have shown that in Calcutta there is a need of 800.000 bricks/day.

The competitive position of “CFBA-BUILDING PRODUCTS” *in relation to existing products.*
From the point of view of application and sales position, there are no real obstacles for commercial success of “CFBA-BUILDING PRODUCTS” in relation to existing products.
The production process is not only to solve the problem of the utilisation of fly-ash but there is also a need of new building products in Calcutta. The social and economic status of India and Calcutta is growing, so it may be expected that the need in the future will increase. As a result there will be a market for new building materials. Moreover when these products have the same ore a better quality than the existing products. On the other hand the government of India has given rules to solve the fly-ash problem. This process helps to solve that problem even on a longer term.

The last question still to be answered concerns the chances of "CFBA-BUILDING PRODUCTS" to gain a reasonable share of the market. This will depend mainly on the competitive position between other building materials and "CFBA-BUILDING PRODUCTS". There are three important criteria in this matter:

1. Quality
2. Availability
3. Sales price

Quality

The production process can be controlled completely and the quality of the end product can be guaranteed. Variations in the composition of the raw materials can be corrected easily by adapting the mixing ratio. The compressive strength of the fired products can be varied from 70 kg/cm^2 to 200 kg/cm^2 depending on the end use.

Products properties of the Calcutta samples:

Compressive strength	**: 80 kg/cm^2.**
Water absorption	**: 20 %**
Bulk density of the fired sample	**: 1,25 10^3 kg/m^3**
Colour of the products	**: from yellow to red.**

Availability

The most of the raw materials for "CFBA-BUILDING PRODUCTS" are so-called residues and non-scarce raw materials. So, there is no lack of availability of raw materials.
The production unit should be built on the same location as the power plant. So, the production of the main raw material and the production of the "CFBA-BUILDING PRODUCTS" are combined.

Sales price

The basic condition for pricing of "CFBA-BUILDING PRODUCTS" is that it should be the same price or cheaper than the traditional building products, because the "CFBA-BUILDING PRODUCTS" are equal in quality compared to ceramic building products. The costs of conventional clay bricks is given as 700 to 1500 Rs/1000 bricks. For bricks made from fly-ash by means of Indian technology, costs of approximately 600 Rs/1000 bricks are given.
Baring in mind the better quality of the "CFBA-BUILDING PRODUCTS" the first two years will be calculated with a price of 1500 Rs/1000 bricks, and after that with a sales price of 2000 Rs/1000 bricks.

4.4. TNO ceramics project case on cold bonded fly ash.

THE KERATON SYSTEM
A NEW COLD BONDED BUILDING MATERIAL OUT OF FLY ASH

THE TECHNOLOGY THE PRODUCTS PRODUCTION PROCESS

THE KERATON TECHNOLOGY

INTRODUCTION

TNO has developed a new lightweight building material. The material has been called "KERATON " on the basis of its properties ("ceramic concrete"). The project has resulted in several innovations:

¥ **The material is completely new among building materials**
¥ **Strength is obtained by low-temperature ("cold") hardening**
¥ **Microwaves are employed for the processing.**

The material can be produced in a variety of building blocks, depending on local markets and regulations. KERATON consists of cheap and ubiquitous raw materials like aluminosilicates, silica and alkalic components, often as fly-ash and other waste materials. These materials are mixed and a bonding agent is added. Mixed raw material is casted in moulds. The moulds are processed in a microwave oven for about 4 minutes. After cooling and de-moulding the building blocks are ready for transport to the building site.

KERATON can be applied as a light-weight material in the house-building industry and utility building, such as stables, barns, garages, etc. Price of one element of 60x30x10 cm for inner walls: ±$3.- Raw material costs per element: ± $2.- Energy costs per element: ¢6

Important is to optimise the product in shape and properties for the local market. Possibilities include elements in various sizes, sheets, bricks. KERATON can be shaped in the desired form by simply adapting the moulds. Thus, a product can be created which is easy for the architect and has a low cost price.

KERATON is a material well-suited for building purposes. A surface treatment or coating is recommended. Strong points are the ability to use waste materials such as fly-ash, the insulation properties and the flexibility to produce KERATON according to market demands.
Production can be done cost-effectively. Initial experiments have shown that also other waste materials can be used to produce KERATON , although properties will change. The full potentials of KERATON have not yet been exploited.

ALL DUTCH PRICE LEVEL!

THE KERATON PRODUCTS

Mechanical and physical properties:

On the basis of the developed recipe and processing technique a number of mechanical and physical properties of KERATON have been determined. When changes are made in the basic components these properties will change. Compression strengths of 1.3 N/mm^2 (density 600 kg/m^3) and 2.5 N/mm^2 (density 800 kg/m^3) were measured and lie in the same range as those for porous concrete. These strengths are suitable for inner building walls. Tensional strengths (3-point tests) are 0.40 and 0.75 N/mm^2, respectively. De elasticity modulus is low (±100 and 175 N/mm^2, respectively). This is to be expected, because KERATON is flexible, whereas concrete is brittle. Hardness of KERATON is about equal to porous concrete. The heat conduction coefficient is low: 0.10-0.15 W/M., compared to 0.17-0.23 for porous concrete. Thus, KERATON has a good heat insulation. Detailed values depend on the moisture content.

The moisture content

The moisture content ranges from 4-5% standard. Total water absorption is low: about 15% (m/m_d). A surface treatment with water repellent can reduce this even further. The capillary height of water in KERATON is small: 8-9 cm. This points to discontinuous capillaries in the material. This is favourable for locations where the materials rests on a humid foundation. Most of the shrinkage takes place in the first 7 days and amounts to 0.3%. After 2 weeks no further shrinkage is observed. A further reduction of the shrinkage time can be achieved when optimal hardening procedures are followed.

Frost-thaw resistance:

Tests according to the same standards prescribed for massive ceramic materials like bricks and roofing tiles in the Netherlands have shown that KERATON is well resistant against at least 30 cycles, with or without forced water absorption. A water repellent is recommended for areas with severe frost-thaw cycles.

Resistance against chemicals:

KERATON is well resistant against acids and bases. Tests have been conducted with hydrochloric acid, lactic acid, sodium hydroxide and ammonia. After 28 days in these solutions the average strength was only 25% reduced. These tests were performed on untreated raw laboratory samples. Coated samples will have a higher resistance.

Fire resistance:

KERATON performed well in standard fire-proof tests on aspects as
flames and smoke, in particular the 800 kg/m^3 type. The less the amount of polystyrene grains, the higher the fire resistance will be. Massive KERATON does not burn (see below).

Resistance against high temperatures:

Heating KERATON at 980°C results in a weight loss of about 15% by loss of water and polystyrene. Surprising is the remaining strength of 0.9 MPa of samples that are no more than a porous body.

Environmental aspects.:

Favourable tests have been conducted on the leaching of Selenium(Se), Cadmium(Cd), Tin (Sn) and lead (Pb). Only Arsenic (As) showed higher leaching concentrations but the values were not problematic..

Sound isolation:

Tests have been conducted to measure the insulation for sound by a KERATON wall. The results are for KERATON of 800 kg/m^3:

thickness wall [mm]	125	R-value at frequency 250	500	1000	2000	RA[dB]{dB(A)}
50	27	31	34	29	32	31
100	32	33	29	33	43	33
200	33	32	35	45	52	38

Summary of keraton properties

Weight: Lightweight variable to produce with a minimum of 600 kg/m^3. Tests and figures below reflect the properties of material with a mass of 800 kg/m^3. Massive layers at the side as a coating are also possible. Fully massive blocks/bricks are possible but not yet thoroughly investigated.

- Strength: about 2.5 MPa
- Tensional strength: about 0.8 MPa
- E-modulus: about 170 MPa
- Water absorption: about 15 %m/m dry
- Shrinkage: 1st week: about 0,3%; thereafter: none.
- Insulation: o.k.
- Sound isolation: 38 dB(A) for a thickness of 200 mm
- Heat insulation: lambda = 0.15 W/m.K; thickness for R=2.5 m^{2}K/W : 8 cm
- Weight: 800 kg/m
- Thermal expansion: 2 x 10^{-6} m/m.K
- Chemical resistant: Resistant against chemicals as Chloric acid, Ammonia, etc.
- Fire resistant: Fire safe
- Environmental tests: o.k.

THE KERATON PRODUCTION PROCESS

Composition:

KERATON consists of a mixture of fly-ash, grit, binder, silica fume, water repellent and polystyrene grains. TNO development has in this stage focused on a recipe which is optimised for strength, density and price. For this purpose a large series of experiments have been conducted. The most important variables that have been addressed were the composition of the binder, the quantity and type of additive materials, and the hardening process. Furthermore, the influence of the size of polystyrene grains has been tested. The quality and quantity of these grains directly influence product properties and cost. Mixing has also been investigated. Important is the combination of silica fume and microwave hardening. A synergetic effect has been found between the quantity of silica fume and the microwave hardening process. This relationship has not been found with conventional (convective) hardening methods.

Heating:

Hardening by means of microwaves takes only minutes, whereas with hot air it takes hours with a poor result (lower strength). The reason for this is the favourable volumetric heating effect of microwaves. The material has to be heated up to 80°C, and should not come above the boiling point of water. The distribution of heat throughout the samples was, however, not homogenous. This can be improved by a better choice of microwave frequency, for instance 915 MHz instead of 2450 MHz. Such radiation has a longer wavelength and thus a better depth of penetration. Also the geometry of the microwave cavity has to be optimised. By adjusting the amount of silica fume and the size and quantity of polystyrene grains, the strength (and cost) of the product can be adjusted to market demands.

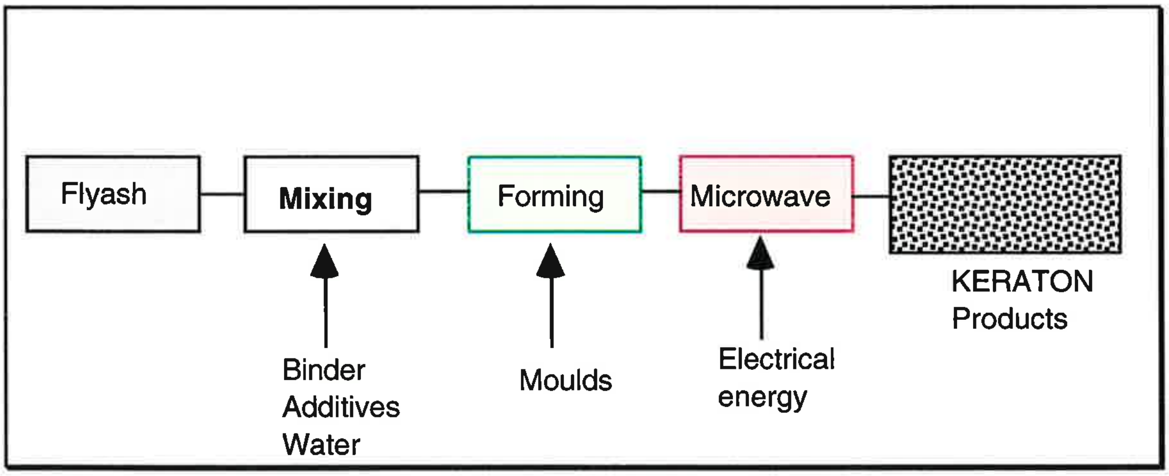
Mould material:

Mould material has to be transparent for microwaves and should have enough stiffness to withstand the pressure during processing. Several materials have been tested, such as Formica, Teflon, nylon, polycarbonate and Korean. Thus far, polycarbonate is most satisfactory. Another possibility is glass fibre-raisin composites which are used for boats etc.

Processing:

On the basis of the research results a processing line has been designed. The expected costs for this line are estimated at ± $3.5 million (Dutch prices). A comparable investment in a porous concrete installation is about $10 million. In addition, energy efficiency is 80% better for KERATON than for concrete. A factory for a production of 2.000.000 elements or 58.000 m^3 or 35.000 tonnes per year would cost in Holland for the technical equipment about $1.5-2.5 million. Doubling the production capacity would require about another $ 1.5 million. For a start a tract of land is necessary of about 5000 m^2 (with an option for another 5000 m^2) Such a factory would consume on the basis of the Dutch KERATON formula about 15.000 tonnes of fly-ash. However, this may be doubled to 30.000 tonnes /year if the formula can be adapted to higher fly-ash concentration.

Schematic diagram of the production process of "KERATON"



Energy:

Only electrical energy required.

5. Other TNO ceramics projects

The research department of TNO's Institute of Applied Physics (TPD) in Eindhoven has wide-ranging experience in the field of ceramics production. It has focused a great deal of attention on environmental impact and energy conservation, in addition to its more obvious research into firing and drying processes. The folowing projects are a example of sutch projects.

5.1 Energy efficient drying of building ceramics

A great deal of money can be saved in the manufacture of building ceramics by a more carefully considered production process. Enhanced control of the drying procedure alone can save a substantial chunk of the energy bill. Major investments are not always necessary – in many cases simple adjustments like the replacement of a burner or changing the atmospheric humidity can make a big difference. These facts have been demonstrated by trial calculations carried out at TNO, where accurate simulation models have pinpointed critical areas within the drying process.

The computer allows the workings of each dryer to be simulated down to the last detail. The precise gains to be made by small adjustments to critical parameters like temperature and airflow speeds can then be determined. And these gains can be considerable: the average producer of building ceramics wastes no less than half its energy consumption on inefficient drying.

The ceramics industry has a traditional character. It has worked for centuries on a trial-and-error basis, with experience and knowledge passed down from father to son. The clay is prepared, moulded, dried and then fired. In more recent times, the TNO experts has noticed a rapidly growing interest in the optimization of the manufacturing process, accompanied by due attention to energy conservation and care for the environment in addition to quality and cost control. That means you have to know exactly what you're doing!. 'If you want to create the ideal process conditions you first need a thorough knowledge of the process itself. That's the only way to improve design and control.'

To achieve the right mix of know-how, TNO's Institute of Applied Physics (TPD) works closely with the ceramics experts at TNO's own Traditional Ceramics section in Eindhoven. Eindhoven has the necessary knowledge of solid state chemistry and materials, while Delft specializes in flow patterns and heat, process control technology and process modelling. TPD in Delft has powerful computers at its disposal, which can run complex physical heat and flow models to simulate every detail of the industrial process. 'The beauty of the system is that its high-tech character is entirely transparent,' Dalhuijsen says reassuringly. 'The most important thing is to extract reliable conclusions that can be applied in a traditional manufacturing company. New ideas have to translate into practical solutions.

The value of model research is illustrated by the simulation of the drying process. Dalhuijsen: 'There's ample room for improvement in this area as far as the production of building ceramics is concerned. The drying process is far from perfect.'
Model research is carried out at a variety of levels. An airflow model has been developed to describe heat transfer. It allows temperature and atmospheric humidity to be calculated in relation to local airflow speed. The airflow model is a tool that can improve uniformity during drying. Uniform drying is critical if crazing caused by shrinkage is to be avoided.

The DRYSIM dryer model is available for studies at macro-level. It uses the findings of the airflow model as input. DRYSIM is designed precisely to simulate the different processes in the dryer. Data on temperature, atmospheric humidity and the weight of the wet product allows the optimum drying parameters to be calculated along with their energy requirement. Apart from information on the drying chamber, the system also contains data on the rest of the drying system, including burners, vents and airways.
The models combine material and process knowledge and are, as one would expect, tested in practical situations to check their reliability. 'Comparison with laboratory measurements carried out in experimental dryers proved highly favourable'. 'To refine DRYSIM, we kept taking wet products from the plant, wrapping them up carefully in plastic and taking them to Eindhoven. We then put them in a laboratory dryer so we could carry out a range of tests on them.'

A specially designed optical shrinkage meter allows the drying shrinkage of wet products to be measured in the lab dryer via video images, thereby avoiding the need for direct contact. The optimum drying curve for each product can then be plotted, so that the product can be dried as quickly as possible without crazing. Knowledge of a product's ideal drying curve is vitally important to manufacturers wishing to improve their drying process.

'We recently used our simulation models to achieve an energy saving of between five and fifteen percent at a fairly new drying plant', Dalhuijsen says. 'The drying time itself remained more or less the same. The saving was achieved via adjustments such as drying at a more uniform rate. More radical changes can result in ten to sixty percent energy savings and a ten to forty percent reduction in drying times.'

5.2. Fluoride problem tackled

The fluoride problem is a live issue in the Netherlands, which is the home of Sphinx and Mosa and the Vereenigde Glasfabrieken plant. Fluorides have been covered by the Netherlands Emissions Directive (NER) since 1994, and European regulations are currently being drafted.In addition to Sphinx, the manufacturers behind the *New Generation of Roller Kilns* project – set to cost twelve million guilders over the next five years – include two ceramics companies, a kiln-builder and a burner manufacturer.

Before the project could get off the ground, the Institute of Applied Physics (TPD) at TNO Eindhoven carried out an extensive preliminary study into the interaction between clay and flue gases. 'To design a better kiln, you first need a detailed understanding of the way fluorides are generated and released. Fluoride emissions from the clay were found chiefly to arise from the action of the water vapour created by the combustion of natural gas in gas-fired kilns. If you use natural gas to cook at home, you will have noticed how the windows quickly steam up. Gas-fired kilns create a lot of water vapour in precisely the same way. The TNO study revealed that the water vapour in the kiln atmosphere reacts with the sintering clay, particularly in the temperature range 800 to 1100 degrees. It is this reaction that causes gaseous hydrogen fluoride to be released. This can be prevented by switching to an enclosed burner system which allows the kiln to remain dry. According to TNO, if the quantity of water vapour in the kiln gas is reduced from fifteen to less than one percent, fluoride emissions can be cut by between seventy and ninety percent. The first step was to review existing fluoride technology. German industry uses a limestone reactor, a large filter installed at the back of the kiln ('end-of-pipe' solution), in which the fluoride is trapped by lime. The calcium fluoride produced in this way has to be disposed of as chemical waste, which is expensive and does not really solve the fluoride problem – it merely shifts it somewhere else. The purchase of a limestone reactor entails an investment of around half a million guilders per kiln, not including the annual operating costs, which currently stand at roughly 300,000 guilders per kiln per year. What's more, the latter can only continue to rise in the coming years as the processing of chemical waste becomes more expensive. TNO thus prefers an alternative, *process-integrated* solution, in which the problem is tackled at source. The new kiln is subject to a whole raft of requirements. To begin with, it has to comply with environmental standards for fluoride: no more than five milligrams of fluoride per cubic metre of gas may be emitted from the flue. In addition, the design must not create a waste problem (unlike the use of filters). The new kiln process must not consume more energy than current modern roller kilns plus filter system, nor must it be any more expensive to purchase and operate. Finally the quality of the ceramic products must be maintained. Taken together, these requirements seemingly add up to a Mission Impossible. A three-year study is currently being proposed into a new kiln design with radiant tube burners operating at very high temperatures (1100 to 1300 degrees Celsius). The tube in which the burner is located carries the burner gases away separately, while the heat of the burner is transferred via the wall of the tube to the products being fired in the kiln. Consequently the burner gases do not come into direct contact with the products and the kiln remains dry. The concept is somewhat reminiscent of old-fashioned muffled baking ovens, in which the burner was located in a closed box and only the heat was conveyed to the oven proper. Sometimes the products themselves were packed in fireproof material to prevent them coming into contact with soot or ash from dirty oil or coal burners. A disadvantage of the tube burner is that it is less energy efficient than an ordinary burner, as only the radiant heat is transferred to the process, while the hot burner gases are carried away separately. The process can be made more energy efficient by reusing the residual energy trapped by the burner gases. The ceramics industry has committed itself through its long-term agreement with the government to achieve a twenty percent reduction in energy consumption (compared to 1989) by the year 2000.

6. List of publications from the ceramic department

1] De Vries, A.H., " Experiments on the preparation of synthetic gravel from fly-ash and harbour mud" TNO report MT 85-06557, 1985

2] De Vries, A.H., " Building products with a high fly-ash content " TNO report nr MT 85-015933, 1985

3] De Vries, A.H., a.o. " Fly-ash in building products " TNO report TPD 753.103-a, 1988

4] De Vries, A.H., Ramaekers, P.P.J., "The TNO- building ceramic department" KleiGlasKeramiek 5 (1988), No. 5, 126-127

5] De Vries, A.H., Van Kasteren, J., "More research on bricks is necessary" Reseach 9(1988), No. 5, p.130.

6] De Vries, A.H., "Whiteware Production and the Environment" Interceram , No. 5 (1988), 57-59

7] De Jong, J., De Vries, A.H., "Laboratory investigation of waste mud from chromium processing at Golden Chemicals Private Ltd (India)" report TNO-TPD Eindhoven no. 853.541, april 1988.

8] A.H. de Vries " Kiln-gas cleaning installation in Germany" , 1988, KleiGlasKeramiek 6 (1988) p. 150-151.

9] J.H. v/d Velden, A.H. de Vries, "Stacking methods for facing bricks in tunnel Kilns" Interbrick (5) no 6, 1989.

10] De Vries, A.H., Reymer, A.P.S.," Utilisation of Microwave technology in ceramic Industry " KleiGlasKeramiek 6 (1989), 220

11] J.de Jong, A.H. de Vries "Current research into the drying process of Dutch Bricks" 1989, Euro-Ceramics , Elsevier Applied Science, pg. 2.631 - 2.635

12] Van der Zwan, J. " The raw material supply for building ceramics industry, an evaluation on clays, additives, and waste materials" TNO report TPD 953.206-a, 1989

13] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Utilisation of chrome sludge in ceramic products. Programme document "No.8 of BIP 35, September, 1989

14] Van der Zwan, J., De Jong, J.W., Gorter, H., De Vries, A.H., " Investigations on energy friendly manufacturing processes in ceramic industry " TNO report TPD 953.032, 1989 "literature survey on forming and drying processes"
TNO report TPD-KM-RPT-90-028 "literature survey on combustable additives"
TNO report TPD-KM-RPT-90-041 "lab. experiments on forming processes"
TNO report TPD-KM-RPT-90-042 "lab. experiments on combustable additives"

15] Van der Zwan, J., De Jong, J.W., De Vries, A.H., " Investigations on raw material supply and alternate raw materials for a brick factory "
TNO reports TPD no. 953.065 -a, -b, TPD-KM-RPT-90-033 / 051 / 062 / 063, 1990. TNO reports TPD-KM-RPT-039 / 067 / 069 / 085 / 086, 1991

16] A.H. de Vries, ing. R. v/d Stel"Calculations of the temperature distribution in clay bricks during firing", 1991, TNO report nr. TPD-KM-RPT-91-084

17] A.H. de Vries, Dr. ir. R. Beerkens "Feasibility study of condensing heat exchangers for ceramic kilns. ,1991,TNO report nr. TPD-KM-RPT-91-100

18] De Vries, A.H.,"Technological Plan for the years 1990-2010 of the Dutch brick and roofing tile industry." TNO report, TPD-KM-RPT-92-056

19] Van der Zwan, J., De Vries, A.H.," Energy and environmental audit of the Dutch roofing tile industry", TNO report, TPD-KM-RPT-92-055

20] Van der Zwan, J., De Vries, A.H.,"Energy and environmental audit of the Dutch brick industry." TNO report, TPD-KM-RPT-92-027

21] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K.,"Utilisation of chrome sludge in ceramic products. Planning of the activities for the preparation of the plan of operations for the remainder of the year 1992 and the full year 1993" TNO report ICC/47/CLRI - 04/92.

22] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products". Part 1 : Programme start document TNO report TPD - KK - RPT - 92 - 080, September 1992.

24] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products. Part 2 : Literature survey " TNO report TPD - KK - RPT - 92 - 100, November 1992.

25] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products. Part 3 : Plan of execution for the period ending december 1994" TNO report TPD - KK - RPT - 92 - 101, November 1992.

26] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products. Part 4 : Experimental work, for the period ending september 1993" TNO report TPD - KK - RPT - 93 - 106, December 1993.39]

27] J.A.M. Denissen, "Reduction firing of building ceramics" part 1, in: ZI Ziegelind. Int. (10) 1993, 636-642 part 2, in: ZI Ziegelind. Int. (11) 1993, 700-706
part 3, in: ZI Ziegelind. Int. (6) 1994, 387-396

28] J.A.M. Denissen, "Reduction firing " KleiGlasKeramiek 14 (12) 1993, 299-305

29] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products. Part 5 : Additional experiments, november december 1994" TNO report TPD - KK - RPT - 94 - 008, January 1994.

30] Van der Zwan, J., De Vries, A.H, Warrier, K.G.K., "Section IV Utilisation of chrome sludge in ceramic products part 6: The technical scale test at Trichur, Kerala" RRL-TNO report TPD - KK - RPT - 94 - 149, August 1994