

Innovative Heat Treatment of Ceramics by using Low O₂ Technology

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1 Introduction

Modern ceramic materials require modern manufacturing processes. Such processes optimise the microstructure and macrostructure of the materials, extend their durability and allow complex geometries.

The necessary shaping processes require adequate plasticization of the ceramic raw material [1]. The traditional plastic raw materials, such as argils and clay, often do not meet the high purity demands of the technical ceramics industry and so they fail to yield the required properties in the finished products.

Synthetic pure raw materials, just like feldspar or quartz, must be classified as inelastic. Nevertheless, they can be used in plastic shaping processes when mixed with plastic raw materials or with organic polymer or binder substances.

Abstract

Interceram 58 (2009) [1]

Modern shaping processes in the production of ceramics require organic binders or polymers to be removed in the later course of the production process by thermal treatment during the debinding phase. It is advisable to link the debinding process with the sintering process in the same plant in sequence without any time interruption or relocation to avoid production time losses as well as relocation damage to the material to be fired. Various transformation processes already take place during the debinding phase, in the course of which different decomposition products are set free. It is necessary to determine these products in advance so as to permit the safe regulation of the debinding process with optimised oxygen content. This shortens the duration of thermal treatment and minimises space requirements, plant size and investment costs.

Depending on the production capacity, both intermittently and continuously operated kiln plants have proved suitable for this application. Both kiln types can be equipped with integrated thermal postcombustion systems ensuring the clean oxidation of all unburnt gases produced during the process, thereby minimising environmental load. The hot and clean combustion products of the thermal postcombustion system are led back to the kiln, where they improve the heat transfer and temperature uniformity. The atmosphere stability marked by the constancy of the oxygen concentration can be obtained by low-O₂ control. Improved product quality and reduced energy consumption are the welcome results.

Keywords: PVA, PEG, plastify, debinding, low O₂ technology, heat treatment

2 Use of binders and their decomposition products [2]

The use of polymers varies with the ceramic process concerned. Different concentrations of polymers are added to suspensions used for slip casting or spray drying. They are used as binders, plasticizers, slip additives and defloculants.

Binders, usually based on polyvinyl alcohols (PVA), polyacrylates, or cellulose, are used in slip casting or during pressing because they give the necessary strength to the green compact by gluing together particles on their interfacial surfaces.

High-polymer components such as cellulose or polysaccharides serve as plasticizers. During extrusion moulding they improve the flowability of ceramic material, but can also fulfil a binder function.

Slip additives are organic auxiliary agents and their functioning is based on the interaction of their hydrophilic groups, i.e. the oxygen atoms of the ether group (C O-C) and the H⁺ ions of the Me-OH groups situated at the surface. Particles of equal charge sliding easily past one another are produced as a result. This improves tension transmission and leads to a higher green density

during dry pressing. A typical internal lubricant is polyethylene glycol (PEG).

Short-chain acids of polyacrylene (PAA) serve as dispersing agents, stabilizers and defloculants for castable slip.

The mentioned organic additives have to be removed as uniformly and completely as possible from the body before the actual sintering process takes place because carbon residues can have a negative influence on the sintering process as well as on the quality of the finished products.

Temperatures for the debinding process range between approx. 150 °C and 500 °C. Debinding has three stages:

- Thermal decomposition of the organic additives,
- Diffusion of the gases through the material pores into the kiln room,
- Oxidation of these gases in the kiln room and in the ceramic body.

The speed of polymer separation should not exceed the diffusion speed of the pyrolysis products in the body since otherwise excess pressure could be generated in the gaseous pyrolysis products which would cause cracks and destruction of the body. A uniform grain size is beneficial for the debinding process whereas

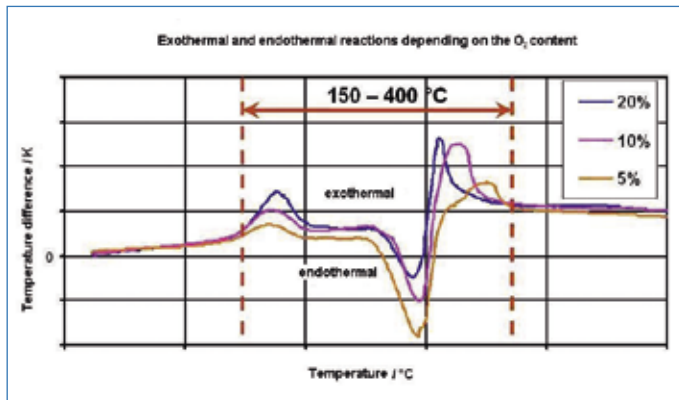


Fig. 1 • Differential thermal analysis

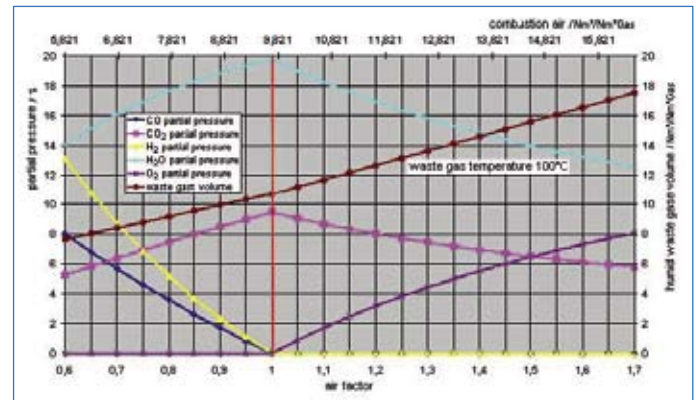


Fig. 2 • Combustion diagram for Russian natural gas

agglomerates or high-density areas have a retarding effect. The use of fine powder accelerates the sintering process, but it also reduces the debinding speed.

In the production process the entire thermal treatment can last up to 80 h, with the debinding process taking place within a time frame of up to 40 h. Long firing times push up energy and space requirements, factors which call for high investment and operating costs and should therefore be reduced to a minimum.

3 Analysis of the debinding processes

Table 1 gives an overview of the temperature range in which the decomposition reactions take place. However, it has to be considered that various ceramic materials have different catalytic effects on the temperature profile of the decomposition reactions of polymers, e.g. Al_2O_3 intensifies the decomposition process of the polymer chains and so the reactions proceed at lower temperatures [3]. During the debinding process the organic additives PVA, PEG and PAA decompose into a wide variety of chemical compounds, as shown in the Tables 2–4 [4].

The thermal reactions proceeding in an industrial application test can be followed very clearly from the diagrams of the differential thermal analysis (DTA) (Fig. 1). While the organic decomposition products are escaping from the material to be fired, very distinct exothermic and endothermic reactions take place in some cases. Mostly the critical temperature range varies from 150–400 °C. An examination of the effect of the oxygen content on the intensity of the reactions reveals that the reactions can be influenced by the kiln atmosphere, which means that, in theory, a tool has been found for product debinding at the maximum possible speed without

risking a decline in quality. In the present case it is advisable to accelerate the debinding process and make it energetically efficient by a low O_2 adjustment.

4 Kiln plants with low O_2 technology

Depending on the production capacity and other factors, continuously operated kiln plants are used for large production quantities, i.e. tunnel kilns in the form of roller kilns, pusher-type kilns with tray conveyance, tunnel kilns with car conveyance, and rotary kilns. For smaller production volumes intermittently operated kiln plants are suitable, such as shuttle kilns, top-hat kilns, elevator and chamber kilns.

In the broadest sense the low O_2 technology can be used for all the above-mentioned kiln plants. The basic principle of the low O_2 technology

demands state of the art atmosphere control in a kiln or in certain kiln areas. If the requested finished product properties are not influenced by specific firing atmosphere conditions, the combustion should always take place under stoichiometric conditions for reasons of energy, i.e. complete combustion of the fuel with the lowest oxygen content. Figure 2 shows the combustion diagram for Russian natural gas, from which it can be seen that e.g. a 5% deviation in the oxygen content in the firing atmosphere from the stoichiometric combustion point causes an approx. 32% increase of the waste gas volume, so the energy consumption will also rise by this amount.

Special firing atmosphere conditions are necessary e.g. in the fast firing process for glaze-firing hard porcelain. In this case fast firing signifies that the complete firing process including cool-

Table 1 • Decomposition ranges of polymers

Organic substance	Decomposition range/°C
PVA	200–300
PEG	150–250
PAA	250–300

Table 2 • Pyrolysis products of PVA

Products of pyrolysis	Molecular formula
Formaldehyde	CH_2O
Acetaldehyde	CH_3CHO
Cotonaldehyde	C_4H_6O
Benzene	C_6H_6
Phenol	C_6H_5OH
Benzaldehyde	C_7H_6O
Toluene	C_7H_8
Styrol	C_8H_8
Cresol	C_7H_8O
Benzofuran	C_8H_6O
Naphthalene	$C_{10}H_8$

Table 3 • Pyrolysis product of PEG

Products of pyrolysis	Molecular formula
Formaldehyde	CH_2O
Acetaldehyde	CH_3CHO
Valeraldehyde	$C_5H_{10}O$
Mono-, di- and trimers of ethylene glycol	$C_2H_4(OH)_2$
Methyl-1,3-dioxolane	$C_4H_6O_3$
Benzene	C_6H_6

Table 4 • Pyrolysis product of PAA

Products of pyrolysis	Molecular formula
Formaldehyde	CH_2O
Acetaldehyde	CH_3CHO
Propionaldehyde	C_3H_6O
2-butanone	C_4H_8O
Benzene	C_6H_6
Xylene	C_8H_{10}
Phenol	C_6H_5OH
Cresol	C_7H_8O

ing is realised within 4 to 8 hours. The desired colour and thus quality of the porcelain products is adjusted and supervised by ensuring a near-stoichiometric, but reducing firing atmosphere (air factor $\lambda \approx 0.95$) in the temperature range of approx. 1100 °C to 1400 °C. The quality of electrotechnical porcelain, such as high-voltage insulators, is influenced in like manner.

The thermal treatment of bulk solids under certain oxygen-deficient conditions can also be carried out in indirectly heated rotary kilns equipped with special sealings (Fig. 3) and with an appropriate lance technology for purging their kiln room e.g. with inert gases.

For larger production capacities of soft ferrites, electrically heated, gas-tight roller kilns and particularly gas-tight pusher-type kilns with tray conveyance are the perfect choice.

The magnetic properties of soft ferrites are obtained by a very quick change from near atmosphere conditions to oxygen ranges of up to 30 ppm. This change of atmosphere is necessary between soaking time at maximum temperature and below Curie temperature. Depending on the product, however, different oxygen contents must already be maintained in the heating-up phase.



Fig. 3 • Indirectly heated rotary kiln with atmosphere control

Roller kilns and pusher-type kilns with tray conveyance are also used for manufacturing other electronic ceramics products and ceramic diesel particulate filters.

For smaller production capacities of soft ferrites intermittent kiln plants are sufficient. The production unit most frequently used for this purpose is the electrically heated gas-tight top-hat kiln (Fig. 4), which also achieves the low oxygen values mentioned above.

Another example among the large number of well-known applications of thermal treatment at low oxygen content is the production of carbon

products. The burning of carbon can be prevented only if no oxygen and, according to the Boudouard equilibrium, no CO₂ gas comes into contact with the carbon products during the baking process. The typical production plant is the ring pit furnace for baking anodes and cathodes. This quasi-continuous plant consists of individual sections filled with products and in-



Fig. 4 • Two electrically heated gas-tight top-hat kilns

intermediate channels of ceramic pit bricks. A burner ramp “moves” at a periodic interval of 26–32 h from one section to the next one. Its burners produce waste gases which are led through the channels, thereby ensuring the indirect heat transfer. Before each section is closed, the product is completely packed in coke to make sure that no oxygen can penetrate.

5 The new low O₂ technology

The new low O₂ technology for innovative heat treatment plants with integrated debinding process differs from the described plants mainly in terms of process engineering.

The new low O₂ technology is a thermal process technology achieving the shortest, energetically most efficient thermal treatment of high-quality ceramic products under near-stoichiometric combustion. A closer examination of the debinding process shows that the most important control variable is the dependence of this process on the oxygen content and the reaction intensity.

Even if the concentrations of the gaseous debinding products are in the non-hazardous ppm range in all cases known up to now, the debinding reactions must be determined for the new low O₂ technology, and the possible concentrations during the debinding process must be calculated in order to prevent deflagrations.

As shown in Tables 1, 2 and 3, the main substance released during the debinding process is formaldehyde, also called methanal. The gases are explosive in a gas-air mixture of from 7 % –

the lower explosive limit (LEL) – up to the upper explosive limit (UEL) of 73 %. The following explosion prevention representation refers to the ternary system of methanal, nitrogen and air as an example (Fig. 5).

The vertices of the three axes with a scale division of 0–100% each define the initial state of a pure component. In order to assign points in the ternary system clearly to the percentages, the reference axes are to be displaced until they meet the required concentration point. The three concentration values of the substances together must always add up to 100 %. To ascertain the concentration of one point, the graphic determination of the percentages of two components is sufficient, the third one can be calculated on this basis. The LEL indicates the minimum percentage of combustible gas in the substance mixture necessary for an explosion. Under the LEL, no explosion is possible as the existing concentration of the combustible substance is too low. The UEL indicates the maximum possible percentage of combustibles in the substance mixture for an

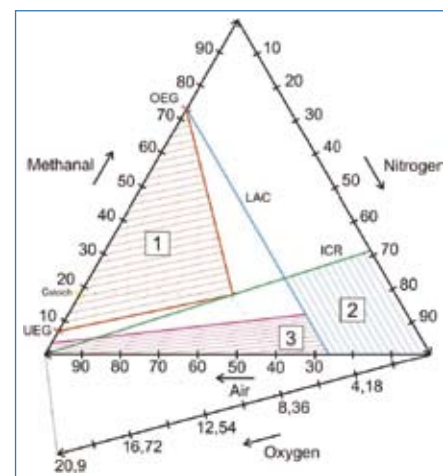


Fig. 5 • Ternary system methanal-nitrogen-air

1 = explosive mixture

2 = inert mixture

3 = safe mixture with variable oxygen concentrations

ignition. Above the UEL an explosion is not possible either, as the existing concentration of an oxidant, mostly oxygen, is too low. Between the LEL and the UEL an explosion must be expected if an ignition source exists. The limits are drawn in Fig. 5.

The LEL and the UEL can be calculated with corresponding formulae [5]. To fix an explosive range, another third point limiting the explosive range is required. This point is calculated with

the same formulae as those used for determining the LEL and UEL by varying the oxygen percentages and it constitutes the interface between the line of stoichiometric combustion and the one for the least possible oxygen percentage for a reaction.

In Fig. 5 the explosive range is marked by area 1. As the transition from non-explosive to explosive can occur very quickly, the limit-air-concentration (LAC) line is added for limiting a transition area which is connected with the LOC (limiting-oxygen-concentration) by the relation $LOC = 0.209 * LAC$

Every mixture to the right of the LOC is not ignitable and also relatively explosion-resistant. As with high methanal contents, however, a low oxygen infiltration can already provoke an explosion; this range is restricted even further by the ICR (inert gas-combustion gas rate) line. This straight line starts at an air concentration of 100 % and runs through the end point of the explosive range. The range determined by this method and limited by the LAC and ICR lines can now be classified as inert and consequently as safe. All other ranges must be considered explosive and thus to be avoided.

The individual debinding components as well as their possible concentrations during the entire debinding process must be determined in preliminary tests as described above. Subsequently an explosion diagram as per Fig. 5 is created for each component if the measured concentrations are above the ICR line. As the measured concentrations of the previous processes have always been in the low ppm range, i.e. far below the ICR line, there is no explosion danger. A reliable oxygen measurement is sufficient for the supervision.

6 Intermittent kiln plants with the new low O₂ technology

To meet the market and product requirements, kiln plants with this innovative technology must have the following features:

- Intermittent and continuous production methods suitable for the required capacities
- Debinding and sintering in one firing process and/or in one plant
- No gas-tight plants but plants meeting the standard and the principles of shuttle kilns and/or tunnel kilns, to be able to resort to proven systems and to minimise investment costs

- Heating by fuel for reasons of process requirements and operating costs
- Precise atmosphere control, particularly during debinding, with due consideration of the regulations for explosion protection
- High and uniform heat transfer with a binder degasification ensuring gentle product treatment
- Use of thermal postcombustion for the binders to reduce energy consumption and thus avoid ecological damage
- Safe operation in the non explosive range.

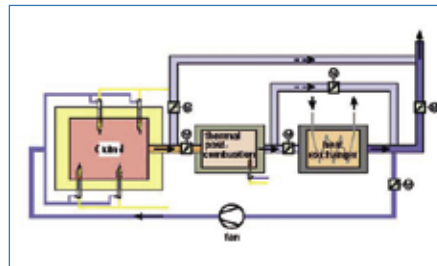


Fig. 6 • Schema of a shuttle kiln with low O₂ technology

The schema of an intermittently operated kiln plant according to the latest low O₂ technology is represented in Fig. 6. The thermal postcombustion system must be heated by fuel to control the oxygen content in the system throughout the process. Its size has to be dimensioned in such a way that the soaking time is long enough to allow for oxidation of the hydrocarbons. The system's heat exchanger can be operated with air or water as cooling medium. The intensive heat transfer of water operation permits the small sizes of heat exchangers frequently specified by customers.

When the kiln has been loaded and charged, the process flow starts with the prescribed purging procedure of the complete plant.

Subsequently the thermal postcombustion system is heated to a temperature which ensures the complete oxidation of all hydrocarbons arising from the upstream debinding stage. The thermal postcombustion atmosphere is continuously checked for its oxygen content and controlled accordingly. Most of the waste gases from the thermal postcombustion are led back to the kiln plant. The intense waste gas circulation and the corresponding burner capacity cause a rapid adaptation of the oxygen concentration in the system to the desired low O₂ value. During the entire process the oxygen content is reliably kept below the explosive range according to the perti-

nent ternary diagram by means of oxygen measuring devices.

The heating-up program for the debinding process in the kiln uses waste gas circulation. Based on the described considerations and the associated tests used for an advance analysis it is possible to adjust the temperature-time-profile of the debinding process as required.

As already mentioned, the concentrations of debinding gases are far below the explosive limits, i.e. within the area 3 in the ternary diagram of Fig. 5, so there is no explosion risk during the debinding process with every possible oxygen concentration.

The debinding process is finished when the O₂ content in the system corresponds to that of the gas/air ratio adjustment of the thermal postcombustion burners. The temperature-controlled main burners of the kiln are switched on for the controlled sintering process and, with a certain time delay, the burners of the thermal postcombustion are disconnected. The kiln plant described is shown in Fig. 7.



Fig. 7 • Shuttle kiln plant with low O₂ technology

7 Continuously operated kiln plants with the new low O₂ technology

From a thermotechnical point of view, the classically operated tunnel kilns are actually two heat exchangers connected in series in which, on the one hand, the hot waste gases from the burners flow in opposite direction to the transport of the material to be fired from the firing zone via the preheating zone to the kiln entrance, thereby giving off their enthalpy to the material to be fired and cooling down themselves. In the cooling zone, on the other hand, the cooling air injected at the kiln entrance also flows opposite to the transport direction towards the firing zone, thereby cooling down the material to be fired and heating itself.

For the low O₂ technology a debinding zone where the gases flow in parallel with the product transport is connected upstream of the kiln

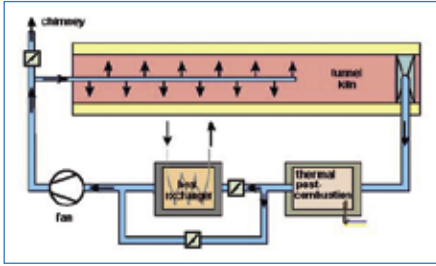


Fig. 8 • Schema of a debinding zone for a tunnel kiln

plant. Thus the gases loaded with hydrocarbons are led to increasing temperatures so that, with a correspondingly low oxygen concentration, most of them already burn up in this zone. The gases flow to the thermal postcombustion section via the chimney installed between the debinding and the preheating zone. In the thermal post-combustion system any residual hydrocarbons are burnt up completely by means of a controlled thermal treatment. Not even condensates can deposit in the waste gas piping due to the high temperature. The clean waste gases from the thermal postcombustion process are led back to the kiln and, supported by special burners, serve the direct heating of the debinding zone.

These special burners acting as injectors for the gases from the thermal postcombustion are used to control the temperature in the debinding zones of the plant as well as the oxygen atmosphere in these zones. The oxygen measurement with the incorporated control guarantees constant low O_2 atmosphere conditions throughout the process. The system thus ensures safe operation outside the explosive limits. The large gas circulation volumes in the kiln channel create good uniform temperatures and constant atmospheric concentrations.

The basic principle of the debinding system described and represented schematically in Fig. 8 has meanwhile become established. It stands out for its low energy consumption, safe operating mode and low waste gas losses with a minimum environmental load limited to the CO_2 particles which cannot be avoided during the combustion of fossil fuels.

With tunnel kilns based on this principle, the duration of the total thermal treatment can be reduced by 50–70 % compared to conventional technology. Other excellent advantages consist in correspondingly smaller, space-saving plant sizes with lower investment costs.

References

- [1] Locher, C., Pfaff, E., Schulz, P., Zografou, C.: Untersuchungen zum Ausbrennen organischer Substanzen im keramischen Scherben. *Keram. Z.* **34** (1982) [7] 361–364
- [2] Becker, F.: Debinding processes – physical and chemical conclusions and their practical realisations. *cfi* **83** (2006) [5] E2–E13
- [3] Ferrato, M., Cartier, T., Baumard, J.F., Coudamy, G.: Der Bindemittelabgang in keramischen Scherben. *cfi/Ber. DKG* **71** (1994) [1/2] 8–12
- [4] Ziegler, G., Willert-Porada, M.: Schadstoffreduzierung durch Prozessoptimierung bei der thermischen Zersetzung organischer Additivsysteme für die keramische Formgebung unter Einbeziehung der Mikrowelleneinkopplung. Report to research project no. 12068 N
- [5] Fuß, O.: Ermittlung und Berechnung der Sauerstoffgrenzreaktion von brennbaren Gasen. Dissertation des Fachbereichs Chemie, Universität Duisburg-Essen, Mai 2004

Received: 10. 12. 2008

New on the Market



Partnership Between Siti-B&T Group and Nuova Fima

Siti-B&T Group and Nuova Fima, two global leaders in the ceramics machinery sector, have signed a partnership which concerns a specific production process, the “end of line”.

The strategic collaboration is born from the wish of both companies to supply the market with top technologic solutions on the whole range, making the most of the experience, the perfections and the extremely high product specialisations of both groups.

The innovative sorting line Dynamic Synthesis is the first result of the new partnership, created from a tight collaboration which seen Siti-B&T Group and Nuova Fima work together, and also includes an engineering, assistance and after

sales service. The commercial policy decided by the two companies will contribute to improving the product offer.

The new sorting line is in complete conformation with the current market demands, equipped with mono stacker with dynamic assignment system and it boasts a highly reliable packing system. It is equipped with Nuova Firma hardware and software and tested electronic equipment.

Dynamic Synthesis will be proposed by Siti-B&T Group for all new complete plants equipped with the adequate specifications (sizes from 15 cm × 15 cm to 60 cm × 60 cm), while Nuova Fima will propose the machine directly to its ceramic clients.

New MICROMATIC System for Cerámica Rioboo

The Cerámica Rioboo brickworks of Pravio (A Coruña) is the last – but not least – brickyard opting for solid fuels in Spain.



This Galician producer of hollow bricks will count in the next weeks with a solid fuel firing system model MICROMATIC that will use petroleum coke as the main fuel in the kiln, for an output of approx. 250 tm/d. The fuel used in the preheating zone will be natural gas.

Beralmar has already supplied more than 200 solid fuel (petcoke, coals, etc.) firing systems over the last quarter of century, the half of which have been installed in the last 8 years alone.

Such boom in the use of solid fuels is not just explained by the price increases of gas and heavy oil, but also by the existence of adequate technologies for their consumption, which are constantly updated.