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ASSISTANCE TO CONSOLIDATE AND DEVELOP THE LIBYAN CEMENT FACTORY, BENGHAZI

TF/LIB/82/002

LIBYAN ARAB JAMAHIRIYA

Technical report: Problems of the ceramic-brick plant

Prepared for the authorities of the Libyan Arab Jamahiriya
by the United Nations Industrial Development Organization

Based on the work of A. R. Marei, special adviser

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ABSTRACT

This project, "Assistance to the Libyan Cement Factory, Benghazi" (TF/LIB/82/002), is being carried out for the authorities of the Libyan Arab Jamahiriya by the United Nations Industrial Development Organization (UNIDO) under a trust-fund agreement. The project, which has been in operation since 1976, represents a new form of technical assistance with direct support to industry. The expert took over as co-ordinator of project activities in May 1980 and in April 1983 was appointed chief co-ordinator of all the UNIDO projects in the field of cement and building materials in the Libyan Arab Jamahiriya. At present he is acting as a special adviser.

This report deals with the ceramic-brick plant, which was built in 1979 as part of the building-materials complex in the Benghazi area and which has been having problems in producing bricks of a steady and reliable quality. The expert examines the raw-material situation and the production processes, describes various tests and experiments carried out on the raw materials and makes recommendations for dealing with the problems.

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INTRODUCTION

This project, "Assistance to the Libyan Cement Factory, Benghazi" (TF/LIB/82/002), is being carried out for the authorities of the Libyan Arab Jamahiriya by the United Nations Industrial Development Organization (UNIDO) under a trust-fund agreement. The project, which has been in operation since 1976, represents a new form of technical assistance with direct support to industry. The expert took over as co-ordinator of project activities in May 1980 and in April 1983 was appointed chief co-ordinator of all the UNIDO projects in the field of cement and building materials in the Libyan Arab Jamahiriya. At present he is acting as a special adviser.

Project background

The cement industry started up in the Libyan Arab Jamahiriya in 1968 with the erection of the El Khums I cement plant east of Tripoli. Since that time the cement industry has been constantly expanding until it reached a capacity of about 6.4 million tonnes per year. About one third of this quantity (i.e. 2 million tonnes) is represented by the yearly cement production of the Libyan Cement Company (LCC) at Benghazi, which started its activities in April 1972 with one production line for 200,000 tonnes per year of normal Portland cement. Consecutive extensions followed with the erection of a second production line (400,000 tonnes per year), which started-up in August 1974 and a third production line, with a similar annual production capacity, which was taken over in January 1977. The last extension in the form of a new cement plant at Hawari with an annual capacity of 1 million tonnes, was provisionally taken over in August 1978. With that extension, the total production in the Benghazi area was brought up to 2 million tonnes per year. Other building-material industries such as a lime plant with two production lines, a paper-bag factory, a concrete-block factory and a ceramic-brick factory were added over the years to constitute a great building-material complex in the Benghazi area. With that rapid expansion, LCC was confronted with a greatly increased need for experienced technical personnel to operate and maintain the various plants. Accordingly, UNIDO was requested for assistance in supplying technical personnel and giving advice on the development and expansion of the industry.

The ceramic-brick plant came into operation as part of the LCC's building-material complex in 1979. The installation of the plant was entrusted to the French firm, Centre d'étude et de réalisation industrielle et commerciale (CERIC). The capacity of this plant is 60,000 tonnes per year of ceramic bricks with a reserve output of 20 per cent. The plant is located near the LCC cement plant.

The ceramic-brick plant has been having special problems mainly in connection with the raw materials used. Although ceramic bricks are not the expert's field of specialization, it was felt that he could analyse the problem and propose a solution. Consequently, since 1983, the expert has been devoting part of his time to studying the problems of this plant.

The output capacity of the machinery and equipment in each department of the ceramic-brick factory can be stated as follows:

Preparation section, 20 tonnes per hour (t/h) or 300 tonnes per day (t/d)
Forming and drying section, 19 t/h or 290 t/d
Burning section, 260 t/d in three shifts of eight hours

As far as the expert could discover, no special data had been provided by CERIC, the plant suppliers, on what characteristics and physical and mineralogical properties could be desirable or undesirable in the raw materials to be used, and in what proportions they should be combined in the raw mixes. Accordingly, the expert thought that an evaluation of the raw materials being used would be an essential preliminary to studying the production processes. He therefore set out to test the raw materials recommended by CERIC for their chemical and mineralogical composition and physical properties.

Since the final properties of the bricks are a reflection of their composition, the expert decided to carry out tests in the laboratory on the following variables:

(a) The use of different types of the raw materials and components in different percentages;

(b) The effect of the water content on the bricks produced from the different types of components and the different percentages applied;

(c) The effect of grain size on the bricks produced;

(d) The effect of different temperatures used in firing the bricks;

(e) The use of one component only in making the bricks, i.e. Militania clay and how the above-mentioned factors affect the quality of such bricks.

Tests on the raw materials used by the ceramic-brick plant were also made by the Academy of Mines and Metallurgy in Krakow, Poland and the results of these confirmed the conclusions reached by the expert.

They found that Militania clay was the most suitable and versatile material but that it would be necessary to carry out further analysis of the carbonate content of the materials and also technological examinations to determine, among other things, the amount of mixing water, drying, shrinkage, water absorption and compressive strength after drying and firing.

For the most part, all these technological tests were subsequently carried out by the expert and the results confirm the fact that the Militania clay is the most suitable clay for ceramic-brick production.

FINDINGS, CONCLUSIONS AND RECOMMENDATIONS

Findings

1. The ceramic-brick plant has its own special raw material problems in that three components are used in the raw mix. The carbonates as well as the silica content of the raw mix are the main factors which affect the quality of the bricks manufactured.

2. Proportioning and mixing are carried out haphazardly without any calculation of the raw-mix designs.

3. There is no background knowledge or information about the raw materials which the plant uses and there are no data on the main clay minerals of the clayey components.

4. The raw materials used have to pass through a two-millimetre sieve to avoid problems arising from the high percentage of limestone pebbles and sand grains.

5. Keeping the raw mix in the stocking silos for 24 hours after the addition of water in order to have a more homogeneous humidity is not done with all the batches. The percentage of water added to the raw mix is changeable and is based on the experience of the operator.

6. The dryers have some special problems due to a lack of spare parts and this is reflected in the quality of the bricks produced.

7. No regular control was exercised in daily production to measure the percentage of shrinkage taking place during drying or firing.

8. There are some special problems with the firing in the kilns, but the expert cannot advise on this as it is outside his field.

Conclusions

1. It is possible to use only Militania clay as the main component in manufacturing the bricks.

2. The grain size of the materials in the raw mix has to be controlled by using a one-millimetre sieve as this will greatly help in improving the quality from the cracking point of view.

3. The effect of the water content on the raw mix (paste) has to be tested before subjecting the batch to drying and firing.

4. The paste has to be set aside and stored for 24 hours at least before use.

5. It is better to fire with temperatures above 850 °C in the kilns. Samples fired at a temperature of 1,000 °C had the best appearance.

6. It is very important to take care when drying the bricks in the plant driers.

Recommendations

1. The ceramic-bricks plant is in need of an expert in ceramics to check the plant's operation and processes. This expert will deal especially with raw-material proportioning, preblending, drying and firing. UNIDO, as agreed

with the Libyan Authorities, will provide the plant with this expert for a short-term mission.

2. There is need of more information concerning the physical properties, mineralogical constituents, grain-size distribution, thermal effects, plasticity, clay minerals etc. of the raw materials and raw mixes used in brick manufacturing as this information will be of great value in assessing the quality of the bricks that might be produced from them.

3. The granulometry of the raw mixes (pastes) has a great influence on the drying and firing of bricks. Accordingly, great care has to be directed to this factor.

1. CLAY AS THE MAIN COMPONENT IN CERAMIC PRODUCTION

Clays are natural, earthy materials with plastic properties when moist, of very fine grain size and composed largely of hydrous aluminium and magnesium silicates. They occur widely in nature and are now extensively used in building materials and ceramics.

Clays can be divided into china clays, ball clays and various kinds of refractory clays such as fire clays and flint clays. China clays are white and composed largely of kaolinite. They are used for the manufacture of white-ware, special refractories and insulators. When impurities such as iron-bearing minerals are present, the clays may become discoloured on burning. Ball clays contain illite and sometimes montmorillonite as well as kaolinite. They have a fine particle size and a high plasticity. They are commonly darker in colour than china clays. They are used in the cement industry. Refractory clays are those in which fusion does not occur until a temperature of 1,500 °C is reached. They generally have a high alumina content.

Clay mineral structure

A clay material consists mainly of clay minerals but also has non-clay minerals such as quartz, calcite and gypsum. Iron-bearing minerals may associate with the clay mineral.

To recognize the properties of clay, the lattice structure has first to be identified and this is not possible with an ordinary microscope but can be done with the X-ray or electron microscope and by other methods.

Clay minerals are classified, in the simplest way, into two structural groups:

(a) Two-layer structures, e.g. kaolinites;

(b) Three-layer structures, e.g. illites and montmorillonites.

The two-layer structures consist of one layer of silica tetrahedra in which the silicon atom is linked to four oxygen atoms in a tetrahedral co-ordination, and another layer of alumina octahedra in which the aluminium atom is linked to six hydroxyl groups.

The three-layer structure consists of two layers of silica tetrahedra plus a layer of alumina octahedra.

Hydroxyls are linked to aluminium in the octahedral co-ordination by a strong chemical bond. Further, in the three-layer structure, aluminium which is trivalent may be replaced by a divalent element such as Ca^{2+} Mg^{2+}. The residual valency is usually balanced by a monovalent alkali metal like Na^+ or K^+. In general K substitutions are characteristic of illites, while Na substitutions are trapped between the structural layers in nests. They can be released and replaced by other cations when clay is suspended in water containing some electrolyte (cation-exchange). However, such interlayer cationic substitutions are held to interlayer water components by a weak bond.

The identification of clay minerals cannot be made using a polarizing microscope due to the extreme fineness of the grains. Non-clay minerals can be identified by using a polarizing microscope. The identity of clay minerals is usually revealed by some other method with more precision such as X-ray analysis and differential thermal analysis (DTA).

The rheological properties of clays

The rheological property of clays refers to their flow and deformation characteristics, i.e. their plastic and viscometric properties.

Plasticity

Plasticity may be defined as that property which enables a material to change its form without rupture, the new shape being retained when the deformatory force is removed. Plasticity is also defined as that property which enables a material to be deformed continuously and permanently without rupture during the application of force which exceeds the yield value of the material. The yield value is the force required to induce fracture. Plasticity implies workability.

There are many theories to explain the nature of plasticity. The molecular attraction theory explains the fundamental source of plastic properties as molecular attraction between the colloidal particles in the clay. The colloid-content conception claims that the plasticity is caused by the adsorbed film of positive plasticity and the clay particle of negative electrical charge. The extreme fineness of the clay grains influences plasticity and the plate formation of the clay particles also creates a large degree of plasticity through the sliding of the plates against each other. The plasticity of illites is generally high, the crystal structure of the minerals is platy.

Plasticity of clay develops largely by aging, i.e. when clay is left for some time. This requires the storage of prepared plastic clay under cool, moist conditions by covering the clay clots with damp sacking in a cool room without ventilation. This causes continued diffusion of the water into the clay grains along the cleavage planes of the minute clay crystals. By providing more "internal lubrication" within the clay, the plasticity or workability is improved. Bacterial action probably also assists in the wetting of the dry internal surfaces.

The workability of clay decreases with the increase of those non-plastics which are usually added to highly plastic clays such as those used in making building bricks to control their plasticity.

Plasticity in general depends on: (a) amount of colloidal content, and (b) type of clay mineral present.

Viscosity

The viscosity of a clay slurry or suspension can be measured by two different methods. In the first method, viscosity is determined as the rate of flow (in seconds) of the clay suspension in the Marsh funnel viscometer. In the second method, plastic viscosity can be measured (in centipoises) by the rotary viscometer. The yield point can also be determined by the use of the rotary viscometer.

Marsh funnel viscometer. This is used for routine determination. It has a specific dimension of 500 ml. Slurry is poured into the funnel and the time of flow is determined by the use of a stop watch. Funnel viscosity is reported in seconds.

Rotary viscometer. Normally, it would be necessary to calculate the shearing stress values with a complicated formula to determine the plastic viscosity and yield point. Using the rotary viscometer, speed and instrument constants are balanced so as to obtain dial readings by which plastic viscosity and yield point can be determined.

Extraction and pre-treatment of clay

A geological survey of a clay deposit should be carried out prior to its industrial exploitation to determine its nature, extent, mode of occurrence and quality. Clays are frequently worked in open pits as costs are lower than for underground mines. The method adopted depends upon the economics and geological nature of the deposit. Various types of mechanical shovels and scrapers are used, though well-lithified deposits may require blasting. High-pressure jets of water are employed in the working of kaolin deposits in England.

The use to which the clay will be put and its economic value determine the pre-treatment to which a clay is subjected. Clay required for the manufacture of structural clay products is generally used with as little pre-treatment as possible. Variation in the raw clay, however, causes variation in the product, so procedures have to be followed to improve the uniformity of the raw material.

Some clays need grinding. This can be done with a variety of different types of commercially-available equipment. Jaw crushers, hammer mills, ball mills and various types of roll crushers are used. Oversize pieces are removed and returned for further grinding by passing the clay through screens of known sieve size. Grinding equipment is sometimes employed in conjunction with an elutriator, the whole operation being continuous. Air and water elutriators are employed for size classification. There are many uses for high-quality clays and their greater value makes it economically worthwhile to use more refined methods of beneficiation to improve the physical or chemical purity of the raw clay. Use is made of the colloidal properties of the clay minerals to separate these from the non-clay minerals. For example, a deflocculated clay remains in suspension almost indefinitely whereas non-colloidal particles soon settle out. Large tanks can be used for this purpose and the refined clay drained off after an appropriate settling time. If the clay is flocculated it soon forms a sediment and can then be siphoned off or decanted. De-watering can also be accomplished by evaporation, filtration or centrifugal action. Iron minerals may be removed magnetically. Froth flotation is much employed in the concentration of ore minerals from gangue. This has been used for beneficiation of minerals such as feldspar which is often used in conjunction with clay in the ceramic industry. Kaolin of high purity has been produced commercially by ultra-flotation using powdered limestone as the carrier of impurities which are removed in the froth.

II. PRODUCTION PROCESSES IN THE CERAMIC-BRICK PLANT

Technical data

The plant was designed for the fully-automatic production of clay bricks.

Output capacity of plant

The designed capacity is for 60,000 tonnes of finished products per year with a reserve output of 20 per cent. This capacity was based on 300 working days per year with three shifts per day for the kiln and two shifts per day for the other sections. The output capacity of machines, production sections, dryer and kiln were calculated on the fired basis.

Range of products

Hollow tiles for ceilings - 50% of production or 30,000 t/a
dimensions: 300 x 200 x 80 mm, 300 x 200 x 120 mm, 300 x 200 x 160 mm, 300 x 200 x 200 mm.

Hollow bricks for walls - 33% of production or 20,000 t/a
dimensions: 250 x 120 x 60 mm, 250 x 120 x 130 mm, 250 x 250 x 60 mm, 250 x 250 x 130 mm, 250 x 250 x 200 mm.

Solid and perforated bricks - 17% of production or 10,000 t/a
dimensions: 250 x 120 x 60 mm.

These products are produced in accordance with the French Standard Specification AFNORNF P/S 301.

Output capacity of the machinery and equipment

Preparation section: 20 t/h, 300 t/d

Forming and drying section: 19 t/h, 290 t/d

Burning section: 260 t/d (with three shifts of eight hours)

Technological processes

Preparation of the clay

The mixing and proportioning of the clays is done in two box feeders, into which the dumpers can unload directly.

The raw mix is conveyed to a wet-pan mill which performs an initial coarse crushing and preliminary homogenization. This machine can accept relatively large-sized pieces. It is an extemely sturdy machine and requires little maintenance.

As the crushed clay mixture emerges from the wet-pan mill, a conveyor belt takes it to the preliminary crushing rollers, where it is ground sufficiently to break up whatever grains remain.

The mixture is then picked up and taken by the conveyor belt to a tempering mixer where it is mixed and homogenized, kneaded and moistened as necessary.

The clay thus prepared is next conveyed either into the storage area or directly to the forming section. The existence of this store of prepared clay enables the factory to be independent of quarry extraction. In addition, it ensures safety in the continuous operation of the plant in the event of incidents occurring in the preparation section.

After rehandling from the storage area, the clay is transported by conveyor belt to a box-feeder and then into two finishing rollers which grind up the clay paste extremely fine and eliminate whatever grains have remained.

Forming section

After going through the finishing mill rollers, the clay has reached the final stage in its preparation. It is next conveyed by a rotating and circular storage feeder to the forming machines.

On top of each auger machine is a large mixer-feeder which puts the finishing touches to the homogenization of the paste and propels it into the extruding press.

The extruder first airs the clay paste in a vacuum chamber to increase its cohesiveness and plasticity and decrease the porosity of the clay products, and then extrudes the paste through dies of the desired shape.

At the exit of each auger machine, an automatic cutter cuts the product emerging from the extruder to the desired length.

Drying of the products

Drying corresponds to the clay's tendency to evacuate its water. There is:

(a) A slow evacuation phase during the shrinkage period;

(b) A fast evacuation phase during the drying period when there is no more shrinkage.

Drying of products is carried out in a fast continuous dryer of the Anjou type, with longitudinal ventilation. Drying is done in two superimposed tunnels in which air is circulated in counter-flow to the products by means of a centrifugal blower. Drying at higher temperatures is done in the lower tunnel, also with the air circulating in counter-flow. The warm-air current flows over the products in a direction opposite to that of the preceding one, but the directions are reversed in an area in which shrinkage has stopped, to prevent cracks from occurring in the products. Cooling is done just before the removal of the products so as to take maximum advantage of dryer length.

Hot air is supplied by means of a combustion chamber located underneath the return canal near the end of the dryer.

The low height of the dryer enables good homogeneity of drying, providing maximum protection against deviations between the upper and lower trays. All products thus benefit from the longest cycle.

The inner speeds of the air are extremely high so as to enable maximum drying of the core of the product. The air cycle with blower relay and special chamber system for hot-air supply enable current consumption to remain low. In addition, the air recirculation system around the chamber allows maximum advantage to be gained from the heat supplied.

As the products emerge from the extruder, they are shunted off, grouped and loaded into a suspended tray via an automatic loader. The dried products coming out of the dryer are also unloaded automatically. The dried products are conveyed to the setting unit of the tunnel on a kiln car via a conveyor belt.

Firing

Firing is carried out in a tunnel kiln in which the loads are mobile and the firing heat steady. The loaded cars are introduced into the kiln where they are preheated gradually and then maintained at the firing temperature. They are then gradually cooled and finally removed from the kiln.

The fuel used is heavy fuel oil, which is distributed to gasification and injection burners spread throughout the firing area. These burners provide a steady, homogeneous firing heat. This kiln is equipped with an automatic temperature-regulation unit.

Both inside the kiln and outside, the handling of the tunnel cars is automatic. The trucks are shunted into the various tracks by electrically-driven transfer cars. The car loaded with dry products is driven into the tunnel kiln and propelled forward by a hydraulic car pusher located at the kiln entrance.

The loading of various types of products onto the kiln cars is done automatically by a setting machine.

Unloading of the tunnel kiln cars has to be done by workers in the following way. The workers stand on a concrete work platform above the truck to be unloaded. At each unloading point, there is a hydraulic pusher car beneath the truck and this pusher will propel the car forward, step by step, as required by the unloaders. It can be moved forward by the unloaders using a push-button panel conveniently within their reach. After unloading, the cars will be moved automatically, one by one, to the loading area by a haulage system.

The storage area

Handling of the wood pallets loaded with fired products between the loading-and-palletization area and the storage area is performed by fork-lift trucks.

Description and performance of the machinery and equipment

Drying section

General characteristics of the equipment:

Main dimensions:	Metres
Overall length	62
Overall width	6.50
Overall height	6
Interior dimensions of the tunnels:	
Width	4.22
Height	1.55
Length of dryer section (two tunnels)	110
Length of cooling section	5

Dimensions of mobile drying racks:
(64 mobile drying racks with four trays)

Useful width	4
Height	1.40
Pitch between trays	.0350
Depth	.55
Pitch between mobile racks	1.80

Production characteristics:

Production (dried products per hour)	9,000 kg
Added humidity	22%
Residual humidity	3%
Humidity extracted in dryer	19%
Water loss per hour	1,710 kg
Weight of frame	10,000 kg
Temperature of the product:	
at the entrance	45 °C
at the exit	65 °C

Ambient air (at 20 °C):

Humidity	7 g/kg

Exhaust air:

Average output	90,000 kg/h
Temperature	35 °C
Humidity	30 g/kg

Burner:

Regular capacity	1,500 Btu/h

Hot air:

Temperature	70 °C at reclaiming fan

A calculation of the thermal balance in the drying section is given in annex I.

The dryers are equipped with an automatic loader-unloader of trays. This device includes:

One 90° transfer driven by a hydraulic device
One conveyor followed by a set of motorized rollers
One transfer table made of shaped tubing and structural steels
(All conveyor belts are powered by the power-reducing set.)
One hydraulic pusher
One palette for setting the products on trays

The extremity of the palette forms a pusher. For each loading there is the corresponding unloading of the same tray. The products are propelled along a rubber conveyor belt driven by its own control motor.

There is one combustion chamber for drying. This combustion chamber is located between the two canals, thereby obviating any obstruction at ground level. The power of the combustion chamber is 3,000 Btu/h. The burner is an automatic one with a regulator. Safety is ensured on one hand by an electric cell and on the other by a pyrometric thermostat which controls the temperature inside the chamber itself. The pressure in the combustion chamber is controlled by a helicoidal fan blower, which also serves to supply warm gas to the dryer.

The trays supporting the products are designed with their structural steels placed in the direction of the gaseous current, so as to provide homogeneous drying of the underneath of the product.

The automatic handling section includes two main functions, load handling and handling of the positioning and removing of the products on the mobile racks. In this type of dryer, the upper part of the mobile racks is equipped with wheels enabling the mobile racks to travel along the full length of the dryer on roller ways. The four trays on the mobile racks are spaced 1.8 m apart and are suspended on two reinforced chains. The load movements are controlled by a power-reducing set which permits ready adjustment of the rotating speed of the mobile racks in accordance with the nature of the products.

Firing section

This consists of a tunnel kiln with two preheaters.

Technical characteristics of the kiln:

	Metres
Total length	112.45
Inner width	4.50
Outer width	6.60
Inner height	3.00
Firing tunnel height	1.75
Outer height	3.60

Cars:

Weight of products per car	9,800 kg
Weight of lining	8 t
Weight of metal frame	1.5 t
Ambient air temperature	20 °C
Moisture rate	7 g/kg (50%)

A calculation of the heat balance in the kiln is given in annex I.

The advantages of the tunnel kiln is that is makes it possible, by accurately adapting the speed of the firing curve to the characteristics of the clay, to obtain the best firing results from the quantity as well as the quality points of view. It is also possible to compose a loading which affords the best distribution of gas circulation and thereby enables maximum loading of single products, varied products, and products with only slight gas circulation (span tiles, solid bricks). It allows considerable operating flexibility and it can be designed in all its elements with sufficient flexibility to enable production to be expanded if desired.

Preheating zone. In addition to the elements required for air draught, this zone in the kiln also has a system for homogenizing and circulating the gases.

The homogeneity of the temperature is regulated by injecting high-speed gases at the top (this prevents the gases from the firing zone from stagnating at the top) and also by sucking the gases out at the bottom of the stack to assist this downward motion. Homogeneity is achieved by regulating the speed of the gases.

Temperature increases are regulated by adjustment of:

(a) The extraction rate and the distribution of the extraction points;

(b) The temperature of the recycled gases and the flow rate at each blower.

The curve is thus maintained and is adapted to what the raw material can bear.

The average temperature in this zone is between 250° and 500 °C

The kiln can be slowed down without difficulty, since, if only a little gas is extracted, the recycled flow remains substantial and ensures normal exchanges in this zone.

Also, products with a short passage (tiles, solid bricks, small products) can be fired, since the penetration of the gas into the load is ensured by the gas-stirring system.

<u>High-temperature preheating zone</u>. In this zone, the CERIC kiln offers a particularly interesting innovation. Traditionally, tunnel kilns suffer from some drawbacks. In kilns using fuel injection in the mass load, the gas injection zone is determined by the temperature at which the fuel can burn. In general, this zone occurs at around a minimum of 650° to 700 °C. As soon as the fuel starts burning, it is injected in large quantities so that the next row in turn is ready to be lit and the heat can be increased. For a high tonnage kiln, nearly one third of the fuel is distributed to two rows.

The draught does not compensate for this phenomenon, particularly in a tunnel kiln in which airtightness is less reliable. Several serious drawbacks then occur such as an overly-steep temperature gradient in a zone in which products are generally fragile, and sharp increases at the base of the stack. In fact, the fuel catches fire badly and generally descends to the bottom. The temperature at the base increases too fast and the products then undergo extensive thermal shock, which results in the products becoming streaked or damaged. The slits are no longer large enough to accommodate all the fuel. Certain clays have endothermic reactions in these temperature zones.

There are enormous amounts of calories from the firing zone leading to circulating a lot of gas. The result is a heavy draught detrimental to air intake. A further result is a large quantity of air drawn from behind the firing zone, which causes too fast cooling and can cause cracking. Hence there is a limitation to the progress of the firing because of the impossibility of increasing the temperature. The variation of temperature between the bottom and the top accentuates the drawbacks listed above. The necessity for lighting the fuel at a low temperature can produce incompletely fired gas and extremely unpleasant smoke, particularly when heavy fuel oils are used.

To remedy all these drawbacks, the CERIC kiln features certain adjustments. In the pre-firing zone, the kiln is equipped throughout with lateral continuous burners. These are designed in an original way to enable the injection into the slits of gases at temperatures barely higher than that of the products to protect them against thermal shock at this stage. This makes it possible to have extremely high-speed first firings and to avoid the preheating accidents encountered in this zone when only the upper burners are used. In addition, by particularly heating the bottom of the stacks, these burners make it possible to enjoy an extremely homogeneous temperature in the pre-firing. Additional slits have been designed, making it possible to move the fire zone if required, or to add to the equipment with a view to increasing production later on. Furthermore, the recirculation system installed in this zone makes it possible to homogenize temperatures by blowing high-speed gases towards the top. The equipment of the zone therefore makes it possible to solve many of the problems connected with starting speeds.

Firing zone. The firing zone proper is equipped with two types of upper burners: two banks (four rows) of gasification burners, and four banks (eight rows) of injection burners. The firing zone is sufficiently long to provide a firing time yielding good longitudinal homogeneity.

Special attention has been paid to temperature regulation. This is performed by pyropetric controls located on every second row of the heating well, which act on the amount of fuel released into each zone. Finally, if these means do not suffice, the kiln is designed to accommodate, in the post-firing zone, fast-cooling tuyeres that are mounted on the blowing apparatus. An overpressure apparatus enables maximum homogenization of the temperatures in this zone. These adjustments thus make it possible to have good control over the post-firing zone.

Production characteristics of the tunnel kiln:

Maximum nominal daily output	260 t/d

Load per car (measuring 2.80 m x 4.50 m) of the following products:

	Approximate unit weight (kg)	Weight per car load (kg)
Hollow bricks (roof):		
300 x 200 x 120 mm	12	7 800
300 x 200 x 160 mm	6	9 800
300 x 200 x 200 mm	8	10 000
Hollow bricks (walls):		
250 x 120 x 60 mm	3.2	14 700
250 x 120 x 130 mm	3.6	12 400
250 x 250 x 190 mm	4	10 700
Solid or perforated bricks:		
250 x 120 x 60 mm	4.2	14 400

Length of firing cycle:

A firing cycle from 30 to 54 hours, according to the various types of products, is advisable. In this case, for a kiln of 40 cars capacity, the firing cycle and daily output for the hollow roof bricks, for example, will be:

Size of roof brick (mm)	Weight per car load (t)	Number of cars leaving kiln per 24 hours	Firing cycle (h)	Daily output (t)
300 x 200 x 120	7.8	32	30	250
300 x 200 x 160	9.8	27	36	264
300 x 200 x 200	10.0	25	38	250

Supplier's guidelines and the experts' comments on each section

1. Preparation section

Supplier's guidelines

The instructions from CERIC stated that brick processing needs raw materials with less than 5 per cent humidity. Therefore, it is necessary to prepare a stack pile to store sufficient raw materials for one month's production, at least, so that the clay is dry enough when it enters the fabrication process.

The instructions added that this kind of preparation (dry process) allows Hawari clay to be used although it contains a high percentage of calcium carbonate ($CaCO_3$) and, therefore, marl and silicate sand have to be added to the Hawari clay to obtain better plasticity and easier drying.

The mixing and granulometry of the mixture should be checked daily. The recommended mixture of raw materials is given as follows:

60-65 %	Hawari clay
20-25 %	Ganfuda marl
10-15 %	Silicate sand

This can be obtained by regulating the speed of the box feeder and opening the flap doors.

To avoid trouble due to the high percentage of $CaCO_3$ stones in Hawari clay, it is necessary to crush the raw material down to two millimetres and accordingly it is very important to check the good condition of the screen wire before starting.

Comments

1. Hawari and Ganfuda are considered to be marly types of clay as they both contain $CaCO_3$ plus the clay minerals.

CERIC gave no information on the clay characteristics and especially on the physical properties of both types of marls. The results of such tests on the individual components and on the raw mix would not only give information on whether the quality of the clay or clays used are adequate for successful production, but also would show the quality of bricks that might be produced from them.

2. The expert agreed to take care of checking the mixing and the granulometry of the raw meal. Special attention must be paid to the stones and pebbles predominating in the clay. As these pebbles are mainly limestone, i.e. somewhat hard, they can be reduced to a manageable size through crushing. These limestone pebbles are a potential source of grave trouble. The expert does not consider it sufficient to crush these pebbles to just under two millimetres as limestone or calcite particles larger than one millimetre may cause lime blowing which disfigures the fired bricks and may even cause them to crack as the individual calcium carbonate ($CaCO_3$) particles will be converted, when fired, to calcium oxide (CaO) or quicklime. Quicklime in turn absorbs atmospheric humidity and the particles being thus converted into $Ca(OH)_2$ grow and burst open like popcorn. Calcium carbonate particles in small quantities may be rendered relatively harmless by fine grinding or by reacting with the silica present in the sand to form C_2S providing the silica is present in large quantities and the raw mix is well designed.

3. Mixing the raw meal components simply in the percentages recommeded by CERIC is not satisfactory as the constituents of all these raw materials are very variable. Therefore, a specific raw-mix design has to be followed for every batch in order to produce high-quality bricks.

4. CERIC recommended that from 20 to 25 per cent of Ganfuda marl should be added to increase the plasticity of the raw mix. The expert has no information on the main clay minerals composing the Ganfuda marl. It is known that montmorillonitic clay is used in low proportions as a plasticizer and to reduce the drying behaviour of the raw meal on firing (montmorillonite is characterized by its poor drying behaviour). It is therefore necessary that the Ganfuda marl should be tested to obtain information on its clay mineral constituents.

2. Fabrication section

The fabrication process can be divided in two parts, humidification and forming or shaping. For forming the cored bricks, CERIC selected an extrusion or stiff-mud process. This extrusion process depends on adding water to this raw meal to make it workable, hence the preliminary humidification.

Supplier's guidelines

The addition of water is to be done for the first time in the water mixer. It is very important to add the water with regularity so that the humidity is even throughout the whole clay. It was recommended that, after this first humidification, it would be better to leave the mix for 24 hours in the stocking silos in order to have a more homogeneous humidity.

The second water addition has to be checked carefully to avoid troubles with the moulder, and it is important to note that the grates need weekly cleaning.

Comments

1. The characteristics of the raw materials which are available from the local quarries affect the choice of product to be manufactured as not all clays are equally suitable for the manufacture of special types of bricks. The extrusion process selected by CERIC has certain disadvantages. The added water causes considerable trouble as it has to be eliminated again later.

2. The expert would also recommend the storing of clay or raw meal to let it age or sour. Moistening of the raw mix and leaving it to age is also recommended but for more than the 24 hours. The moistening and aging of the moistened raw mix will certainly improve its workability.

3. It is also recommended that sufficient reserves of clay should be kept in the dry season (summer) as in winter the wet clays can be blended with these.

4. The expert agrees with CERIC that the percentage of water to be added in the mixer must be checked as the percentage needed will vary depending on the original water content of the clays and the percentage of the clay minerals predominating in the raw-meal batch. It is recommended that only the percentage of water necessary to give good workability of the clays should be used.

5. The workability could be determined through measurement of the clays' plasticities, which would also give helpful information for the forming process. Plasticity could be improved by fine grinding of the raw mix when

clays with poor plasticity are used and is also affected in this case by the presence of free silica. Generally, illitic clays have higher plasticities than kaolins.

3. Drying section

Supplier's guidelines

CERIC recommended a certain procedure for starting up and stopping the dryer. The starting of the dryer must be done in two steps:

(a) Ventilation. Start the reclaiming fan, then the draught fans, then the burner fans. The fans must be started one by one to avoid overloading;

(b) Burning. Regulate the drying temperature, then start the burner.

At the end of the working day, the dryer must be stopped as follows:

(a) Stop the burner;

(b) Stop the fans one hour later, to allow the burner to cool off.

For any longer stoppage (more than 15 minutes), the burner will be stopped, but to avoid a lack of balance in the drying process the ventilation must stay on.

The operator of each moulder has to take care of the dryer.

Comments

1. The raw meal manufactured by the extrusion process must be dried before it is permitted to enter the kiln. The drying properties of the clay are important in determining whether the clay will be dried quickly and safely without cracking and warping or not. Warping is usually caused by the presence of montmorillonite clay, which not only absorbs water greedily, but absorbs more of it than any other harmless or beneficial clay mineral. Therefore, the potential for unfavourable drying behaviour can normally be detected by the water content required to develop a given consistency.

2. Drying and firing shrinkage has to be determined before extrusion. This can be done quite easily by using a metallic mould measuring 15 x 5 x 2 cm. The raw-mix paste specimen is moulded. Drying shrinkage may then be calculated as the ratio (percentage) of the dried specimens to the original dimensions. Of equal importance is the shrinkage caused by firing which can be calculated from the difference between the dried and the fired dimensions of the specimen. Any clay or raw meal with a combined drying and firing shrinkage greater than 7 per cent in relation to a water absorption of about 15 per cent will need shorting, that is, addition of lean clays or more sand.

3. The drying process is always affected by particle size and amount of liquid in the solid interior. Safe drying, in this case, must be slow to avoid strains and cracks at this stage and also later in the kiln.

3. Firing section

Supplier's guidelines

CERIC had given the following information on the firing of bricks:

Kiln-rate regulation:

The pusher is used to enter and to move the kiln cars
The string of cars advances one step (half a car) every pushing

When the rate of the kiln must be changed, it is necessary to regulate any overpressure

Normal temperature and pressure regulation:

Temperature of draught smoke must be between 100 °C and 140 °C
Pressure in the kiln must be around 1 mm H_b in the first zone.

For important variations, it will be necessary to regulate the delivery of the burners. The main parameters to check are:

Smoke temperature
Preheating temperature
Firing temperature
Cooling temperature
Pressure in the firing zone
Firing time

Daily maintenance:

The work of the brickburner on this kiln with automatic regulation is reduced to:

Moving the kiln cars
Checking, in detail:
  Burner. Cleaning of the atomizer, lining up jets
  Fuel-circuit. Pressures, tanks, temperature level, cleanness of filters, fuel-return-circuit pressure, use of safety pump
  Loading
  Level in the sand pit
  Cleanness of the kiln
  Kiln car movement
  Kiln car loading in the firing zone
  Any problem with pusher
  Re-starting after electricity cut
  Progress of burning

Any important problem should be reported to the person in charge.

Daily checking:

This must be done by the man (or shift) in charge of fabrication or burning to see that all instructions have been thoroughly followed up. The following must be checked:

Loading
Sand pit
Maintenance of filters, atomizers, burner position
Draught and overpressure
Rate of the kiln
Cleaning of kiln cars
Burning book

Kiln safety:

To ensure safety in the kiln, it is necessary to check the good running of the vault-cooling fans and of the kiln-car cooling fans.

In the event of an electricity cut, a power generator can supply electricity for the vault cooling fans, the kiln-car cooling fans, the fuel-circuit pumps and the two firing zones.

If it is impossible to start these fans (for instance, if the power generator is out of action), the man in charge of running the kiln must check that the two registers of natural ventilation are opened. As soon as the cooling fans start again, these registers should be closed.

Kiln control:

The tunnel is the only unit of the factory actually working 24 hours a day. It regularizes production, which most of the time is not continuous. To be most efficient, the kiln must work as regularly as possible. It is important to avoid variations in the kiln rate.

Loaded kiln-car storage:

The difference of working time between the kiln and the other sections in the factory makes it necessary to have loaded kiln cars ready to go into the kiln. For example, for a production of two cars per hour in the fabrication section, the rate of the kiln during the week must be:

$$\frac{24}{8 \times n \times 2} \quad \text{where } n = \text{number of shifts}$$

For an extended discussion of kiln temperatures and the firing reactions of clays, see annex II.

Comments

1. The physical and chemical composition of the raw materials is the most important factor in determining the firing schedule. In general, the firing process should be slow, about 10 °C per minute to avoid cracking, especially during the evaporation of water, crystallization, quartz transformation and mullitization of clays. Higher firing temperatures and short vitrification range may result in over-firing and the collapse of the body.

2. Maintaining the right firing temperature increases glass translucency, mullite development and quartz solution and develops more homogeneous structure. However, a certain minumum temperature is necessary to obtain vitrification, regardless of the length of soaking time. Gradually increasing temperature is more effective in reducing porosity.

3. Good brickmaking clays seldom require firing temperatures above 1,050 °C but there are exceptions, of course. From 20-300 °C, water held in the mix is expelled, followed by the decomposition stage which can take place between the tenth and twenty-fourth hour, i.e. up to a temperature of 900 °C. Clays decompose over 500 °C, combined water being expelled, leaving an amorphous residue sometimes called metakaolinite. Any free alfa quartz is converted to beta quartz above 573 °C. Carbon and sulphur must be burned out as vitrification in the last stage will prevent their later escape and leave the brick black-hearted. Full firing, which lasts for 12-18 hours up to 1,200-1,400 °C, can be done for special types of bricks. In this stage, the

formation of silicates probably proceeds from 1,000 °C onwards and the upper permissible temperature depends on the progress of this vitrification. Silica and alumina are converted to higher-temperature modifications and combine to form mullite at temperatures above about 1,100 °C. The top temperature depends on the proportion of fluxes present. Under-firing leaves the centre friable and weak. Over-firing may induce slumping and certainly causes high susceptibility to thermal shock. Bricks made from most shales usually require 1,050 °C or even higher firing temperatures, especially if they are fired to low-water absorption, but the average for normal masonry, or even low-grade face bricks, lies between 900 °C and 950 °C.

4. Water absorption is a good indicator of the mechanical strength of the fired clay. It can be determined by boiling the fired and previously weighed specimen in water for at least two hours. The water absorbed is quickly calculated from the difference in weight between the dry and the boiled specimen.

5. The fired specimen is judged by its colour. A clean, reddish colour is desired if the bricks are not to be covered by any mortar or stucco coating. If only masonry bricks that will be hidden behind stucco are to be made, the fired colour is less important. The same is true for any scumming tendency, which manifests itself through the formation of a white, or sometimes yellowish, "veil" on the brick surface. Again, the presence of such scum renders the bricks unsuitable for facing, though it does not affect their use as masonry bricks. It should be remembered, however, that a clean red colour is a powerful sales stimulant even when the bricks are to be hidden under stucco or whitewashed.

6. The tunnel kiln instruments must be carefully maintained and serviced.

7. CERIC considers the kiln to be divided into three parts and that the maximum firing temperature needed is 850 °C. The expert believes that more heat is required to decompose the limestone pebbles and particles and to assist chemical reaction between CaO and SiO_2 to form calcium silicate. This will only happen at a temperature around 1,000 °C.

III. ANALYSES AND TESTS OF RAW MATERIALS

No specific data was available on the characteristics or physical and chemical properties of the raw materials used in the ceramic-brick plant. It seemed important to the expert that this sort of information should be made available to the technical staff in the plant to help them to tackle some serious problems of the plant such as producing a high percentage of cracked bricks.

The main raw materials used in the brick plant are Hawari marl, Ganfuda marl, and Gialo sand.

During the past years, and due to the problems caused by using Hawari marl as the main component, the plant has also tried to use another component called Militania clay. This type of clay predominates in the area surrounding Al Marj, about 90 kilometres east of Benghazi. It contains a low percentage of carbonates. It is not clear why the plant stopped using this type of clay in brick manufacture when it contains such a low percentage of carbonates and huge quantities were stored near the plant ready to be used. The expert believes that this type of clay is very suitable for brick manufacture. Taking all this into account, it was decided that a complete study of the raw materials should be carried out and their chemical and mineralogical composition analysed.

Mineralogical composition could be determined by microscopic studies, X-ray and differential thermal analysis (DTA).

A complete silicate analysis using standard methods as well as new techniques for accurate determining of oxides of iron titanium, alkalis and free silica should be carried out. Beside this, information on the grain size distribution of the clay constituents as well as the liquid phase and melting point of the clay samples was also required.

Two sets of tests were carried out. Firstly, some raw-material samples were given to Prof. Kudowski of Krakow University in March 1983. They were analysed in the Academy of Mines and Metallurgy and the test results were received on 12 July 1984. Secondly, some tests and analyses were carried out in both the LCC and brick plant laboratories. For these tests, the expert, assisted by chemist A. Selim, collected the following samples in January 1983:

200 kg of Hawari marl
100 kg of Ganfuda marl
100 kg of Gialo sand

These samples were sent to be analysed in the LCC laboratories.

Analyses carried out in the LCC and brick-plant laboratories

Chemical analysis

The results of the analysis of chemical composition are given in table 1.

Granulimetric analysis

The grain-size distribution of Gialo sand was carried out in the brick plant's laboratory. Every grain size was then chemically analysed. Table 2 shows the grain size distribution of Gialo sand as well as the carbonate and the silica content of every size fraction.

Table 1. Chemical composition of the samples analysed in the LCC laboratories
(Percentage)

Raw material	LOI	Moisture	Insoluble residue	$CaCO_3$	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	CL^-
Ganfuda clay	24.83	9.10	0.25	43.00	20.40	4.50	21.35	25.76	1.20	1.50	--	--	0.01
Hawari marl	14.94	10.38	0.59	18.38	45.56	6.20	17.98	11.76	0.60	0.048	0.34	1.02	1.42
Gialo sand	12.39	2.66	0.35	24.75	68.13	0.60	1.93	15.12	0.20	0.37	0.17	0.13	0.71

Table 2. Grain-size distribution, carbonate and silica content of Gialo sand

Sieve aperture (mm)	Amount remaining on each screen (g)	Amount remaining on each screen (%)	Carbonate content (%)	Silica content (%)
4.76	0.8	0.217	..	..
2.36	24.4	6.603	4.5	96.37
1.18	38.8	10.500	5.0	87.66
.60	43.8	11.854	6.5	89.05
.30	42.4	11.475	30.0	67.17
.15	106.9	28.932	40.0	58.68
.10	112.4	30.419	32.0	56.61
Total	369.5	100.00		

Two other marl samples as well as Gialo sand samples were subjected to carbonate analysis and it was found that the carbonate content of these samples were as follows:

Hawari marl	14.5%
Ganfuda marl	38.0%
Gialo sand	27.0%

Three samples of Hawari, Ganfuda and Militania marls were taken (132.6 g, 159.70 g and 161.30 g respectively). These were thoroughly washed with water on a sieve 0.1 mm. The quantities of each remaining on the 0.1 mm sieve were established as 8.130 g (6.13%), 4.029 g (2.52%) and 1,216 g (0.75%) respectively. The samples were then dried and subjected to sieve analysis. The quantity retained on each sieve (.1, .15, .3, .6, 1.18, 2.36) is shown in table 3.

Table 3. Grain-size distribution of Hawari, Ganfuda and Militania marls

Sieve aperture (mm)	Hawari marl (g)	Hawari marl (%)	Ganfuda marl (g)	Ganfuda marl (%)	Militania marl (g)	Militania marl (%)
2.36	4.801	59.05	.642	15.93	.223	18.34
1.18	1.160	14.27	.519	12.88	.225	18.50
.60	.709	8.72	.459	11.39	.203	16.69
.30	.102	1.25	.568	14.10	.233	19.16
.15	.694	8.54	1.268	31.48	.220	18.10
.10	.664	8.17	.573	14.22	.112	9.21
Total	8.130	100.00	4.029	100.00	1.216	100.00

In order to compare the sieve analysis of the samples with the raw mixes used in brick manufacture in the plant, a sample of 103.4 grains was taken from the raw mix used in the brick plant on 2 February 1983. The same procedure for washing, drying and sieving was followed. Table 4 shows the sieve analysis of the plant's raw mix.

Table 4. Grain-size distribution of the brick plant's raw mix

Sieve aperture (mm)	Quantity remaining on each sieve (g)	Quantity remaining on each sieve (%)
2.36	.227	1.60
1.18	3.240	22.60
.60	2.817	19.66
.30	2.015	14.06
.15	3.697	25.80
.10	2.333	16.28
Total	14.329	100.00

The sieve analysis shows that the main constituents of Militania clay are clay minerals whereas the Hawari and Ganfuda marls have higher proportions of carbonate and sandy materials. There is no clear relation between the grain-size distribution of the raw materials shown and the raw mix used.

The fact is that Hawari marl has its own special characteristics from the geological and sedimentation points of view. These were studied by the expert who subjected representative Hawari marl samples to mineralogical investigation.

Mineralogical analysis

This showed that the samples were made of microcrystalline calcite and aragonite and dolomite fragments in a matrix of carbonate. In this matrix, it is possible to identify quartz grains present in appreciable amounts (fine to very fine, angular, sub-angular to sub-rounded) and feldspar crystals. Clayey material is represented as dispersed matter consisting of micaceous clays and limonitic substance.

As a confirmatory tool, differential thermal analysis (DTA), thermogravimetry (TG) and differential thermogravimetry (DTG) analyses were carried out on the samples. An exothermic effect at about 905 °C was shown in the thermal curve.

The endothermic effect with peak temperatures at 100 °C and 140 °C in the sample was due to humidity and inter-layer water losses from montmorillonite and illite. It should be noted that the endothermic peak at 140 °C represented in the thermographs of marls were found to be less by at least 20 °C than a corresponding peak of DTA curves of a clay sample (160-170 °C). Shifting of the peak towards a lower temperature range may be due to the presence of impurities or of a considerable amount of carbonate in the marl sample. Also, in the clays, most of the free water is strongly absorbed on the clay layers, i.e. absorbed by the Van-der-Waal forces. On the other hand, in marl, the free water is less strongly absorbed so it requires less energy for its removal.

The difference in physical (particle size and surface area) and chemical nature between clay and marl is responsible for shifting the peaks. Grim (1953) reported that the first shift taking place occurs in the range 100-200 °C and the second shift at about 700 °C. This may be attributed to several factors such as the nature of absorbed contents on the clay minerals, other clay-mineral impurities, coatings of amorphous impurities as well as the amount of iron and magnesium replacing the aluminium. Grim, added that large replacements of the endothermic reactions (of montmorillonite) occur from 700 °C down to somewhere between 550 °C and 600 °C. Other montmorillonites with moderately high Mg contents may also show lowering of this dehydration temperature.

The endothermic reaction peak at 555 °C was due to the loss of the structural hydroxyl group (OH^-) from montmorillonite, kaolinite and illite lattices.

The weak endothermic peak at 580 °C may be due to illite dehydroxylation or quartz transformation. In case of quartz, the reaction represents the transformation of α to β quartz. (Foust [1948] and others)

The endothermic peak recorded at about 710 °C may be due to dehydroxylation of montmorillonite or to the presence of carbonate impurities.

The endothermic effects at 790 °C and 880 °C may correspond to the decomposition of carbonate minerals present. The last exothermic peak at about 905 °C may be attributed to new phases formed and alumina.

The total loss in weight in the case of this sample is about 20 per cent. In the low temperature region (25 °C to about 250 °C), the loss in weight (5%) is mainly due to humidity and inter-layer water losses from montmorillonite and illite (Grim, 1968). The shoulder-shape deflection at about 185 °C on the DTG curve may be due to partial dehydration of a small amount of gypsum.

The loss in weight of the sample, indicated by a very weak peak on the DTG curve at about 280 °C, is due to water loss of the colloidal constituents such as gel of silica or alumina.

A weight loss of about 5 per cent detected in the temperature range between 500 °C and 640 °C on the DTG curve can be attributed to dehydroxylation of a clay mineral such as kaolinite. This was confirmed by the strong endothermic reaction peak on the DTA curve of the sample. The DTG curve showed overlapping stages of weight losses in the temperature range between 640 °C and 1,000 °C at around 710 °C and 790 °C. The first loss in weight represented by the peak at about 722 °C may be due to montmorillonite dehydroxylation.

The last (sharp) weight loss stages may be attributed to carbonate dissociation.

In general terms, Hawari marl is a loose rock, light brown in colour. Petrographically, as previously mentioned, it is formed of a detrital part and a microcrystalline part.

Analyses carried out in Krakow

Chemical composition

The chemical composition of the raw-material samples (including Militania clay) is given in table 5.

Table 5. Chemical composition of the samples analysed in Krakow, Poland
(Percentage of weight)

Raw material	Loss on ignition	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	P_2O_5	TiO_2
Militania clay	7.86	59.84	6.01	17.60	1.59	2.85	1.30	0.42	0.35	0.25	--
Ganfuda clay	30.82	30.82	4.40	9.95	26.03	2.04	0.58	0.32	1.21	--	0.50
Hawari marl	12.66	52.96	5.71	14.48	5.08	5.39	1.75	0.56	0.30	--	--
Gialo sand	10.88	72.39	0.43	1.68	12.54	0.20	0.24	0.23	1.26	--	0.25

Granulometric composition

The granulometric composition of samples is given in tables 6 and 7. Grain sizes greater than 0.06 mm were determined by the wet method on the screens (table 6) and the smaller sizes were identified using a sedimentation balance (table 7).

Table 6. Screen analysis of grain-size distribution of samples in Krakow
(Percentage of weight)

Sieve aperture (mm)	Amount retained on each sieve			
	Militania clay	Ganfuda clay	Hawari marl	Gialo sand
2.0	.2	1.3	7.8	3.3
1.02-2.0	.35	1.0	1.55	22.7
.5-1.02	.2	.8	.7	11.55
.12-.5	.35	3.2	2.0	50.0
.06-.12	4.6	.9	5.4	12.3
.06	94.3	92.8	82.35	.15
Total	100.0	100.0	99.8	100.0

Table 7. Sedimentation analysis of grain-size distribution
of samples in Krakow
(Percentage of weight)

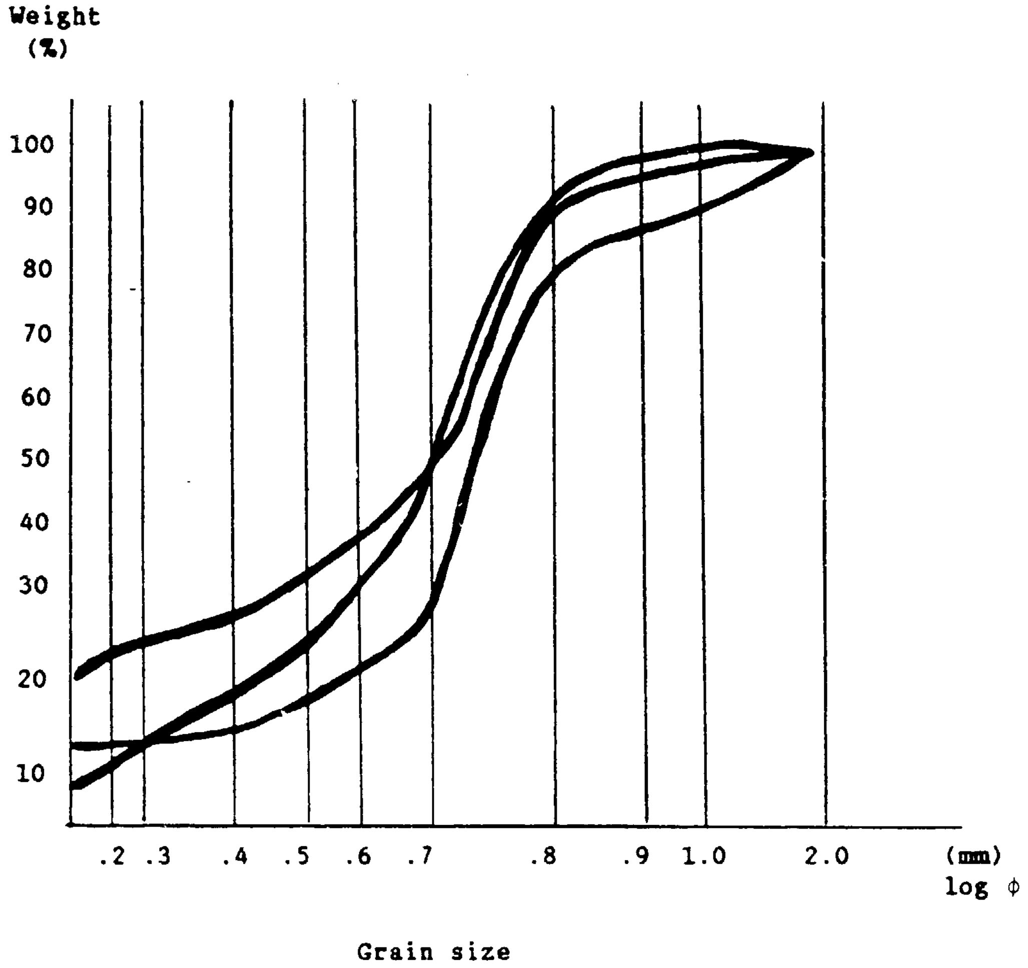
Grain size (m)	Amount in each grain size		
	Militania clay	Ganfuda clay	Hawari marl
60	5.7	7.2	17.6
30-60	36.1	39.4	48.5
20-30	21.9	11.2	11.4
10-20	16.1	11.2	8.5
5-10	9.8	3.6	1.5
5	10.4	27.4	12.5
Total	100.0	100.0	100.0

Curves for the granulometric composition of all the raw materials are shown in figure 1.

Mineral composition

Figure 2 shows the X-ray analysis of all the raw materials. In table 8, the mineral phases occurring in these raw materials are listed in order of decreasing amount.

Figure 1. Curves of the grain-size distribution of the raw materials



Key: △ Militania clay
N Ganfuda clay
S Hawari marl

Figure 2. X-ray diffraction analysis of raw materials

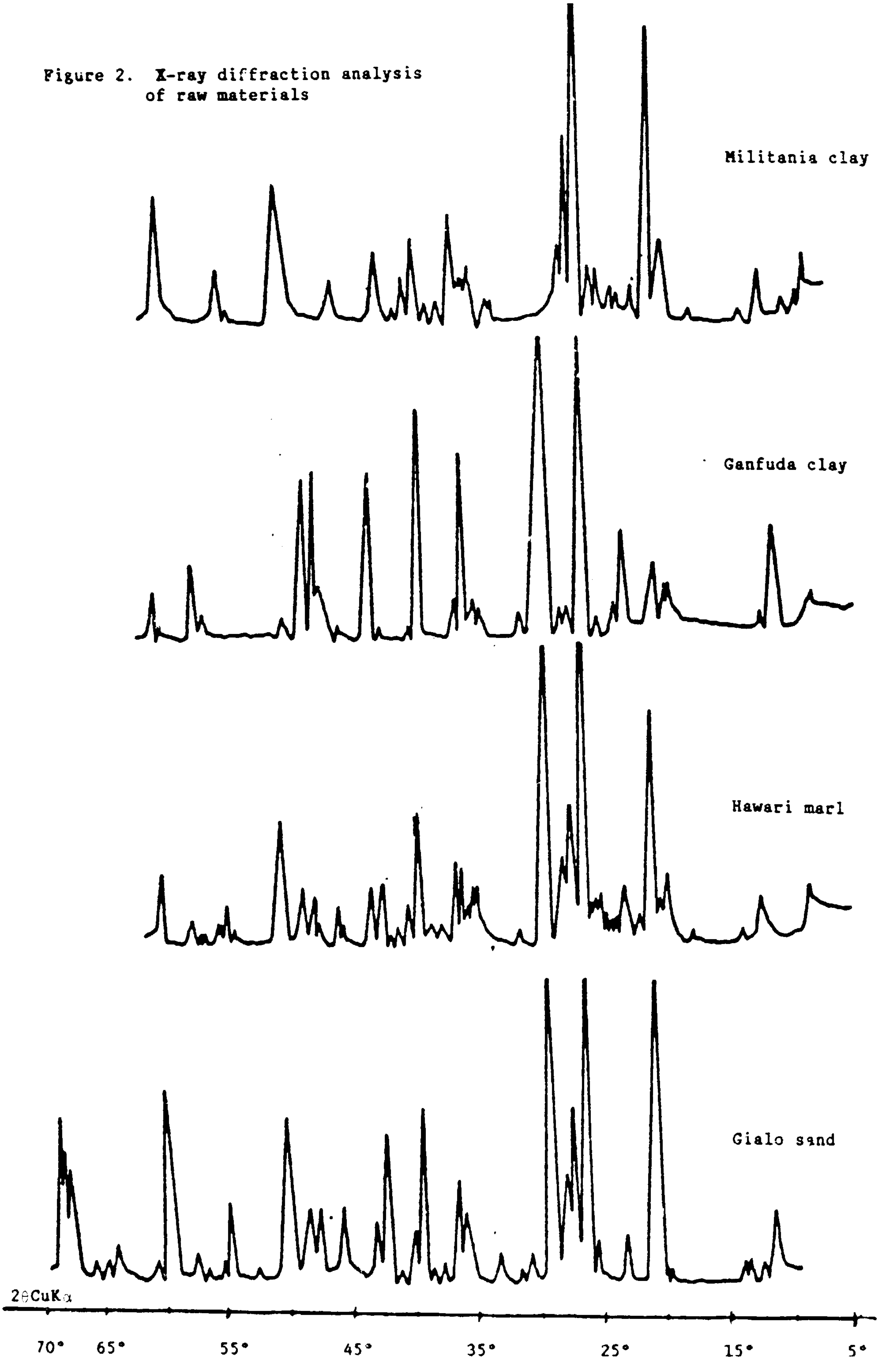


Table 8. Mineral composition of the samples

Raw material	Mineral components given in order of decreasing proportion in material
Militania clay	illite, kaolinite, quartz, calcite, gypsum, pyrite
Ganfuda clay	calcite, kaolinite, illite, quartz, feldspar, gypsum, pyrite, carbonates
Hawari marl	illite, quartz, kaolinite, calcite, feldspar, carbonates, pyrite, gypsum
Gialo sand	quartz, calcite, aragonite, orthoclase

To provide more detailed information about the mineral composition of the clay, the smallest grains (i.e. less than 5 μm) were separated out from the three raw materials, Militania clay, Ganfuda clay and Hawari marl by the sedimentation method. These fractions were subjected to X-ray analysis under special conditions. The diffraction patterns obtained made it possible to establish that illite prevails in all the three samples with a smaller amount of badly crystallized kaolinite. The greatest amount of kaolinite occurs in the Militania clay. All the samples (except the sand) contained small amounts of organic substances. Figure 3 shows the X-ray diffraction pattern of the Militania clay sample. Figure 4 shows the thermal curves of all the samples, based on differential thermal analysis and thermogravimetry.

Liquid phase and melting point of samples

Figures 5a, b and c give scanning micrographs of the four raw materials. Figures 6a, b and c show the behaviour of pellets made from samples as seen under a high-temperature microscope and figure 7 illustrates the changes in the surface of the samples.

The following shows the intervals between the sintering and the melting temperatures of the raw materials.

Raw material	Interval between the sintering and melting temperature (°C)
Militania clay	190
Ganfuda clay	40
Hawari marl	80

Suitability classification

Using the data of the chemical analysis, we can also classify clays according to their suitability for certain applications. This type of classification, proposed by I. A. Awgustiniuk, is illustrated in figure 8.

Figure 3. Example of X-ray diffraction pattern of Militania clay

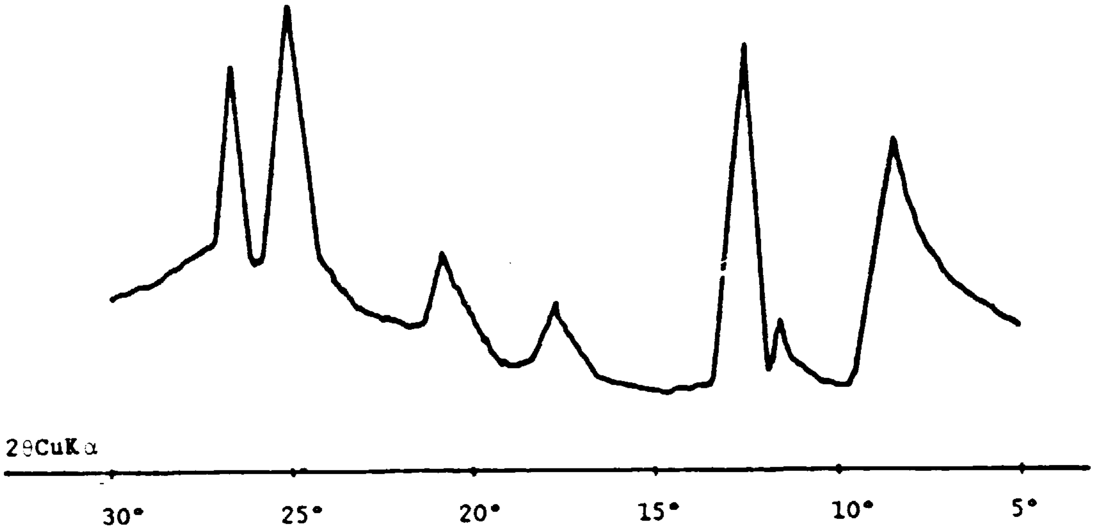


Figure 4. Thermal curves of the four raw materials

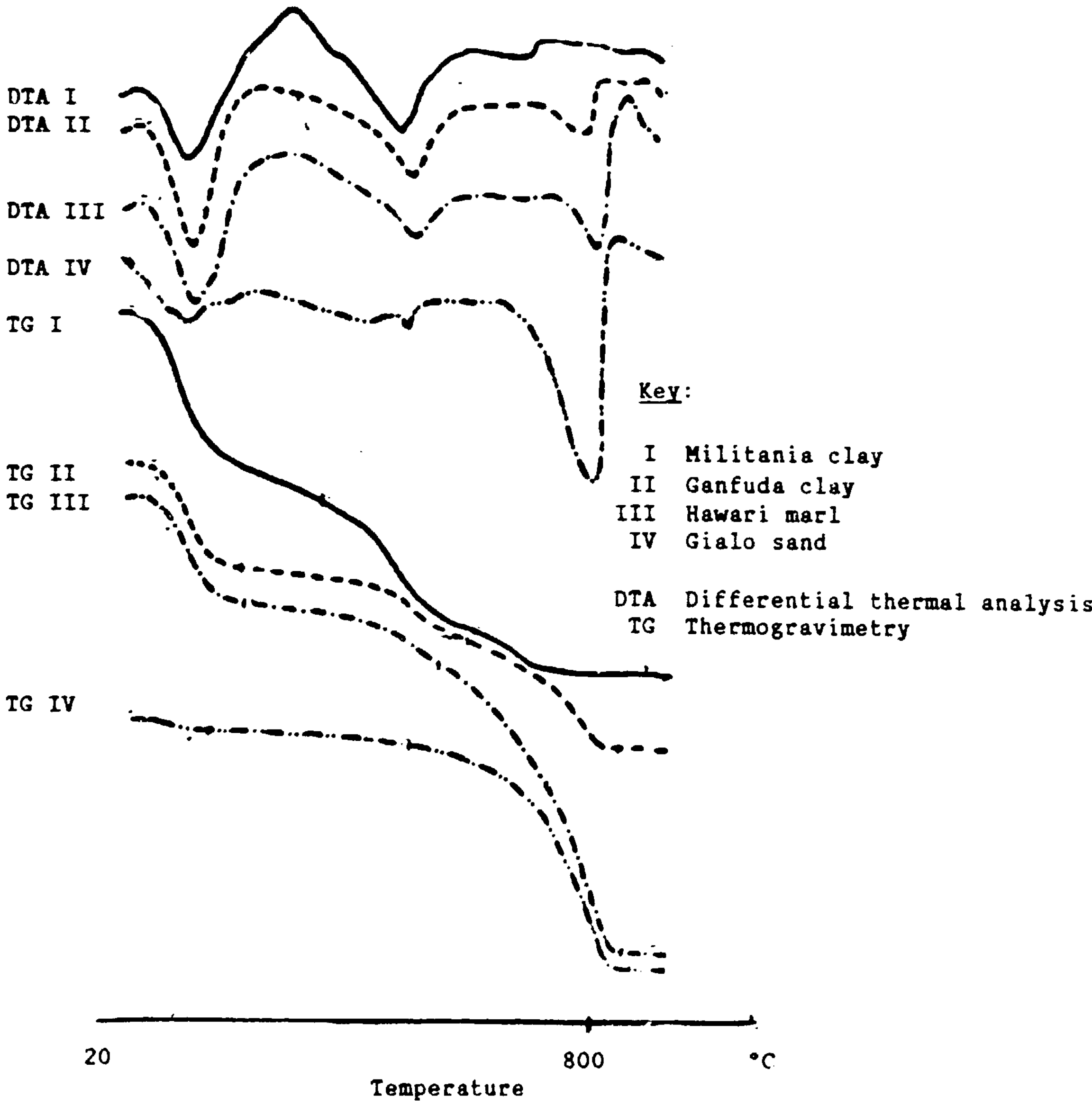
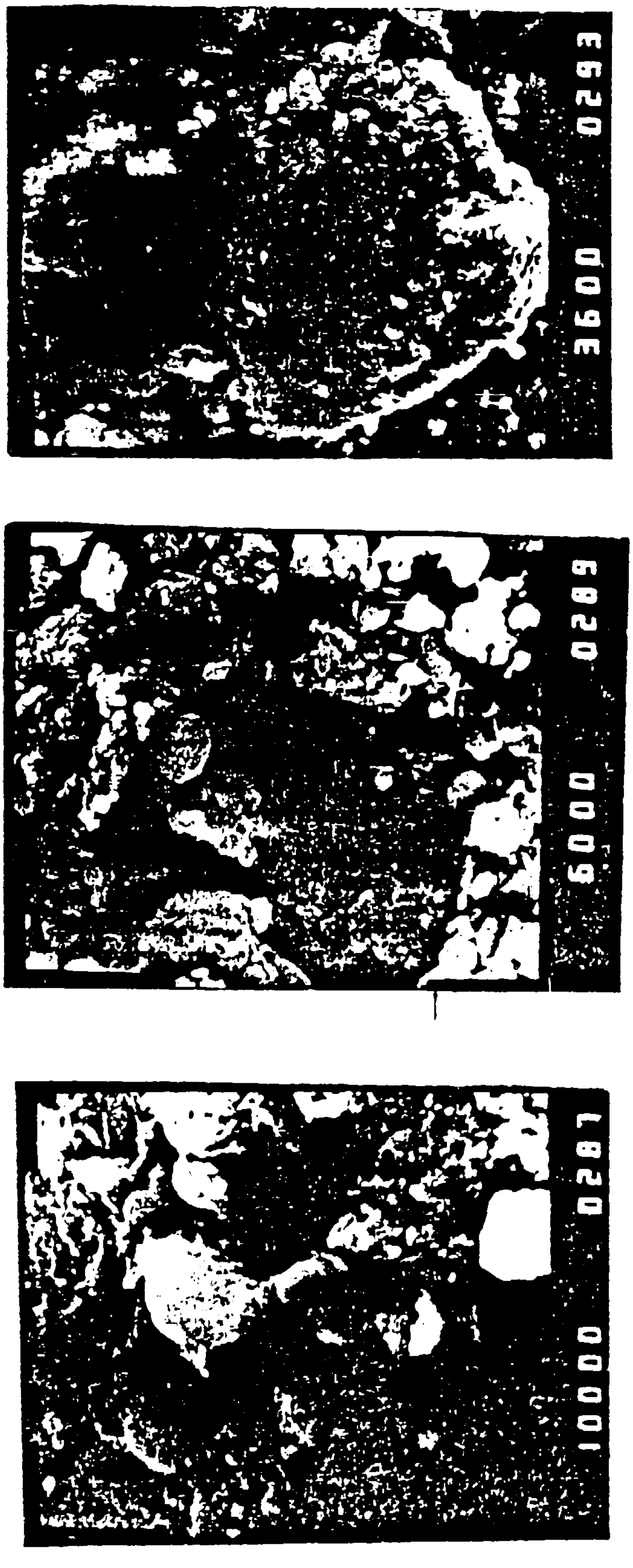
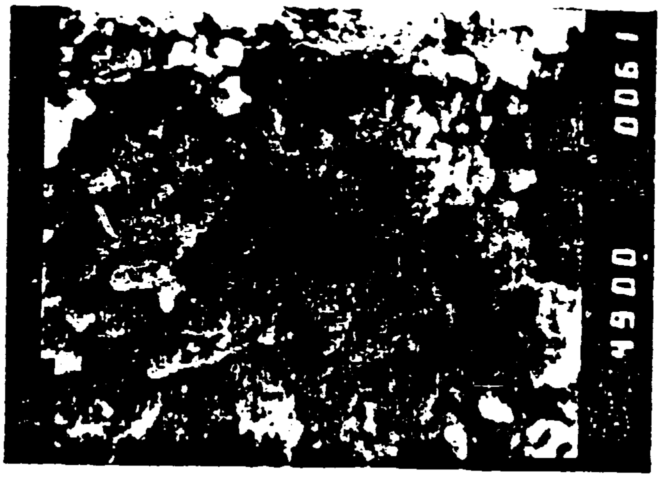


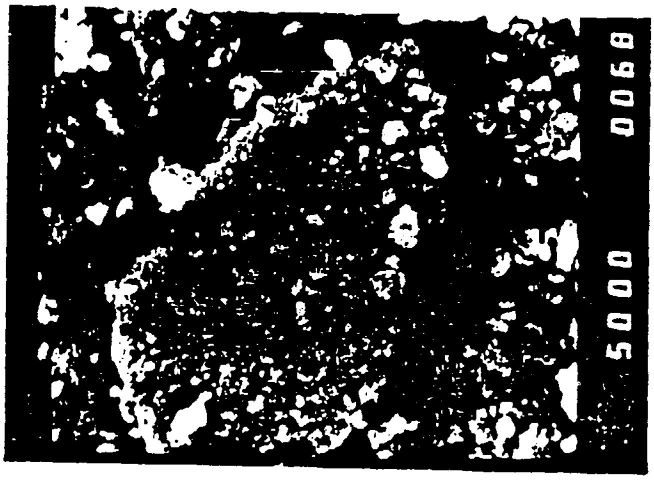
Figure 5. Scanning micrographs

A. Militania clay

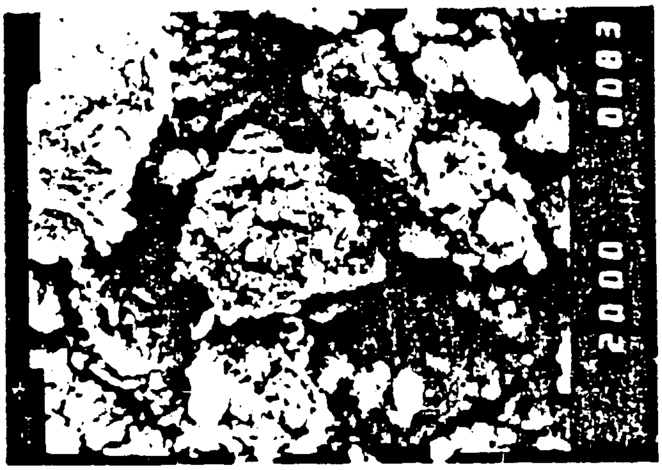


B. Ganfuda clay

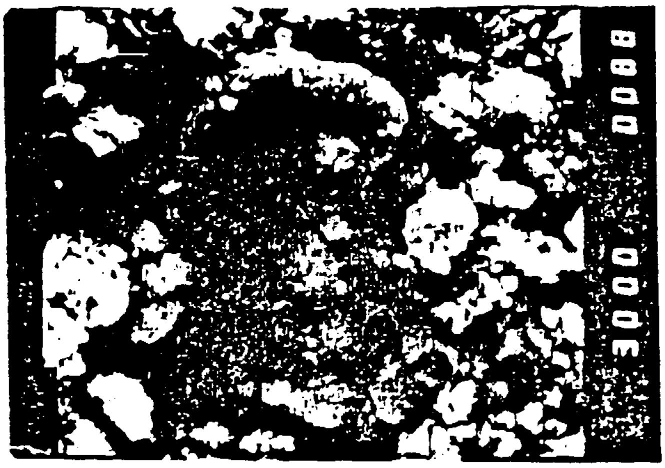




C. Hawari marl and Gialo sand



Hawari marl



Hawari marl

Gialo sand

Figure 6. Sample pellets seen under a high-temperature microscope

A. Militania clay

Kiln temperature 20°

680°

820°

840°
Beginning of sintering

900°

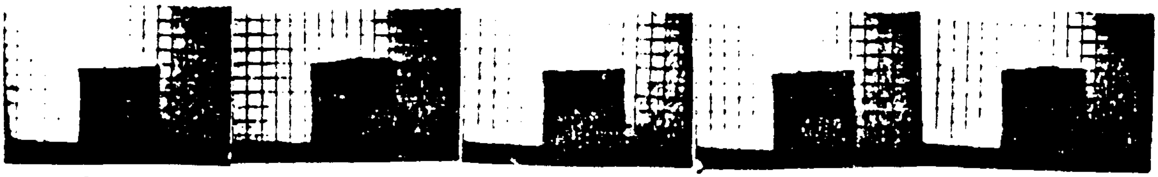
920°

980°

1,060°

1,100°

1,130°
Maximal sintering



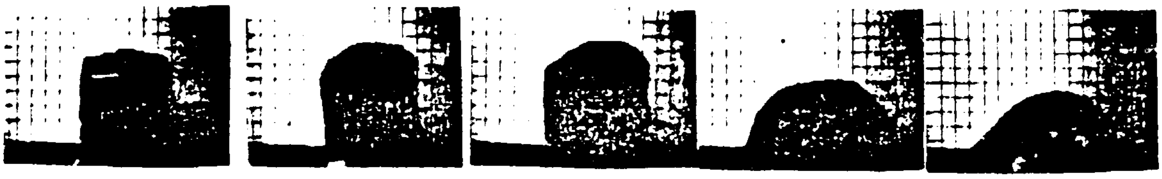
1,150°
Softening temperature

1,160°

1,170°

1,180°
Beginning of thermal expansion

1,200°



1,220°

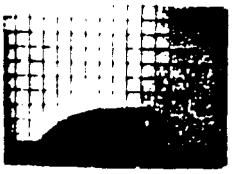
1,260°

1,260°
Maximal expansion

1,320°
Melting temperature

1,330°

$$S = \frac{P_{max}}{P_o} = 1.3$$



1,330 °C
Flowing temperature

B. Ganfuda clay

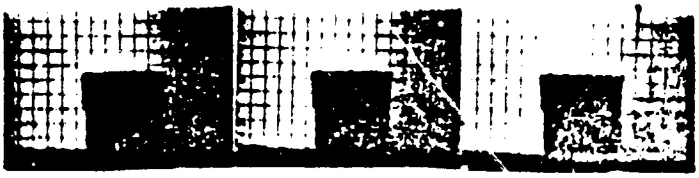
Kiln temperature 200°

600°

800°
Beginning of sintering

820°

860°



(defective picture)
Sample starting to melt

960°

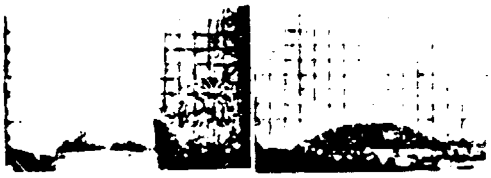
1,000°

1,060°

1,080°

1,080°
Maximal sintering

(defective picture)



1,090°
Softening temperature

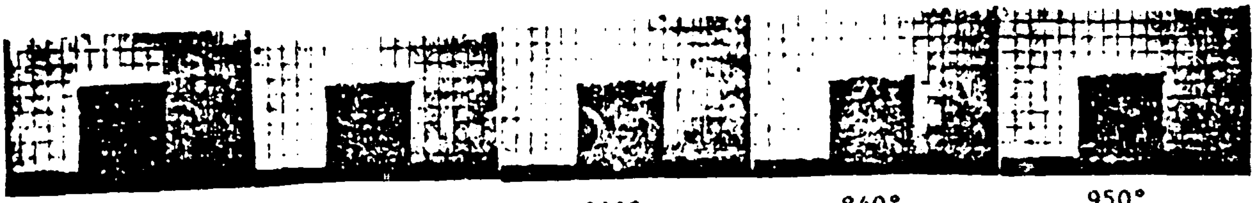
1,100°

1,115°

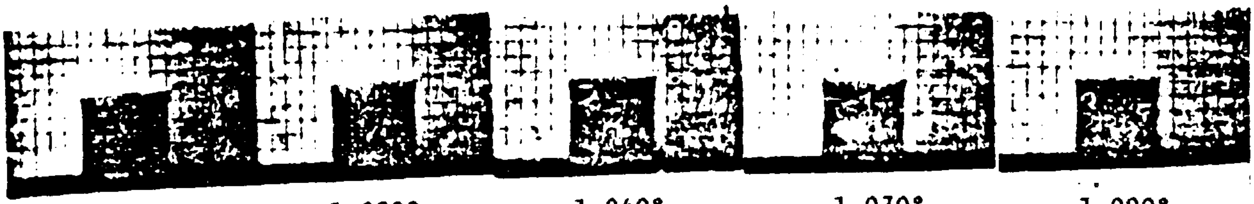
1,120°
Melting temperature

1,130 °C
Flowing temperature

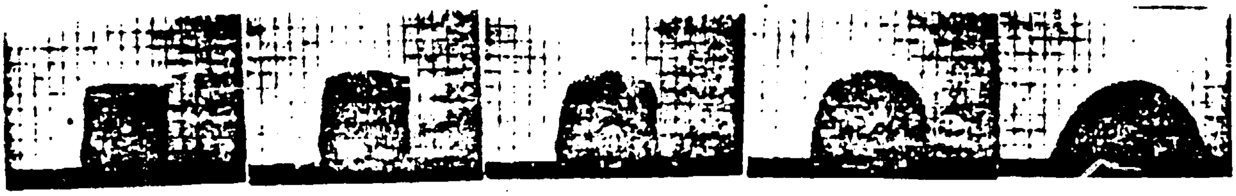
C. Hawari marl



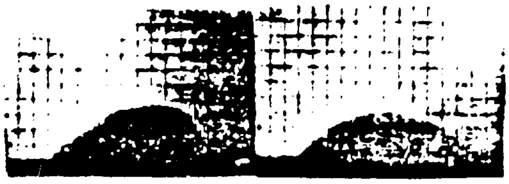
Kiln temperature 20° 580° 800° 840° Beginning of sintering 950°



1,000° 1,020° 1,040° 1,070° 1,090° Maximal sintering



1,120° Softening temperature 1,130° 1,140° 1,160° 1,170° Melting temperature



1,180° 1,185°C Flowing temperature

Figure 7. Changes in the sample surfaces

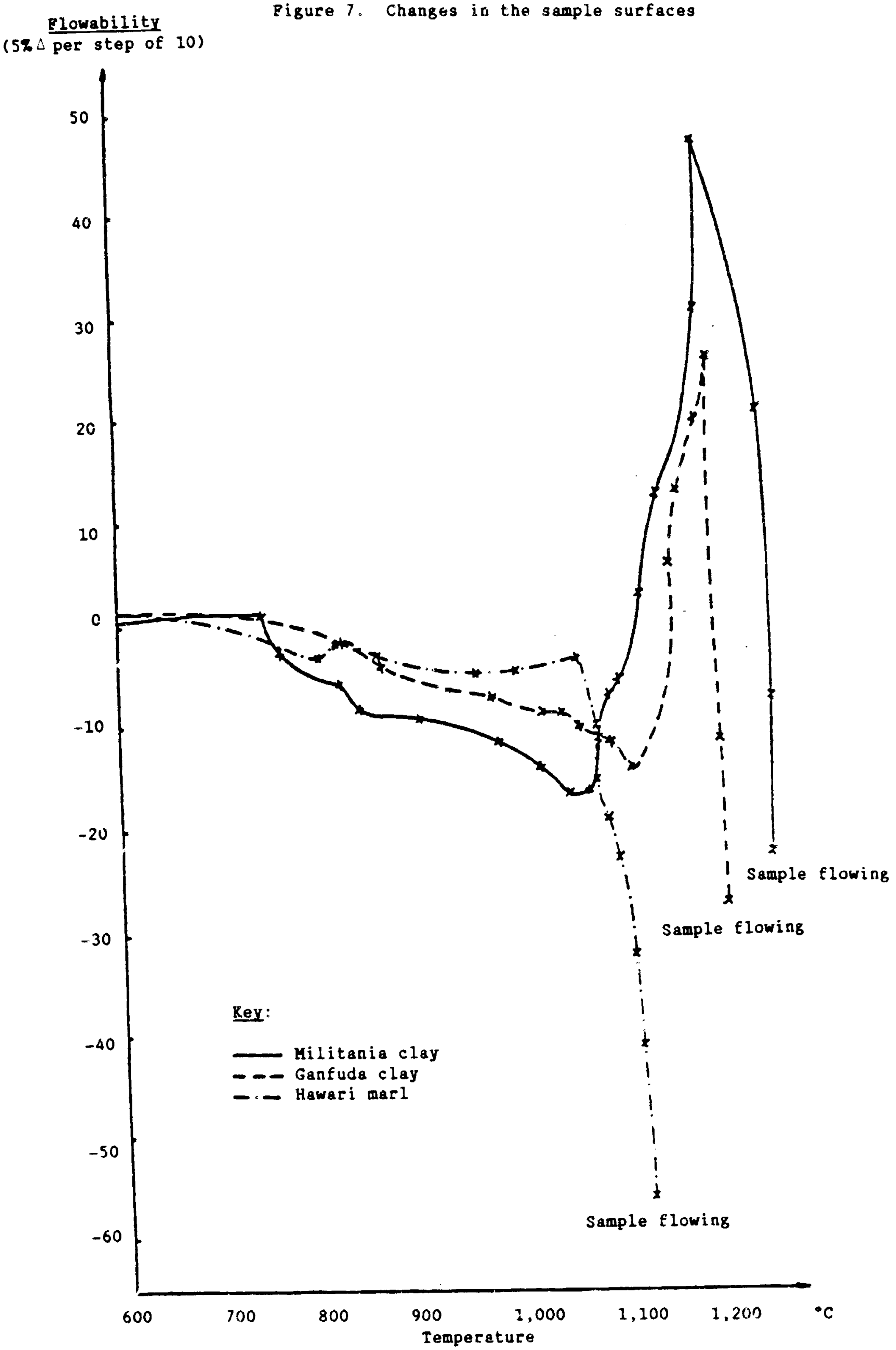
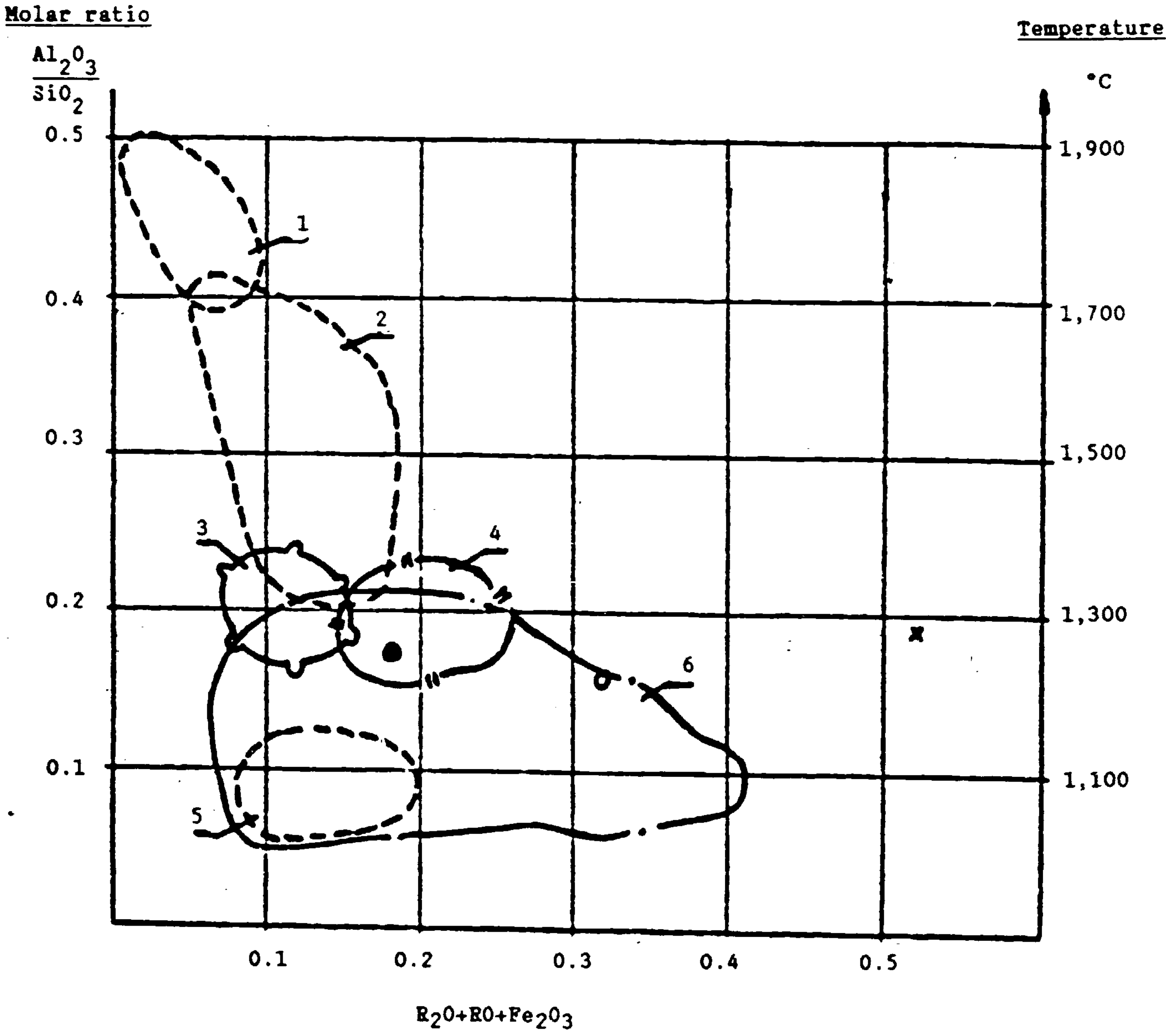


Figure 8. Classification of clay suitability for different products according to composition of material (Awgustiniuk)



Molar flux composition

Key:

- ● Militania clay
- X Ganfuda clay
- O Hawari marl

Suitable applications:

Area 1 - refractory products
Area 2 - floor tiles, pipes, stoneware, acid-proof materials
Area 3 - pottery and terracotta products
Area 4 - roofing tiles
Area 5 - clinker
Area 6 - brick production

The basis for the classification is the molar ratio Al_2O_3/SiO_2 and the sum of the flux moles, i.e. alkalies, alkaline earth metals and iron oxides. In this system of co-ordinates, Awgustiniuk distinguishes six fields of raw materials with different technological properties.

Kaolinites and clays suitable for the production of refractory products occupy area 1. Clays which can be used for the production of floor tiles, sewage pipes, acid-proof materials and stoneware fall in area 2. Pottery clays and terracotta products occupy area 3, clays for roofing tiles are in area 4, and in area 5 there are clinker clays. The clays for brick production occupy the largest area, 6.

Militania clay has the molar ratio Al_2O_3/SiO_2 equal to 0.17 and the sum of the flux moles $Fe_2O_3 + MgO + CaO + Na_2O + K_2O$ equal to 0.18. Ganfuda clay has the ratio Al_2O_3/SiO_2 equal to 0.19 and the sum of flux moles equal to 0.52. Hawari marl has the ratio Al_2O_3/SiO_2 equal to 0.16 and the sum of the flux moles equal to 0.32.

Two of the raw materials examined, Militania clay and the Hawari marl, are found, according to this classification, in area 6, which is suitable for brick production. From the point of view of this classification, the best of these materials is Militania clay, which is also found in area 4 and is therefore suitable for the production of roofing tiles as well. Ganfuda clay, which, on account of a high content of aluminium oxide, cannot even be located in any area proposed by Awgustiniuk, may be used for the production of ordinary bricks. Hawari marl (area 6) is suitable for the production of ordinary bricks and probably also of cellular bricks.

All the materials examined are plastic. They contain a great number of fluxes (Militania clay 12.77%, Ganfuda clay 33.37%, Hawari marl 18.49%).

All three materials are distinguished by low sintering temperatures (Militania 1,130 °C, Ganfuda 1,080 °C, Hawari 1,090 °C) and melting temperature (Militania 1,320 °C, Ganfuda 1,120 °C, Hawari 1,170 °C). The intervals between these temperatures is also narrow (190 °C, 40 °C and 80 °C respectively).

The thermal properties of these raw materials make it difficult, with the standard production methods, to use them for the production of sintered ceramic.

It should also be noted that the Gialo sand contains a considerable admixture of calcium carbonate (exceeding 20%).

For a full evaluation of the applicability of the clays for the production of building ceramics, it would have been necessary to carry out technological examinations to determine, among other things, the amount of mixing water, drying shrinkage, water absorption and compressive strength after drying and firing. These investigations were not carried out on account of the small amount of the sample material.

Further tests in the laboratory

As stated previously, no adequate technical information had been provided by the plant's suppliers as a basis for their proposal as to the raw materials to be used or the proportions in which they should be mixed. Their proposed mix was 60-65% Hawari clay, 20-25% Ganfuda marl and 10-15% silicate sand, the mix to be obtained by regulating the speed of the feeder and opening the flap doors. There are several objections to this. Firstly, Hawari marls are saline deposits, which have been deposited in lagoonal areas and are composed mainly of calcareous loam mixed with oolitic limestone. The chemical composition of the marl always varies from place to place vertically and laterally. It is impossible to use a regular percentage of this marl because of this variation in its chemical composition and, therefore, the raw-mix design of every batch used in brick manufacturing has to be re-calculated on the basis of the chemical variation.

Secondly, there is no clear technical basis for using Ganfuda marl. No data was available as to its physical properties and it appears to contain a high percentage of carbonates.

Thirdly, the sand used is also chemically variable as its carbonate content changes from place to place. This also necessitates changes in the mixture used to adjust the silica content required to react with CaO to form silicate. The grain-size distribution of this sand also changes from place to place and these changes will affect the drying as well as the firing processes.

Fourthly, the plant had not been advised to use the Militania clay, although the expert believes that this type of clay is very suitable, being mainly composed of clay minerals and having a low carbonate content.

Even after the laboratory analyses in LCC and Krakow, many questions remained unanswered as to the suitability of the materials from a technological point of view. To complete the information and provide a scientific basis for manufacturing the ceramic bricks, the expert decided to proceed with some applied laboratory tests and experiments on the raw materials presently in use and including Militania clay as a fourth component. It was hoped to carry out these experiments in the bricks-plant laboratory but unfortunately, after many attempts, it was found that it was impossible to carry them out there.

As there was another ceramic-brick plant located in the El-Sawani area near Tripoli, and this plant was equipped with a special pilot plant for research and investigation into brick technology, the expert decided to carry out the additional experiments in this plant.

Procedure for testing

The experiments started on 17 April 1983 in the El-Sawani ceramic-brick plant laboratories with the assistance of A. Selim. Representative samples of all the raw materials were dried and then passed through a 2-mm sieve. A number of raw-mix designs were made up as follows:

Raw-mix designs I-IV

Sample I (The same raw mix as used in the plant)

	Kilograms	Percentage
Hawari marl	3.25	65
Ganfuda marl	1.00	20
Gialo sand	0.75	15

900 grams of water used in mixing (18%).

Sample II

	Kilograms	Percentage
Hawari marl	4.24	85
Ganfuda marl	0.50	10
Gialo sand	0.20	5

900 grams of water used in mixing (18%).

Sample III

	Kilograms	Percentage
Militania clay	2.5	50
Hawari marl	2.25	45
Gialo sand	0.25	5

900 grams of water used in mixing (18%).

Sample IV

	Kilograms	Percentage
Militania clay	1.7	45
Ganfuda marl	1.9	50
Gialo sand	0.19	5

836 grams of water used for mixing (22%).

After being thoroughly mixed with the water, the samples were stored in closed plastic bags for 24 hours. The pastes were then conveyed to a small pilot-plant mixer/feeder. This mixer put the finishing touches to the homogenization of the paste and then propelled it into the extruding press. The extruder aired the clay paste in a vacuum chamber connected to a vacuum pump.

The paste was extruded through a slot opening (3.8 x 2.8 cm) and the extruded bricks were cut by hand into 10 centimetre lengths.

The bricks produced from each raw mix were put into a dryer for 40 hours at 80 °C. The measurements of the bricks were then taken and recorded.

The bricks were then introduced into a laboratory furnace and subjected to a burning temperature of 950 °C, which had been raised gradually according to the special instructions of the furnace.

An identical sample of bricks was introduced into another laboratory furnace and subjected to a burning temperature of 1,000 °C which had also been raised gradually. The two different furnaces were used to study the influence of raising the temperature and to compare the influence of both temperatures on the bricks produced. The bricks were heated in the furnace from normal temperature up to the required temperature of 950 °C or 1,000 °C and then cooled down till they reached the normal temperature again, following the timetable shown in table 9.

Table 9. Schedule of time and temperature in the experimental firing

Furnace I (950 °C)			Furnace II (950 °C)		
Time		Temperature	Time		Temperature
hour	minute	(°C)	hour	minute	(°C)
8	30	100	8	30	100
9	30	200	9	30	200
10	30	250	10	30	250
11	30	300	11	30	300
12	30	350	12	30	350
13	30	400	13	30	400

continued

Table 9 (continued)

Furnace I (950 °C)			Furnace II (950 °C)		
Time		Temperature	Time		Temperature
hour	minute	(°C)	hour	minute	(°C)
14	30	450	14	30	450
15	30	500	15	30	500
16	30	550	16	30	550
17	30	600	17	30	600
18	30	700	18	30	700
19	30	800	19	30	800
20	30	900	21	15	900
21	30	950	23	00	1 000
22	30	Stopped	24	00	Stopped

The weight of all the brick samples was taken after moulding, after drying and, finally, after firing. Table 10 shows the results. Table 11 gives the dimensions of the samples at these stages.

Table 10. Weight of samples after moulding, drying and firing (Grams)

	Weight		
Raw mix	Moulded	Dried	Fired
I	211	183	155
II	212.5	179	155.5
III	220	192	166
IV	221	190	160

Percentage of weight lost in firing:
I = 26.5 II = 26.8 III = 24.5 IV = 27.6
Average weight loss = 26.3

Table 11. Dimensions of the samples after moulding, drying and firing (Centimetres)

Furnace I (950 °C)					Furnace II (1,000 °C)				
Raw mix	Dimension	Moulded	Dried	Fired	Raw mix	Dimension	Moulded	Dried	Fired
	Length	9.8	9.4	9.3		Length	10.1	9.7	9.6
I	Height	2.8	2.7	2.6	IA	Height	2.8	2.7	2.6
	Width	3.8	3.5	3.4		Width	3.8	3.5	3.4

continued

Table 11 (continued)

Furnace I (950 °C)					Furnace II (1,000 °C)				
Raw mix	Dimension	Moulded	Dried	Fired	Raw mix	Dimension	Moulded	Dried	Fired
II	Length	10.2	9.6	9.4	IIA	Length	10.1	9.7	9.4
	Height	2.8	2.7	2.7		Height	2.8	2.7	2.6
	Width	3.8	3.5	3.4		Width	3.9	3.6	3.5
III	Length	10.6	10.0	9.7	IIIA	Length	10.2	9.7	9.5
	Height	2.8	2.7	2.6		Height	2.8	2.7	2.6
	Width	3.8	3.5	3.4		Width	3.8	3.6	3.5
IV	Length	10.6	10.0	9.8	IVA	Length	10.4	9.8	9.7
	Height	2.8	2.7	2.6		Height	2.8	2.7	2.6
	Width	3.8	3.5	3.4		Width	3.8	3.5	3.4

Table 12 shows the percentage of shrinkage of the samples after drying and after firing.

Table 12. Shrinkage in the drying and firing stages
(Percentage)

Furnace I (950 °C)				Furnace II (1,000 °C)			
Raw mix	Dimension	After drying	After firing	Raw mix	Dimension	After drying	After firing
I	Length	4.0	5.1	IA	Length	4.0	4.9
	Height	3.6	7.1		Height	3.6	7.1
	Width	7.9	10.5		Width	7.9	10.5
II	Length	5.9	7.8	IIA	Length	4.0	6.9
	Height	3.6	7.1		Height	3.6	7.1
	Width	7.9	10.5		Width	7.7	10.3
III	Length	5.7	8.5	IIIA	Length	4.9	6.9
	Height	3.6	7.1		Height	3.6	7.1
	Width	7.9	10.5		Width	5.3	7.9
IV	Length	5.7	7.5	IVA	Length	5.8	6.7
	Height	3.6	7.1		Height	3.6	7.1
	Width	7.9	10.5		Width	7.9	10.5

Certain results were observed after the samples had been fired:

(a) Samples of group I and IA were characterized by the presence of cracks in all directions;

(b) Samples of group II and IIA were of good shape;

(c) Samples of group III and IIIA contained longitudinal micro-cracks in the lower part of the brick;

(d) Samples of group IV and IVA were of very good shape, indeed were the best shaped bricks;

(e) All bricks fired at 1,000 °C, (IA, IIA, IIIA, IVA) were more solid and of better appearance than those bricks fired at 950 °C (I, II, III, IV).

Raw-mix designs V-XVI

Another group of different raw-mix designs was prepared for testing as shown in table 13. The same procedure for testing was followed as with the previous designs.

Table 13. Composition of raw-mix designs V-XVI

	Hawari marl		Militania clay		Ganfuda marl		Gialo sand		Water used
Raw mix	(kg)	(%)	(kg)	(%)	(kg)	(%)	(kg)	(%)	(ml)
V	3.25	65			1.00	20	0.75	15	575
VI	4.25	85			0.50	10	0.25	5	800
VII	2.25	45	2.50	50			0.25	5	650
VIII			1.70	45	1.90	50	0.19	5	525
IX			5.00	100					625
X	1.19	17	5.60	80			0.21	3	950
XI			5.60	80	1.19	17	0.21	3	1 000
XII	1.75	25	4.90	70			0.35	5	950
XIII			4.90	70	1.75	25	0.35	5	1 050
XIV	2.25	45			2.25	45	0.50	10	650
XV	0.65	13			4.00	80	0.35	7	750
XVI	4.50	90					0.50	10	650

Parts of the raw-mix samples V, VI, VII, VIII, XIV, XV and XVI passed through the extruder with a space between the two cylinders ranging from .6-.8 mm, whereas the other raw-mix samples were left to pass normally, i.e. the space between the two cylinders ranging from 1.0-2.0 mm. Some samples were therefore finer than the normal fineness.

The samples were placed in a dryer. The temperature of the dryer was raised gradually from normal until it reached 90 °C. Raw-mix samples V, VI, XI, XII and XIII were left in the dryer for 109 hours. Raw-mix samples VII, VIII, XIV and XV (normal fineness) were in the dryer for 79 hours. Raw-mix samples XVI (normal fineness), IX, XIV (fine) were dried for 67 hours. Samples XV and XVI (fine) were dried for 62 hours only. Sample X was omitted altogether.

The samples were fired in two furnaces, one reaching a temperature of 950 °C and the other a temperature of 1,000 °C. The samples were then left to cool again. Table 14 shows the firing times and temperatures.

Table 14. Firing schedule for samples V-XVI

Furnace I (950 °C)			Furnace II (1 000 °C)		
Time		Temperature	Time		Temperature
hour	minute	(°C)	hour	minute	(°C)
5	30	50	5	30	50
6	00	100	6	00	100
7	00	200	7	00	200
8	00	250	8	00	250
9	00	300	9	00	300
10	00	350	10	00	350
11	00	400	11	00	400
12	00	450	12	00	450
13	00	500	13	00	500
14	00	550	14	00	550
15	00	600	15	00	600
16	00	700	16	00	700
17	00	800	17	00	800
18	00	900	18	00	900
19	00	950	19	00	1 000
20	00	Stopped	20	00	Stopped

The dimensions of the samples were recorded after moulding, i.e. before drying, after drying and firing. The results are shown in table 15.

Table 15. Dimensions of the samples after moulding, drying and firing (Centimetres)

Furnace I (950 °C)					Furnace II (1 000 °C)					
Raw mix	Dimension	Moulded	Dried	Fired	Raw mix	Dimension	Moulded	Dried	Fired	Remarks
	Length	10.0	9.8	9.4		Length	10.0	9.8	9.4	fine
V	Height	1.8	1.7	1.6	VA	Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
	Length	10.0	9.7	9.5		Length	10.0	9.7	9.4	fine
VI	Height	1.8	1.7	1.6	VIA	Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
	Length	10.0	9.6	9.3		Length	10.0	9.6	9.3	fine
VII	Height	1.8	1.7	1.6	VIIA	Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
	Length	10.0	9.7	9.6		Length	10.0	9.7	9.5	
VIII	Height	1.8	1.7	1.6	VIIIA	Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	

continued

Table 15 (continued)

Furnace I (950 °C)					Furnace II (1 000 °C)					
Raw mix	Dimension	Moulded	Dried	Fired	Raw mix	Dimension	Moulded	Dried	Fired	Remarks
IX	Length	10.0	9.7	9.5	IXA	Length	10.0	9.7	9.5	fine
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	1.7	1.6		Width	2.8	2.7	2.6	
X[a]	Length				XA[a]	Length				
	Height					Height				
	Width					Width				
XI	Length	10.0	9.5	9.1	XIA	Length	10.0	9.5	9.1	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XII	Length	10.0	9.8	9.2	XIIA	Length	10.0	9.8	9.2	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XIII	Length	10.0	9.7	9.5	XIIIA	Length	10.0	9.7	9.5	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XIV	Length	10.0	9.8	9.4	XIVA	Length	10.0	9.8	9.4	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.7	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XV	Length	10.0	9.8	9.4	XVA	Length	10.0	9.8	9.1	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XVI	Length	10.0	9.7	9.5	XVIA	Length	10.0	9.7	9.5	Normal fineness
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XIV	Length	10.0	9.5	9.4	XIVA	Length	10.0	9.5	9.3	Fine
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XV	Length	10.0	9.5	9.4	XVA	Length	10.0	9.5	9.3	Fine
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	
XVI	Length	10.0	9.7	9.5	XVIA	Length	10.0	9.7	9.5	Fine
	Height	1.8	1.7	1.6		Height	1.8	1.7	1.6	
	Width	2.8	2.7	2.6		Width	2.8	2.7	2.6	

[a] Raw-mix samples X and XA were excluded and were not treated thermally.

The percentage of shrinkage of all the samples are shown in table 16. Table 17 shows the weight loss of the samples after drying and firing.

Table 16. Shrinkage after drying and firing, samples V-XVI
(Percentage)

Furnace I (950 °C)					Furnace II (1 000 °C)			
Raw mix	Dimension	After drying	After firing	Drying and firing	Raw mix	After drying	After firing	Drying and firing
V	Length	2.0	6.0	4.08	VA	2.0	6.0	4.08
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
VI	Length	3.0	5.0	2.06	VIA	3.0	6.0	3.09
	Height	5.56	11.11	5.88		5.56	11.11	1.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
VII	Length	4.0	7.0	3.13	VIIA	4.0	7.0	3.13
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
VIII	Length	3.0	4.0	1.03	VIIIA	3.0	5.0	2.06
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
IX	Length	3.0	5.0	2.06	IXA	3.0	5.0	2.06
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XI	Length	5.0	9.0	4.2	XIA	5.0	9.0	4.2
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XII	Length	2.0	8.0	6.12	XIIA	2.0	8.0	6.12
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XIII	Length	3.0	5.0	2.06	XIIIA	3.0	5.0	2.06
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XIV	Length	2.0	6.0	4.08	XIVA	2.0	6.0	4.08
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XV	Length	2.0	6.0	4.08	XVA	2.0	9.0	7.14
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	5.14	3.7		3.57	7.14	3.7
XVI	Length	3.05	5.0	2.06	XVIA	3.0	5.0	2.06
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.70

Table 16 (continued)

Furnace I (950 °C)					Furnace II (1 000 °C)			
Raw mix	Dimension	After drying	After firing	Drying and firing	Raw mix	After drying	After firing	Drying and firing
XIV	Length	5.0	6.0	1.05	XIVA	5.0	7.0	2.10
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XV	Length	5.0	6.0	1.05	XVA	5.0	7.0	2.10
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7
XVI	Length	3.0	5.0	2.06	XVIA	3.0	5.0	2.06
	Height	5.56	11.11	5.88		5.56	11.11	5.88
	Width	3.57	7.14	3.7		3.57	7.14	3.7

Table 17. Weight of the moulded samples and losses after drying and firing

Raw mix	Weight of moulded paste (g)	Weight after drying (g)	Loss in weight after drying (%)	Weight after firing (g)		Weight loss between paste and fired mould (%)		Weight loss between dried and fired mould (%)	
				at 950 °C	at 1 000 °C	at 950 °C	at 1 000 °C	at 950 °C	at 1 000 °C
V	100	86	14	73	73	27	27	15.12	15.12
VI	100	84	14	73	72	27	28	13.1	14.29
VII	100	83	17	74	74	26	26	10.84	10.84
VIII	100	84	16	77	76	23	24	8.33	9.52
IX	103	86	14	77	77	25.24	25.24	10.47	10.47
XI	95	80	15.79	72	72	24.21	24.21	10.00	10.00
XII	100	85	15	74	74	26.00	26.00	12.94	12.94
XIII	100	84	16	76	76	24.00	24.00	9.52	9.52
XIV	100	86	14	70	70	30.00	30.00	18.60	18.60
XV	104	81	22.11	67	64	31.73	34.52	17.28	20.99
XVI	103	87	15.53	76	75	23.30	24.27	12.64	13.79
XIV	100	84	16	73	71	27.00	29.00	11.90	15.48
XV	100	82	18	67	65	33.00	35.00	18.29	20.73
XVI	100	85	15	74	74	26.00	26.00	12.94	12.94

Annex I

CALCULATION OF THE HEAT BALANCE IN THE DRYER AND THE KILN

A. Heat balance in the dryer

Heat supply (kcal/h)

Fuel	1,500,000
Clay	79,200
Total	1,579,200

Heat loss (kcal/h)

Exhaust air	1,579,200

The contribution of water to the heat balance is considered negligible.

Fuel supply	average output of the burner = 1,500 (therm/h)
Clay supply	output of the moulder Δt x 0.22 = 79.2 (therm/h) Δt = temperature difference between the product and the ambient air

(Note: 1 therm = 1,000 kcal)

Energy consumption per kg of expelled water: $\frac{1,579,200}{1,710} = 923.5$ kcal

Energy consumption per tonne of dried product: $\frac{1,500,000}{9}$ = 166,000 kcal/t = 166.7 therm/t

B. Heat balance in the kiln

Figures used for these calculations:

Specific heats (therm/h):

Air	0.24
Product	0.22
Car refractory lining	0.20
Car metal frame	0.12

Ambient air:

Temperature	20 °C
Moisture content	7 g/kg

Quantities of materials entering the kiln (t/h):

Product	8.3
Car refractory lining	6.5
Car metal frame	1.25

Heat-loss calculations

1. Heat losses by radiation/convection of kiln envelope

The kiln can be divided into three parts:

(a) The first part is the temperature-raising area, where the temperature is raised from 20 °C to 800 °C;

(b) The second part is the firing area itself, where the temperature is raised from 800 °C up to the maximum firing temperature, i.e. 850 °C, and then lowered back to 800 °C (temperatures required to transform carbonate to oxides are not reached);

(c) The third part is the cooling area where the temperature is lowered from 800 °C to 20 °C.

The temperature-raising and cooling areas are considered thermally identical as far as the kiln frame is concerned.

Thus, the calculations are based upon a two-part division of the kiln:

(a) An area between 20 °C and 800 °C;
(b) An area where the temperature rises above 800 °C.

A. Heat losses inside the firing area through convection/radiation

(i) Heat losses by convection inside the firing area

Actual length (X) = 25 m, height (h) = 3.6 m width (l) = 6.6 m

Heat losses ($\Phi 1$) on vertical walls

$\alpha = P\,(T_{wall} - T_{air})^{0.25}$
$T_{wall} - T_{air} = 30$ °C
$P = 1.59$
$\alpha = 1.59\,(30)^{0.25} = 3.72$ kcal/h/m^2/°C
ϕ = thermal flux across the wall

$\phi = \alpha\,(T_{wall} - T_{air})$
$= 3.72 \text{ x } 30 = 111.6$ kcal/h/m^2
Φ_1 = total thermal flux dissipated through convection across the walls
$= \Phi \text{ x } h \text{ x } X \text{ x } 2 = 111.6 \text{ x } 3.6 \text{ x } 25 \text{ x } 2$
$= 20{,}088$ kcal/h
$\Phi_1 = 20.088$ therm/h

Heat losses ($\Phi 2$) across kiln top

$\alpha = P\,(T_{kiln\ top} - T_{air})^{0.25}$
$T_{kiln\ top} - T_{air} = 30$ °C
$P = 2.15$
$\alpha = 2.15\,(30)^{0.25} = 5.03$ kcal/h/m^2/°C
$\phi = \alpha(T_{kiln\ top} - T_{air})$
$= 5.03 \text{ x } 30 = 150.9$ kcal/h/m^2
Φ_2 = total thermal flux dissipated across the kiln top
$= \Phi \text{ x } l \text{ x } X = \text{x } 6.6 \text{ x } 25$
$= 24{,}750$ kcal/h
$\Phi_2 = 24.75$ therm/h

Thus the total heat loss (Φ_3) inside the firing area by convection is given by

$\Phi_3 = \Phi_1 + \Phi_2$
$= 20.088 + 24.75$
$= 44.83$ therm/h

(ii) Heat losses inside the firing area through radiation

$$\varepsilon = C \frac{(T_{wall}/100)^4 - (T_{air}/100)^4}{T_{wall} - T_{air}}$$

where C is the emissivity ratio = 4.88, T is the thermodynamic temperature in kelvins, and ε is the emissivity of kcal/m^2/h)

Thus,

$$\varepsilon = 4.88 \frac{(323/100)^4 - (293/100)^4}{323 - 293} = 5.72 \text{ kcal/h/m}^2/°\text{C}$$

$4 = \varepsilon(T_{wall} - T_{air})(2h + 1)X$
$= 5.72 \times 30 \times (2h + 1) \times X$
$= 5.72 \times 30 \times (2 \times 3.6 + 6.6) \times 25$
$= 59{,}202$ kcal/h
$\phi_4 = 59.202$ therm/h

(iii) Overall heat losses (ϕ5) in the firing area

$\phi_5 = \phi_3 + \phi_4$
$= 44.83 + 59.202$
$\phi_5 = 104.03$ therm/h

B. Heat losses in the temperature-raising and cooling areas through convection/radiation

Site measurements taken on various kilns show that overall average losses (ϕ_6) through radiation and convection amount to 200 kcal/h/m^2 from the actual surface of the kiln casing. This value includes all sources of heat emission through the kiln casing for bath areas:

$\phi_6 = 200 \times L \times (2h + 1)$
$= 200 \times 90 \times (2 \times 3.6 + 6.6)$
$= 248{,}400$ kcal/h
$\phi_6 = 248.4$ therm/h

C. Overall heat losses (ϕ7) through kiln casing

$\phi_7 = \phi_5 + \phi_6$
$= 104.03 + 248.4$
$\phi_7 = 352.43$ therm/h

2. Heat losses from products

A. Transformation heat

Firing one tonne of clay requires 120 kcal/kg = 120 therm/h

ϕ_8 = weight of 1 car (kg) x 120 (kcal/kg)
$= 8{,}300 \times 120$
$= 996{,}000$ kcal/h
$\phi_8 = 996$ therm/h

B. Heat (ϕ9) emitted by products at kiln exit

At kiln exit, the cars are not yet completely cold, so a certain quantity of heat is emitted to the air.

The ambient temperature is 20 °C and the product temperature is 30 °C higher, i.e. 50 °C.

The heat loss calculation is as follows:

$$\Phi_9 = W_{car} \times 30 \times 0.22 \text{ th/h}$$
$$= 9.8 \times 30 \times 0.22$$
$$\Phi_9 = 64.68 \text{ therm/h}$$

In fact, at a low throughout rate, there is no heat emitted by products at kiln exit.

C. Overall heat loss (Φ10) from products

$$\Phi_{10} = \Phi_3 + \Phi_9$$
$$= 996.00 + 64.68$$
$$\Phi_{10} = 1{,}060.68 \text{ therm/h}$$

3. Heat losses from cars

A. Heat loss resulting from the cooling under cars

This is caused (i) by forced convection and (ii) by radiation.

(i) Forced convection with downward flux

$$\alpha = p\ (1 + 0.74V)\ (T_w\ T_a)^{0.25}$$

The difference in temperature between air and cars is 40 °C (this has been repeatedly checked through site measurements).

p = coefficient corresponding to a horizontal surface and downward flux = 1.13
V = air circulation speed = 2.5 m/s
T_w = car temperature (surface)
T_a = air temperature

$$\alpha = 1.13\ (1 + 0.74 \times 2.5)\ (40)^{0.25}$$
$$\alpha = 8.1 \text{ kcal/m}^2\text{/°C/h}$$

Thus,

$$\Phi = \alpha\Delta\ T = 8.1 \times 40 = 324 \text{ kcal/m}^2\text{/h}$$

The cooled surface has width = 6.6 m and length = 25 m

$$\Phi = 324 \times 1X$$
$$= 324 \times 6.6 \times 25$$
$$= 53{,}460 \text{ kcal/h}$$
$$\Phi = 53.46 \text{ therm/h}$$

(ii) Radiation

$$\Phi = \alpha(T_w - T_a)$$

$$\varepsilon = 4.88\ \frac{(T_w/100)^4 - (T_a/100)^4}{40}$$

Air temperature rises from 20 °C to 60 C
Car frame temperature falls from 100 °C to 60 °C
Thus, assumes various values between 6.1 and 8.54

If the highest value (8.54) is taken into account, then

$$\phi = 8.54 \times 40 = 342 \text{ kcal/m}^2\text{/h}$$

The total heat loss (ϕ_{11}) from cooling under cars is given by

$$\begin{aligned}\phi_{11} &= \text{(radiation + convection)}\\ &= (342 + 324) \times L\\ &= (342 + 324) \times 25 \times 6.6 = 109{,}890 \text{ kcal/h}\\ \phi_{11} &= 109.89 \text{ therm/h}\end{aligned}$$

B. Heat losses from firing accessories

$$\phi_{12} = W1 \times 30 \text{ °C} \times 0.22 \text{ therm/h}$$

where W1 is the weight of firing accessories (t)

$$\phi_{12} = 1 \times 30 \times 0.22 = 6.6 \text{ therm/h}$$

C. Heat emitted by cars at kiln exit

Car linings are hotter than ambient air (about 80 °C)
Car frames are cooler as they are cooled inside the kiln (about 60 °C)
Heat loss is due to the heat (Q_l) from the car linings and the heat (Q_f) from the car frames:

$$\begin{aligned}Q_l &= \text{weight of lining} \times 80 \times 0.20 \text{ therm/h}\\ Q_l &= 6.5 \times 80 \times 0.20 = 104 \text{ therm/h}\\ Q_f &= \text{weight of frame} \times 60 \times 0.12 \text{ therm/h}\\ Q_f &= 1.25 \times 60 \times 0.12 = 9 \text{ therm/h}\end{aligned}$$

Total heat losses (ϕ_{13}) on kiln cars at exit is given by

$$\begin{aligned}\phi_{13} &= Q_l + Q_f\\ &= 9 + 104\\ \phi_{13} &= 113 \text{ therm/h}\end{aligned}$$

D. Overall losses (ϕ_{14}) through kiln cars and firing accessories

$$\begin{aligned}\phi_{14} &= \phi_{11} + \phi_{12} + \phi_{13}\\ &= 109.89 + 6.6 + 113\\ \phi_{14} &= 229.49 \text{ therm/h}\end{aligned}$$

4. Heat losses resulting from smoke emission

The smoke flow has to be determined first. It consists of the cooling air of various elements: products, car and firing accessories and the combustion products.

A. Cooling air

The flow of cooling air is equal to the flow of materials entering the kiln, less car frames (as car frames are separately cooled). Using the values for flow of product (8.3 t/h), accessories (1 t/h) and linings (65 t/h) given above, and taking into account the respective specific heat ratios, then the cooling air flow Y is given by

$$Y = \frac{8.3 \times 0.22 + 1 \times 0.22 + 6.5 \times 0.20}{0.24}$$

$$= 13.94 \text{ t/h}$$

The air at the kiln entrance is supposed to be at a temperature of 20 °C, with a moisture content of 7 g/kg.

B. Combustion air

The approximate air flow for combustion is 8,000 kg/h.

To this is to be added the water vapour discharged during firing of the products, i.e. 94.3 kg/t of fired products, or 782.69 kg/h.

C. Smoke characteristics

The composition of the smoke is as follows:

Cooling air flow (Y_1)	= 13,940 kg/n
Combustion air flow	= 8,000 kg/h
Total air flow (Y_2)	= 21,940 kg/h

The air contains 7g water vapour per kilogram of air. Thus Y_3, the water vapour flow is given by:

$$Y_3 = Y_2 \times 0.007 = 21{,}940 \times 0.007 = 153.58 \text{ kg/h}$$

The total water vapour flow (Y_5) emitted during product firing:

$$Y_5 = 782.40 + 153.58$$
$$= 935.98 \text{ kg/h}$$

Thus the water content of the smoke is

$$Y_6 = 935.98/21{,}940 = 42.6 \text{ g/kg smoke}$$

D. Total losses resulting from smoke emission

At kiln exit, the temperature is 120 °C.

The smoke specific heat is given by:

$$Q = 0.24\ \Delta T + \text{water content } (0.46 \times \Delta T)$$
$$Q = 0.24 \times 100 + Y_6\ (0.46 \times 100)$$
$$= 0.24 \times 100 + 0.042\ (0.46 \times 100) = 25.93 \text{ kcal/kg smoke}$$

The overall losses (Q) through smoke emission is given by:

$$Q = 25.93 \times 21{,}940 = 568{,}904 \text{ kcal/h}$$
$$= 568.9 \text{ therm/h}$$

5. Summary of thermal balance

		therm/h
Losses through kiln envelope	=	352.43
Losses from products:		
transformation heat	=	996.00
heat emitted by products	=	64.68
Losses from cars and firing accessories	=	229.49
Losses through smoke emission		568.9
Total	=	2,211.50

Energy consumption per tonne of fired products = 266.4 therms

Annex II

THE FIRING REACTIONS OF CLAYS

When clay minerals are heated, they lose most of their surface adsorbed water around 100-120 °C. The temperature at which water is lost by dehydroxylation varies with the heating rate, the water-vapour pressure and other experimental conditions. Illites dehydroxylate between 350 °C and 600 °C. Montmorillonites dehyroxylate at about 500 °C (the reaction is complete at about 750 °C) and kaolins dehydroxylate in the 500-600 °C temperature range.

Water vapour has been found to have a self-retarding influence on the dehydroxylation of kaolinite. Above the temperature of dehydroxylation, kaolinite retains a two-dimensional order in the crystal structure and the product is termed metakaolin. According to Brindley, this is transformed at a temperature of 925 °C to an Al-Si spinel-type phase at a higher temperature of 1,050-1,100 °C. He reported that the spinel is transformed exothermally into mullite with the loss of silica which appears as cristobalite.

This reaction continues up to 1,400 °C with the products developing better crystallinity. The dominant mechanism in the changes was considered to involve migrations of cations with adjustment of the oxygen framework.

$$\text{kaolinite} \xrightarrow[\text{endothermic}]{\text{about 500 }^\circ\text{C}} \text{metakaolin} \xrightarrow[\text{exothermic}]{\text{about 925 }^\circ\text{C}} \text{spinel} + SiO_2$$

$$\xrightarrow[\text{exothermic}]{\text{1 050-1 100}^\circ\text{C}} \text{mullite + cristobalite} \xrightarrow{\text{1 200 - 1 400 }^\circ\text{C}} \text{mullite + cristobalite}$$

Different decompositions have been reported on heating mica-type clay minerals. This is thought to result from failure to reach equilibrium, differences in initial consumption and presence of water. According to Grim illite dehydroxylates between 200 °C and 600 °C. Spinel appears above 850 °C and increases in crystallinity and amount up to 1,200 °C when it is replaced by mullite.

$$\text{illite} \xrightarrow{\text{200-600 }^\circ\text{C}} \text{anhydrous modification} \xrightarrow{\text{850 }^\circ\text{C}} \text{spinel} \xrightarrow{\text{1 200 }^\circ\text{C}}$$

$$\text{mullite} \xrightarrow{\text{1 300 - 1 400 }^\circ\text{C}} \text{fusion}$$

A commercial clay product is fired only long enough to develop properties required for its use. Equilibrium in the chemical or mineralogical sense is generally not achieved. Phase diagrams are of great use. They provide the first criteria for the deduction of the behaviour of the materials on firing and prediction of the composition and properties of the products.

Mineralizing agents such as borates lower the viscosity and facilitate crystallization. Fusion is promoted by fluxes. Firing mixtures which contain mica-type clay minerals and feldspars liberate alkalies which act as fluxes. An increase in the proportion of such minerals leads to an increase in the proportion of glass and mullite develops at lower temperatures and in smaller amounts than in more kaolinitic mixes. Cristobalite forms at the expense of kaolinite but when illite is present the fluxing action of interlayer cations is thought to be responsible for the generally-observed reduction in amount of cristobalite and increase in glass content. Quartz tends to persist on firing and under these conditions is not readily converted to cristobalite.

The development of the glassy phase is associated with shrinkage of the article and closing of the pores. If heating is continued for too long this may lead to eventual bloating due to expansion of trapped gases or vapour.

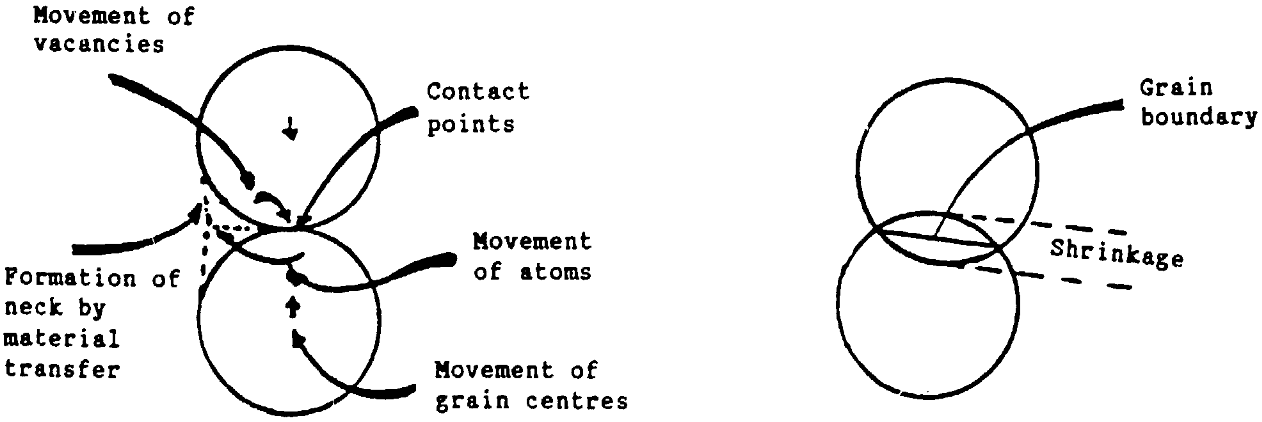
The firing process may involve sintering. This term refers to the formation of a weld or union between particles of powder at a temperature below the melting point. Sintering is generally accompanied by shrinkage and a decrease in void space and surface area. It was originally thought that sintering always took place in the absence of liquid but a fluid phase is now known to be present in some cases so the terms wet sintering and dry sintering have come into use. Viscous and ionic diffusion probably take place during wet sintering. Significant variables in the process are viscosity, surface tension and pore size.

The viscous mechanism is of major importance when there is a considerable amount of glass formed as is the case in the firing of a great many of the ceramic articles which contain clay. In dry sintering, the mechanism involves a solid-state process. It is considered that structural vacancies or point defects move in one direction while a corresponding movement of atoms or ions occurs in the opposite direction. As a result, material is transferred from point contacts to form a connecting neck between particles.

It is an important process in the formation of certain single-phase ceramics such as ferro-electric and magnetic ceramics.

The mineralogy of the raw material is related to the composition of the fired product and significantly affects the optimum conditions of manufacture and properties of the fabricated article. The mineralogical changes which take place on firing are accompanied by increase in strength of the product.

Schematic illustration of sintering



Solid-state sintering

Changes that occur during the firing process are related to changes in grain size and shape, and pore size and shape. A compact powder, before it has been fired, is composed of individual grains separated by 25-65% volume percent porosity depending on the material used and the processing. For maximizing properties such as strength, it is desirable to eliminate as much of the porosity as possible.

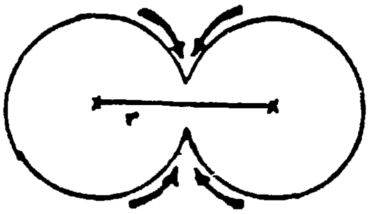
Driving force for densification

The free energy change that gives rise to densification is the decrease in surface area and lowering of the surface by the elimination of solid-vapour interfaces, which is accomplished by the formation of low-energy solid-solid interface. The net decrease in free energy occurring in the sintering of one-micron size particles is one calorie per gram. If the particle size, and consequently the radius of curvature is small, these effects may be of substantial magnitude. They become large when the radius of curvature is less than a few microns.

The driving force, which is related to surface energy, is achieved through different mechanisms such as evaporation, condensation, viscous flow, surface diffusion, grain boundary or lattice diffusion and plastic deformation. The most important of these are diffusion and viscous flow.

Evaporation condensation

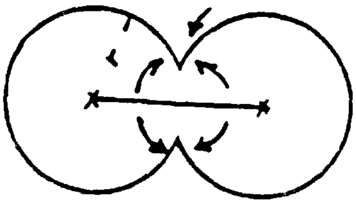
During sintering, there is a tendency for material transfer, because of the difference in surface curvature and consequently the difference in vapour pressure at various parts of the system. With two adjacent particles, the vapour pressure between the neck area and the particle surface tends to transfer material into the neck area. The pore shape is affected.



The variables that affect the process are the particle diameter and the temperature. This type of sintering is common in halide systems.

Diffusion

The difference in free energy or chemical potential between the neck and the surface area and the surface of the particle provides a driving force which causes the transfer of material by the fastest means available.



Diffusion is equivalent to the migration of lattice vacancies in the opposite direction. The neck surface acts as a vacancy source. Material migrates from the surface boundary between particles to the neck area with an equivalent motion of the particle centres to one another, giving rise to simultaneous changes in pore shape and size and a correspondingly overall decrease in porosity, and is accompanied by shrinkage.

The important variables are time, particle size and temperature. Control of grain growth is important as it lowers densification rate. This type of process is important in pure-oxide systems.

Sintering with a reactive liquid

The presence of an appreciable amount of liquid acts to bring the particles into contact for the sintering process. Therefore, the liquid must wet the solid particles also. The solid phase shows a certain limited solubility in the liquid at the sintering temperature.

Reprecipitation of solids gives increased grain size and density. As the liquid brings the particles into contact, substantial compressive stresses are developed across the thin film between the particles, leading to solubility at these points and a material transfer by diffusion to the liquid film between the particles, resulting in densification.

This sintering process is important in cements.