PROPERTIES OF REFRACTORY CASTABLES FOR MICROWAVE DRYING

Moritz B.K. Fritzsche, Christian Dannert
Forschungsgemeinschaft Feuerfest e. V., Höhr-Grenzhausen, Germany

Ralf Wagner, Albrecht Schmidt, Patrick Hunhold, Anne Tretau
Materialforschungs- und -prüfanstalt an der Bauhaus-Universität Weimar, Weimar, Germany

ABSTRACT

Microwave technology is a promising approach to electrify drying processes in the refractory industry. The temperature-dependent dielectric properties of refractory castables determine the energy input required to achieve sufficiently high temperatures for drying, i.e. for removing the physically and chemically bonded water.

Two basic refractory castables, based mainly on either corundum or andalusite, have been investigated regarding their dehydration behaviour, technological and dielectric properties in microwave drying up to 800 °C. The latter are described by the complex permittivity, comprising a real part and an imaginary part (dielectric loss), both of which change with temperature. Permittivity measurements at 915 MHz and 2.45 GHz were performed using a resonator method. During the initial heating, residual pore water strongly absorbs microwave energy. The dissipation factor was found to vary significantly among materials under investigation. Technological properties that directly affect the risk of explosive spalling of castables, such as permeability and vapor pressure build up within the material, were investigated. The dehydration reactions identified by thermoanalytical analysis (MMH) are reflected in changes of dielectric loss of the refractory concretes.

INTRODUCTION

Drying of refractory castables

Most monolithic refractory products are typically manufactured and pre-dried by refractory producers before on-site installation. This way, physically and chemically bonded mixing water is removed from the pores and hydrate phases after curing, which otherwise could cause "explosive spalling" or at least microstructural damage in service. Therefore, pre-drying is generally carried out at temperatures up to 400 to 600 °C, to ensure that all CA-hydrates have been dehydrated. Most commonly the used drying systems are powered by natural gas. In such conventional dryers, heat up at the surface and conductive heat transfer towards the inside will progressively end with a completely dried refractory product. The limiting factors are heat conductivity to the inside and moisture transport to the outer surface. In very dense, slow-drying refractory castables, in which moisture remains in the innermost core for a long time, high vapor pressure can lead to explosive spalling. To avoid such damage during pre-drying due to high vapor pressure, long and energy-intensive heating protocols with slow heating rates and long holding times are common practice.

Compared to conventional heating, the heating in microwave dryers occurs more volumetrically, delivering energy directly to the interior of the refractory products being dried. Microwave drying prevents the formation of a pronounced thermal gradient from the exterior to the interior of the product. The temperature and moisture distributions are rather inverse compared to conventional drying. This can accelerate the transport of water to the outer surface because the higher vapor pressure on the inner side will push the moisture outside towards the colder surface. Faster moisture removal and, as a result, absence of water inside of the material at higher temperatures helps to avoid high vapour pressures at the end of the drying process.

This study aimed to establish a basic understanding about the differences of the drying process in microwave dryers compared to conventional drying, and to assess the relevance of temperature-dependent dielectric properties of typical refractory materials for process control and simulation of microwave drying.

Microwave drying of refractories

Microwaves are electromagnetic waves in the range of 300 MHz to 300 GHz. For commercial applications in industry, two frequencies at 915 MHz and 2.45 GHz are commonly used. When a wet, dielectric material is exposed to an electromagnetic field, energy is transferred by rapid polarization and depolarization of physically bonded water [1]. This results in heat dissipation within the material. Even after the moisture has been removed, the refractory material continues to absorb microwave energy, resulting in ongoing heating. According to accessible literature, microwave drying of refractory products has not yet been implemented broadly in industrial practice, although it seems to be a promising technology for electrifying the drying of refractory castables. Some literature suggests that microwave assisted drying has been successfully used for drying of monolithic ladle linings [2,3]. Nevertheless, there are only few studies that deal with the microwave drying of prefabricated refractory components made of refractory castables [4,5,6]. These studies are limited to tests on a laboratory scale. This brings up the question: What are the barriers preventing refractory manufacturers from operating microwave dryers? Especially, when considering the benefits of such a drying technique compared to conventional drying, such as [1,2,3]: environmental sustainability via renewable energy utilization, reduced energy consumption, rapid heating rates and short processing times, as well as volumetric heating directly inside the material.

The authors assume that the answer to the question raised above is two-fold and most likely the lack of fundamental knowledge about i) a safe process control which avoids inhomogeneous or to intense local heating (hot and cold spots), and ii) the extent to which microwave drying can be used as an universal drying method for all types of refractory products. The latter is particularly important for refractories, considering the broad range of raw materials, and variations of geometrical shapes and product dimensions, compared to other ceramic industries, e.g., the production of sanitary ceramics or building bricks.

In practice, a hybrid system that combines microwave heating with convective air heating seems most promising to increase the energy efficiency compared to a single-microwave system [1]. A combination of microwave and hot air drying also resulted in longer service lifetime for monolithic ladle linings [2]. Additional hot air convection probably leads to a better homogenization of heat within the drying furnace chamber and promotes uptake of water from the surface of the material being dried for removal.

Dielectric properties of refractory materials

Systematic studies on the temperature dependence of the permittivity of refractory materials and the influence of grain size and density are limited [7,8,9]. For reliable simulations and process control of microwave dryers, it is necessary to consider the changes in temperature-dependent permittivity in connection with the technological properties. After pore water removal, the imaginary part of the permittivity may become very small, as in pure corundum, slowing further heating due to the low absorption of microwave power. Conversely, some materials with low microwave absorption at low temperatures may exhibit a sharp increase in the loss factor at higher temperatures, as observed in glass raw materials and clays [8], requiring careful management of critical temperature ranges to avoid excessive heating. Therefore, temperature-dependent measurements on both wet and dried refractory castables are necessary to assess the contribution of residual mixing water to dielectric permittivity.

MATERIALS AND METHODS
Raw materials and castable compositions

Four Low-Cement-Castables (LCC) were investigated here, mainly based on one of two selected refractory raw materials: corundum (Cor) and andalusite (And). The deflocculants (Defloc. A[5], B[6], and C[6]) and main components are summarized in Tab. 1 and Tab. 2, respectively. All mixtures contain 5.00 wt.-% Calcium-Aluminate-Cement (CAC; Secar® 71[1]) and 0.05 wt.-% popypropylene fibers (PP-fibers; 2,8/6[2]), except one composition (*Cor-II*). Three castables (*Cor-I, Cor-II, Cor-III*) are, composed of highly pure Al_2O_3 (Tabular Alumina T60/T64[3], CTC20[3], and RG4000[3]) and differ only in their water content and additives (deflocculants, PP-fibers). Castable *And-I* is based on 80 wt.-% Analusite (60 wt.-% Durandal 59[1] and 20 wt.-% Kerphalite KF[1]). The Matrix of *And-I* also contains Microsilica® 971-U[4] (3.50 wt.-%) and calcined alumina CT 800 FG[3] (11.50 wt.-%). Deflocculant C was used in combination with citric acid and Li_2CO_3 to adjust the setting kinetics. All castable formulations were designed in a way to have a similar flow behaviour under vibration and a sufficient setting for demoulding after approximately 24 hours.

Tab. 1: Deflocculants (Defloc) used for the different LCC formulations.

Deflocculant		Wt.-%
A	Polycarboxylate (PCE): Castament FS60[5]	0,065 %
B	Sodium tripolyphosphate (STPP): N 25-15[6]	0,150 %
C	Sodium hexametaphosphate (SHMP): Budit 4H[6]	0,150 %
	+ citric acid	0,030 %
	+ Li2CO3	0,002 %

Tab. 2: Summarized composition of the different LCC. The amount of water in wt.-% refers to the total amount of solids.

Name	Main comp.	Fines	Water	Additives
Cor-I	T60/T64 (95 wt.-%)	Reactive alumina	5.4 %	Defloc. C, PP-fibers
Cor-II			5.4 %	Defloc. C
Cor-III			4.6 %	Defloc. A, PP-fibers
And-I	Durandal 59 (60 wt.-%)	Andalusite, Calcined alumina, Microsilica	6.2 %	Defloc. B, PP-fibers

[1]Imerys S.A., France; [2]STW Kautzmann GmbH, Germany; [3]Almatis GmbH, Germany; [4]Elkem ASA, Norway; [5]BASF SE, Germany; [6]Chemische Fabrik Budenheim KG

Analytical methods

Thermal analysis by the Method of Monotonic Heating (MMH) [10] in combination with Thermal Gravimetric (TG) Analysis and in situ measurement of gas pressure (P) at the center of the specimen were conducted after a curing period of 24 h at 20 °C and 90 % relative humidity. The cylindrical specimens for MMH-TG-P-testing (diameter: 65 mm, height: 140 mm) were heated in a conventional electrical furnace with a heating rate of 250 K/h up to 700 °C. Modulus of Rupture (MoR) was determined by testing flexural strength of prismatic test pieces (width: 40 mm, length: 160 mm, height: 40 mm) after curing and drying at 110 °C, 220 °C, 340 °C, 530 °C, and 800 °C. The temperature levels were selected to frame temperature ranges of the mineral phase changes that have been detected by MMH measurements. The halved prisms were used to determine open porosity (water absorption method). To determine gas permeability, cylindrical test pieces (diameter: 100 mm, height: 20 mm) were produced and measured for each temperature level. After drying at 110 °C, the first gas permeability measurement was performed at room temperature using the vacuum decay method [11]. The specimen was then dried at the next temperature level and measured again. This procedure was carried out up to the last temperature level to obtain a consistent dataset on the evolution of the gas permeability during drying of the materials. The evaluation procedure was based on the model proposed for pressure decay

measurements from Innocentini et al. [11] that was adapted for the vacuum decay data.

Measuring the permittivity of samples at high temperatures requires thermal decoupling between the sample and the measurement apparatus. Therefore, either very small samples [12,13] or antenna arrangements [14,15] are used. Another option are temperature-compensated resonator arrangements, as described, for example, in [16]. A measurement arrangement based on a coaxial cavity resonator (copper) was developed that can determine the permittivity up to approximately 1000 °C at the two frequencies relevant for microwave applications, 915 MHz and 2.45 GHz. Specimens large enough to represent the behaviour of an entire refractory castable were used. The cylindrical, temperature-controlled test specimens with a diameter of 20 mm are briefly inserted into the water-cooled resonator after curing and at various dehydration stages. Permittivity and sample temperature are determined during insertion and removal.

RESULTS AND DISCUISSION
Effective thermal diffusivity and gas (vapor) pressure

Thermal diffusivity data, shown in Fig. 1a, show exothermic and endothermic signals in the form of upward or downward directed peaks that can be correlated with specific reactions. These signals indicate the ebullition of water and the thermal decomposition of hydrate phases during drying, like those described by Simmat et al. for LC and MC castables [10,17,18]. Exothermic signals between about 70 °C and 120 °C were attributed to the rapid hydration of residual CAC. Endothermic reactions above approximately 130 °C can be assigned to the thermal decomposition of different hydrate phases (AH_3, C_3AH_6, $C_4A_3H_3$, AH) at certain temperatures, summarized in Tab. 3. Signal assignment in MMH was guided by plausibility considerations and informed by literature data on known hydrate phases and their reported thermal decomposition temperatures [19].

Temperature variations of the same dehydration reaction reflect differences in permeability, which in turn results in distinct hydrothermal conditions during heating. The fast heating rate and low permeability of dense castables with low permeability lead to high gas pressure (vapor pressure) in the pore structure up to a recorded maximum of about 40 bar at 260 °C for *Cor-II* (cf. Fig. 1b). These hydrothermal conditions with high vapor pressure stabilize hydrate phases to higher temperatures and therefore affect the temperature range at which hydrate phases will decompose. A sharp increase in the effective thermal diffusivity is interpreted as the end of the evaporation (and ebullition) of free water. At this temperature, there is no liquid water present in the pore space, and the endothermic evaporation process is finished which results in an immediate increase in the temperature. This correlates well with the gas pressure drop below the vapor pressure curve (Antoine equation) after the maximum is reached at the end of evaporation.

Tab. 3: Temperatures from MMH-signals attributed to the dehydration reactions occurring in the LCCs.

Phase	Cor-I	Cor-II	Cor-III	And-I
AH_3	164 °C	166 °C	175 °C	Not detected
C_3AH_6 or $C_4A_3H_3$	330 °C	348 °C	352 °C	302 °C
AH	520 °C	545 °C	540 °C	Not detected

Technological properties

MoR and Open Porosity (OP) were measured at room temperature after curing and drying. The results are shown in Fig. 2 as a function of the drying temperature. The corundum based castable with PCE as deflocculant (*Cor-III*) has the lowest amount of water, the highest strength and lowest OP after drying at 110 °C and 220 °C. However, with increasing drying temperature, the MoR becomes even smaller than those of *Cor-II* and *Cor-III* after treatment at 800 °C. *And-I* also showed a decreased MoR with rising temperature. In general, there is a clear trend that the OP increases with rising temperatures for all castables. These observations can be explained by the fact that the

strength-forming hydrate phases decompose, i.e., dehydrate at elevated temperatures. This causes a drop of MoR up to 530 °C for most test specimens and an increase in OP up to 800 °C.

An increase of MoR after drying at 800 °C can be recorded for *Cor-I*, *Cor-II*, and *And-I* and is related to first sintering reactions.
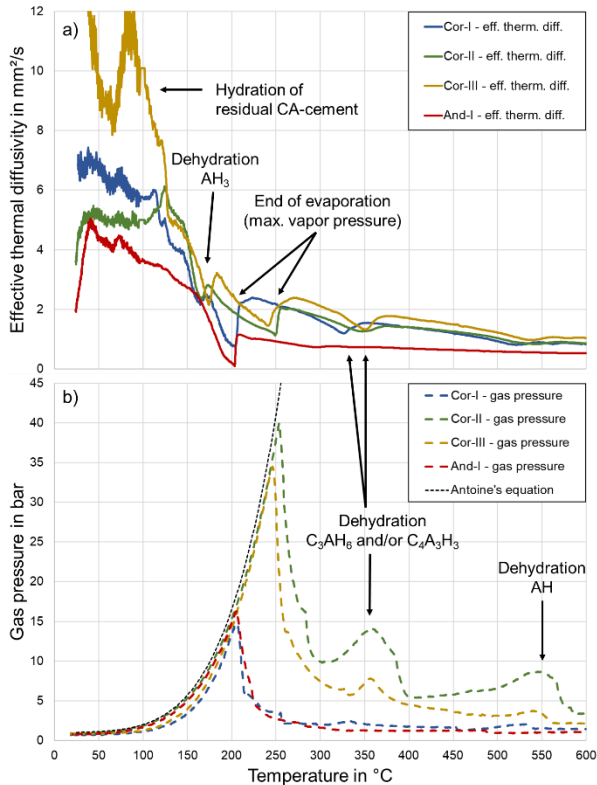

Fig. 1: Thermal diffusivity (a) and gas pressure (b) measured using a combined MMH-TG-P-Setup during heating (250 K/h) to 700 °C after curing.
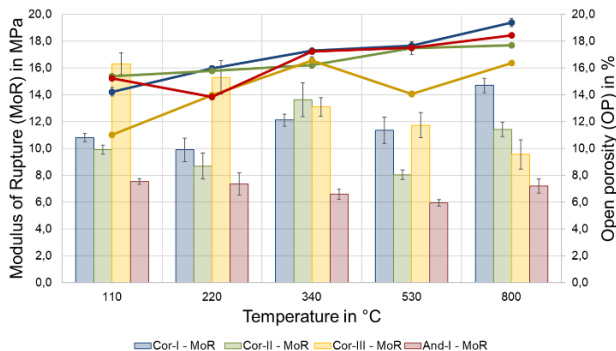

Fig. 2: Modulus of Rupture (MoR) and Open Porosity (OP) for each LCC after curing and subsequent drying at the indicated temperature.

Gas permeability
Quantification of gas permeability was done by evaluation of vacuum decay data according to the Forchheimer equation. A clear dependence of the drying temperature on the Darcy permeability can be noticed in Fig. 3. The non-Darcian (inertial permeability) was observed to reflect the same qualitative relationship, which is why these values are not shown here. Considering the logarithmic scale on the y-axis in Fig. 3, it becomes clear, that the increase of permeability is mainly due to the addition of PP-fibers (melting temperature at about 170 °C). They form a well-connected pore network that significantly enhances permeability, whereas OP does not exhibit a comparable increase (cf. Fig. 2). However, one can still observe (see data of *Cor-II*) that the progressive decomposition of hydrate phases with increasing temperature results in a further enhancement of permeability. The permeability data reflect the

maximum gas pressure during heat up in MMH-TG-P tests. In general, high permeability allows fast water removal which in turn leads to an end of evaporation at lower temperatures.
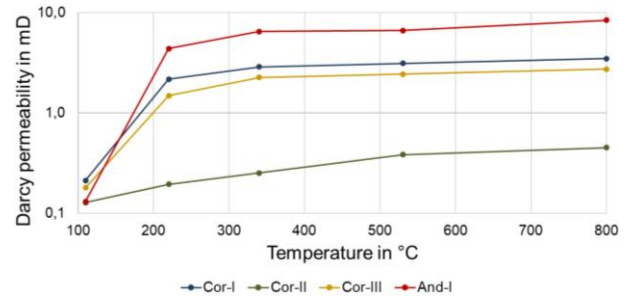

Fig. 3: Darcy-permeability for each LCC after curing and subsequent drying at the indicated temperature.

Dielectric properties of refractory castables
The real part of the permittivity of the test specimens decreases from room temperature to a temperature of approx. 140 °C (cf. Fig. 4a and b). This decrease is associated with a decrease in mass (cf. Fig. 5), which suggests that the (initial) pore water is released up to this point. The first inflection point in the TG curves within this temperature range marks the end of the main evaporation phase. The imaginary part also tends to decrease up to 140 °C due to the reduced amount of water. The decreasing trend is superimposed by the increasing value of the imaginary part of water with increasing temperature. In contrast to *And-I*, the imaginary part of *Cor-III* rises significantly again. This increase in the imaginary part up to 250 °C can also be observed for the dried sample during a second heating.
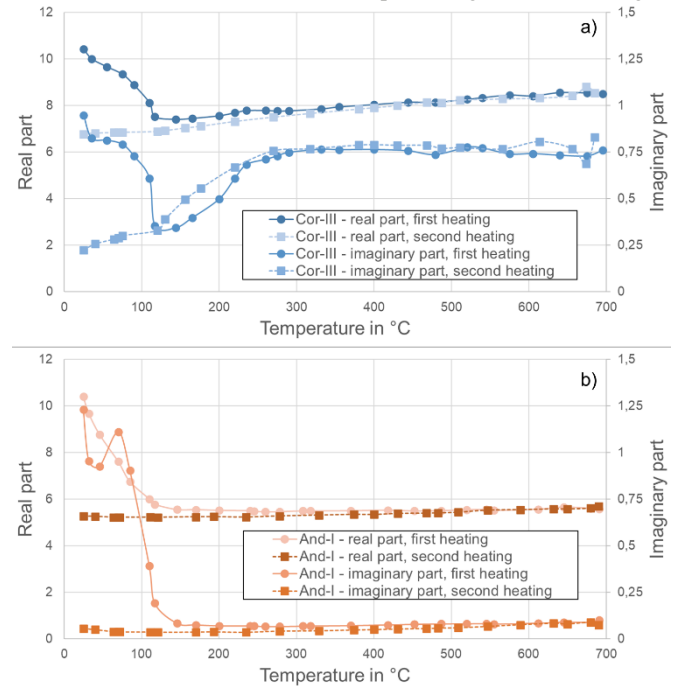

Fig. 4: Real and imaginary part of permittivity of cured and dried samples based on corundum (a) and andalusite (b).

The weight loss observed above 140 °C can be attributed to the release of chemically bound water from the decomposition of CA hydrate phases. This release is also reflected in the permittivity measurements. The slightly higher values in the real part during the first heating compared to the dried sample are caused by the presence of residual bound water. The real part continues to converge in the higher temperature regime. Thus, the permittivity in the second heating corresponds to that of the solid material without the contribution of water (physically and chemically bonded) at this temperature. Interestingly, the results reveal a significantly stronger temperature dependence of the permittivity for the corundum-based castables (illustrated here for *Cor-III*), even after drying. The

imaginary part increases from 0.35 to about 0.78 between 100 °C and 300 °C and then remains almost constant. In contrast, the andalusite-based material (*And-I*) shows a more linear and smaller increase in the imaginary part with increasing temperature, with overall lower absolute values below 0.1. The absorption of microwave energy should therefore be lower for the andalusite-based material. In initial successful heating experiments conducted in a laboratory microwave oven with the castables presented here, the resulting temperature profile reflects the results for the dielectric properties. The corundum-based casting compounds reach much higher temperatures with the same energy input.

When comparing the results of permittivity and MMH-TG-P, it should be noted that the measurement setup for the dielectric properties required a cylindrical sample with a length of 100 mm and a diameter of 20 mm, and that the specimen was alternately heated and measured. This results in an 'earlier' release of pore water in relation to temperature compared to the MMH-TG-P measurements with larger test samples and continuous heating. This accounts for differences, such as the temperature at which no initial pore water remains. The permittivity for the first and second heating for both castables differ slightly above about 300 °C. In general, slightly higher real and imaginary parts between 130 °C and 300 °C during the first heating are be explained by the hydrate phases that are still present, which subsequently decompose. However, there is no clear explanation yet as to why the imaginary part in *Cor-III* is higher during the second heating and needs further research.
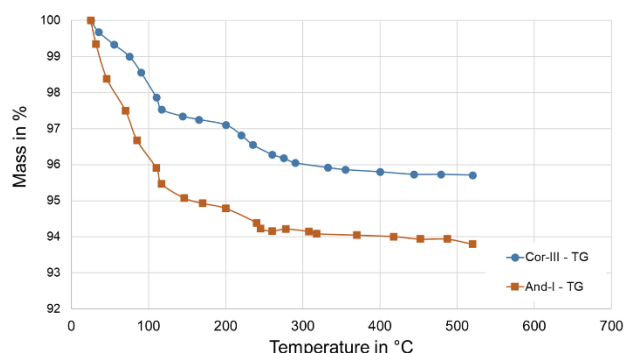

Fig. 5: Normalized mass during drying as function of the applied temperature during permittivity measurements, up to 520 °C, as no further dehydration was observed above this temperature.

CONCLUSIONS AND OUTLOOK

The results demonstrate how different raw materials of refractory castables affect their drying behaviour, and particularly the vapor pressure, hydrate phase content and permittivity. Strong differences in permittivity need to be considered for microwave drying for safe and economic operation. The material properties shown here and results from additional laboratory tests indicate that the energy input in microwave dryers must be dynamically adjusted to the materials and their water content to achieve sufficiently high temperatures for dehydration and at the same time to avoid explosive spalling.

Further research will be conducted on the subjects of:

– Dielectric properties of broadly used refractory raw materials.
– Comprehensive simulations to optimize microwave drying.
– Adaptive process control to avoid explosive spalling.
– Upscaling from laboratory scale to pilot plant scale dryers.
– Concepts for microwave assisted dryers on an industrial scale.

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