

# Safety Processes for Tempering Carbonaceous Refractory Products

E.-G. Hartung

Every year several million tons of carbon containing refractory products are produced worldwide. Even if different production processes are used, all of them follow the same basic principle: a ceramic granulate is mixed with a carbonaceous binder, pressed and subsequently submitted to a tempering process. In most cases the ceramic granulate is MgO and internationally these products are referred to as magnesia carbon (MgO-C). In other cases aluminium oxide is used and the products based on this compound are designated as alumina carbon.

## Tempered products

The aim of the tempering process is always the evaporation of volatile matter from the binder to obtain a final product with a content of pure carbon in the end.

Two main groups of carbonaceous products can be distinguished:

- pitch-bonded products
- resin-bonded products

The pitch-bonded bricks are mainly produced in Europe.

In former times, only pitch obtained from coal tar was used for pitch-bonded bricks. Nowadays, many manufacturers use the material CARBORES® with only low emission of harmful vapours during preparation and shaping. Tempering temperatures of 300–350 °C are typical for pitch-bonded products. The binder that is mainly used for resin-bonded products is phenolic resin which, however, has the disadvantage of a lower carbon content which means that larger amounts have to be used to obtain the same carbon content in the final product. The typical tempering temperatures for this process are 180–250 °C.

## Existing tempering processes

Magnesia carbon and alumina carbon always require thermal treatment in a tempering kiln, however with significant regional differences in the type of construction and equipment of these kilns. These differences are due to the completely different safety and emission regulations and standards in

the individual countries. Here the following aspects are to be stated: safety, work safety and environmental protection

### Safety

The first one is the safety aspect as during the tempering process flammable vapours are always released which, under unfavorable conditions, could lead to fire or even to an explosion of the kiln. To avoid this risk, the atmospheric conditions in the process area have to be controlled and adapted to the running process. This is already general practice in modern tempering plants, however a large number of plants are still in operation worldwide in which the process atmosphere is neither controlled nor regulated.

### Work safety and environmental protection

The other aspect is work safety and environmental protection as the tempering process always leads to the production of noxious substances. Pitch-bonded products release hydrocarbons and the benzopyrene developing at tempering processes over 300 °C has been known to be extremely carcinogenic for a long time.

When tempering resin-bonded products formaldehyde is released which, in higher concentrations and with prolonged exposure, is toxic for the human organism. For the before-mentioned reasons the waste gases from such kilns have to be subjected

to afterburning in nearly all industrial countries. However, still today, a large number of tempering kilns without any waste gas cleaning is in operation around the world. The fact that kilns, which have been in operation without any control system for some time, need to be retrofitted with a thermal postcombustion system due to the introduction of new emission laws can always entail great risks. Now the waste gas volume determining how much purging air has to be introduced into the kiln to prevent the formation of an explosive atmosphere suddenly plays an important role.

The quite understandable attempt to reduce the costs of the post combustion system by reducing the volume of purging air could easily lead to a dangerous binder concentration in the kiln room. Therefore a precise control of the kiln atmosphere is indispensable in this case.

## Atmosphere measurements in tempering kilns

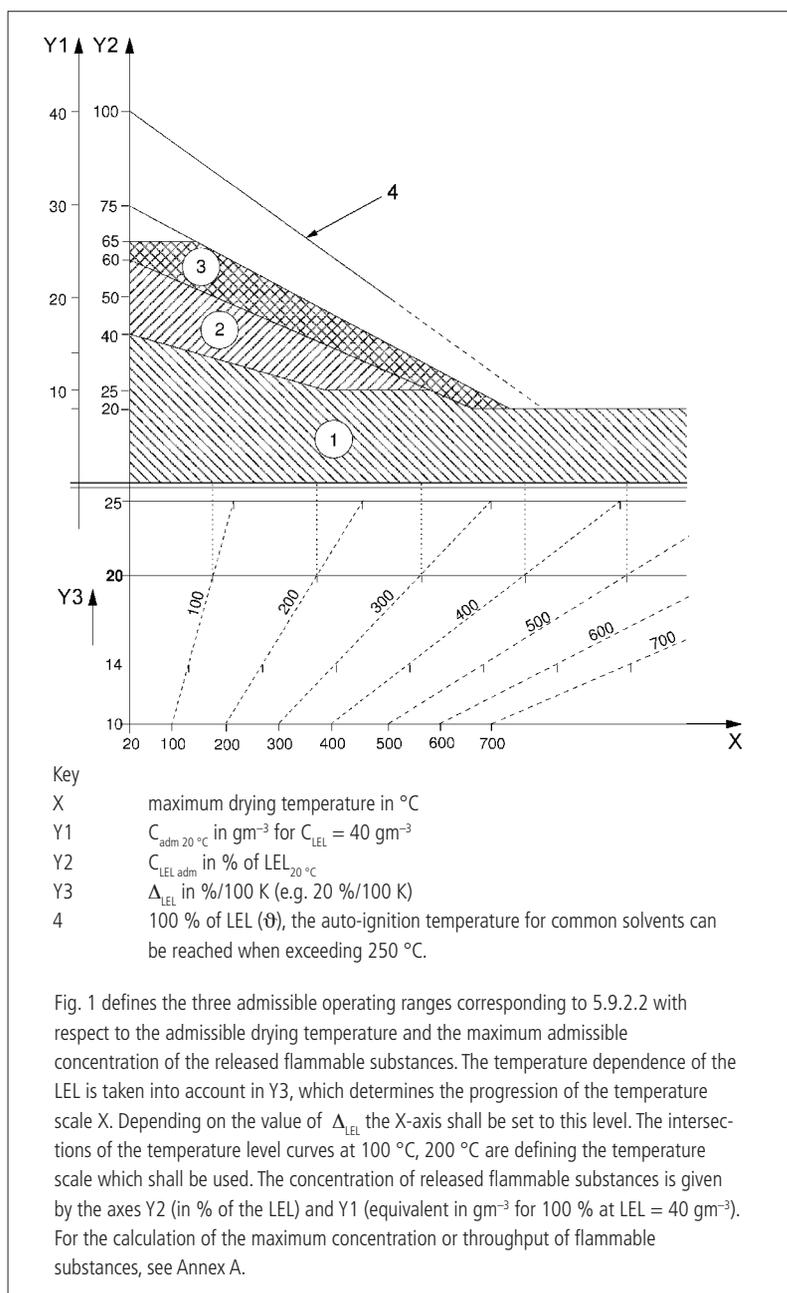
For the kiln atmosphere measurement in tempering kilns different systems are available on the market. A comparably cost-efficient system consists of infrared or diffusion sensors coming from the mining industry which have been developed for the measurement of hydrocarbons in the air.

Infrared sensors are generally limited to an application temperature of max. 80 °C which is not enough for a normal tempering process. Diffusion sensors are available for a temperature up to 200 °C which can be quite sufficient for the waste gas flow of a

Ernst-Georg Hartung  
Riedhammer GmbH  
90411 Nürnberg

E-mail: ernst.hartung@riedhammer.de  
www.riedhammer.de

Keywords: tempering kiln, magnesia carbon, safety processes



**Fig. 1 Operating ranges for type A dryers**

(Source: DIN EN 1539 Dryers and ovens, in which flammable substances are released – Safety requirements)

tempering kiln. Unfortunately such sensors are not suitable for continuous measurements as they are highly sensitive to condensates from the waste gas.

Another, considerably more expensive solution consists in the Flame Ionization Detectors (FID), which can be used for measuring hydrocarbons. This type of measurement is actually well suited for tempering processes as a large percentage of flammable substances can be recorded, however, the suit-

ability of these devices has to be checked for each different process application. In all cases, these devices need regular and careful maintenance due to the fact, that for this measurement a certain volume of the kiln atmosphere has to be extracted from the kiln into the measuring unit, being cooled down at the same time. Suitable filters have to be used to avoid blockage of the measuring line by condensation or damage to the measuring sensors.

## Operation with excess air as per EN 1539

In the EU the safety of such plants is defined by the EN 1539 standard. This standard defines the safety requirements for dryers and ovens in which flammable substances are released.

In this context the plants are subdivided into 2 different types, on the one hand type A covering all plants operated with excess air and on the other hand type B for plants operated oxygen-free. Type A is the normal operating mode with which nearly all tempering kilns are operated nowadays. Fig. 1 shows the diagram for dryers of type A.

The diagram shows the ranges of the admissible concentration of flammable substances. Since the gases released from the refractory products are chemically altered by the thermal treatment and therefore the exact composition cannot be determined during operation, a LEL of 40  $\text{g}/\text{m}^3$  is assumed in practice at approx. 300 °C, that means from this concentration there is a direct risk of explosion.

In order not to have to operate too close to this limit, a safety factor  $\times 4$  is required, according to which the maximum possible concentration of flammable gases in the kiln should not exceed the value of 10  $\text{g}/\text{m}^3$ . In order to reduce the concentration to the set value of 10  $\text{g}/\text{m}^3$ , the kiln must be flooded with a corresponding quantity of fresh air, the so-called dilution air.

The dilution air increases the exhaust gas quantity significantly; in view of the fact that the exhaust gas must be completely combusted, the amount of dilution air plays a central role in the energy consumption of a tempering kiln.

In the case of a continuously operated tempering kiln, in which the evaporation of the flammable gases is largely constant with a constant kiln power, the energy consumed in the post combustion can be recovered in large quantities in the heating of the kiln by using modern kiln technology.

It is much more difficult to operate a periodic tempering kiln, in which the flammable gases suddenly evaporate in large quantities and in a short time, generally in the temperature range between 100–250 °C. In this range of the tempering curve, the concentration of flammable gases in the kiln rises sharply, so that the dilution air must have a high volume, in order to keep the

concentration in the kiln below the required 10 g/m<sup>3</sup>. This requires a very large exhaust system and a large post combustion system. Since, in practice it is not possible to measure the concentration of flammable gases in a process-compatible and reliable manner, the dilution air cannot be constantly adapted to the highly fluctuating current concentration of gases, but must be maintained at a relatively high level for safety reasons. This leads to a very high fuel consumption.

**Operation under oxygen deficiency**

The EN 1539 standard also allows operation under oxygen deficiency. This kind of tempering is referred to as dryer type B. In this case, the oxygen content must be limited to such a degree that the released, flammable substances cannot be ignited under any circumstances. The inert gas required for this purpose must be efficiently kept in the kiln and any unintended leakage must be prevented.

In the normal temperature range for tempering kilns above 150 °C the maximum permissible oxygen concentration must be determined based on the ignition limits of the flammable gases. In case of the binders commonly used in the production of MgO-C-bricks, an oxygen content of less than 4 % is generally sufficient. The inerting of the kiln atmosphere can be carried out in the case of directly heated kilns by the CO<sub>2</sub> coming from the combustion. This is not possible with indirectly heated kilns; here the inerting process should be carried out by means of inert gas (CO<sub>2</sub> or N<sub>2</sub>), which has a negative impact on the cost-efficiency of the tempering kilns.

Since directly heated kilns have been established on the market in recent years due to their low energy consumption and their safety-related advantages, and indirectly heated kilns (with exception of dolomite production) are hardly ever used, an inert atmosphere can be generated by means of

**Tab. 1 Average gas consumption of different tempering kiln types**

Tempering kiln, continuous, directly heated, excess air operation	10–12 Nm <sup>3</sup> /t
Tempering kiln, continuous, indirectly heated, excess air operation	16–18 Nm <sup>3</sup> /t
Tempering kiln, periodic, directly heated, excess air operation	20–22 Nm <sup>3</sup> /t
Tempering kiln, periodic, directly heated, low-oxygen-operation	14–16 Nm <sup>3</sup> /t

a correspondingly regulated modern burner system. In the case of periodic kilns in particular, the low oxygen operation offers advantages in fuel consumption due to the absence of dilution air, which can be significant in a medium-sized kiln. In this respect, such a kiln can even keep up with a continuous kiln.

Tab.1 shows average values in the gas consumption of the various types of tempering kilns, always based on natural gas as fuel at a tempering temperature of 300 °C and a capacity of 100 t/d. However, in the design of such a tempering plant, the lack of a safety margin between normal operation and possible critical conditions of the plant must be carefully considered.

While a safety factor of 4 is to be used for excess air operation in accordance with the requirements of EN 1539, such a margin is missing for this functional principle. As a control range, only the range of 0–4 % oxygen is used, above 4 % a flammable and therefore also explosive range is reached very quickly. The operation in a strongly reducing range is also not advisable, since this generates larger quantities of CO.

This very narrow safety range requires a very precise system control. For the measurement of the oxygen in the kiln atmosphere safe and reliable instruments are available on the market. This measurement should be failsafe, since the oxygen content is the decisive parameter for this process. However, the plant must also be secured in other areas, e.g. in the event of a power failure. Since at the same time the inert gas generator fails due to the failure of the

burners, the plant must be purged by an externally supplied inert gas, such as CO<sub>2</sub> or N<sub>2</sub>, in order to prevent the formation of an explosive atmosphere.

Whether a product can be tempered in a low-oxygen kiln is essentially due to the amount of evaporation substances. If the amount is too high in a certain time, the concentration increases too much which can lead to overtemperatures in the post-combustion system.

**Summary**

The high safety requirements for tempering kilns in most industrialized countries have made the operation of these potentially risky kiln plants considerably safer. The necessity of very cost-intensive safety technology is essentially connected with the obligation to treat the exhaust gases in such a way that environmental pollution is kept to a minimum. The resulting need to limit the exhaust gas volume, to minimize the cost of this exhaust gas purification makes the control of the process significantly more demanding and also significantly more expensive.

However even today more than half of the MgO-C products manufactured worldwide are tempered in kilns that do not have either an exhaust gas purification or any significant safety technology. In this case such a kiln can be produced at low cost, which, of course, also makes the final product significantly cheaper. In the end, however, due to official regulations, a conversion to environmentally friendly and safe systems for these kinds of plants will be necessary.