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ORIGINAL ARTICLE

Direct observation of the moisture distribution in calcium aluminate cement and hydratable alumina-bonded castables during first-drying: An NMR study

Ahmed J. Barakat¹ | Leo Pel¹ | Olaf Krause² | Olaf C. G. Adan³¹Eindhoven University of Technology, Eindhoven, Netherlands²Koblenz University of Applied Sciences, Koblenz, Germany³TNO, Eindhoven, Netherlands**Correspondence**Leo Pel, Eindhoven University of Technology, De Rondon 70, 5612 AP, Eindhoven, Netherlands.
Email: l.pel@tue.nl**Funding information**

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Abstract

The drying behavior for various calcium aluminate cement and hydratable alumina-bonded refractory castables was investigated in the first-drying temperature range (100°C–300°C). Using a specialized high-temperature Nuclear Magnetic Resonance setup, we were able to directly and nondestructively measure the spatially and temporally resolved moisture distribution, while simultaneously measuring the temperature distribution as well. These measurements show that the drying front position is a linear function of time, which can be explained on the basis of a simplified model where only vapor transport is considered. Based on the measurements and the model, one can directly determine the permeability at high temperatures. Moreover, the results demonstrate that the drying front speed and temperature strongly correlates with the control of key material parameters (eg, water demand, binder content, etc). In particular, microsilica fume-containing low-cement castables displayed the highest vapor pressures, while regular castables generated the lowest vapor pressures reflecting the permeability of these materials.

KEYWORDS

castables, first-drying, high-temperature NMR, phase transitions, porous media

1 | INTRODUCTION

Calcium aluminate cement/hydratable alumina-bonded castables still pose a serious challenge with regard to removing the physical and chemically bound water components from the porous network prior to their application in steel ladles. Due to the high risk of generated steam pressures destroying the material at temperatures above 100°C, castables must be predried under conservative heating schedules below 1°C/min to ensure safe evacuation of the moisture. In particular, the dangerous ebullition stage and hydrate phase decomposition stage pose the greatest concern during heat-up. Therefore, a quantitative understanding of the transport physics in the range of first-drying, that is from 100°C to 300°C, will help guide industrial producers and refractory

engineers in selecting suitable heating schedules for a given set of materials.

Furthermore, recent spalling events suggest that controlling key parameters, such as material selection, that is, binder content, additives, etc, curing time and environmental conditions, are critical to ensure adequate refractory performance.¹ The stability of the chemical hydrates, for instance, depends much upon the curing time, temperature, and ambient environment of castable preparation.² Evermore, the mixing time, water demand, binding phases, for example, calcium aluminate versus hydratable alumina, as well as the use of additives for improving rheology and flow characteristics also affect the properties of these materials, for example, porosity, permeability, etc.^{3,4}

However, the exact contribution to mechanical failure, from the respective dewatering stages of drying already alluded to above, are not quantitatively understood. On one hand, the release of physically free water from the pores is intensified by the ebullition stage of drying, due to the pressure-limited escape of water from the pores. Since there is fast formation of vapor at some distance from the surface, as more liquid is located at greater depths within the material, the balance between internal gas development and removal from the surface, for a given applied heating rate, material permeability, and material thickness, is not easily attained.³ Moreover, at higher temperatures the hydraulic bonds release their water molecules, thereby generating increased porosity and diminishing the mechanical strength of the material.⁵

Therefore, in order to evaluate the likelihood of spalling, destructive and indirect methods are often employed to characterize the dehydration and mass change of water (DSC/TGA); or phase morphology (eg, by XRD). Unfortunately, these techniques are limited by a lack of access to information due to inadequate sample sizing, thereby preventing development of a temperature gradient, or destruction of the specimen. More importantly, vital information for deriving transport properties, such as the position, temperature, and speed of the boiling front, and thus the associated vapor pressure, cannot be obtained through these conventional experimental techniques. Additionally, extracting reliable empirical data on the moisture distribution throughout first-drying will help narrow the assumptions that are often made in conceptual modeling, which until now have been mostly based on second-guessing the internal transport dynamics, such as the relationship between vapor/liquid mass flux.^{6–8}

Recently, a high-temperature nuclear magnetic resonance (NMR) setup was developed and characterized demonstrating that the moisture distribution can be directly measured for regular castables (RC).^{9,10} As NMR is a resonance technique, it can be specifically made sensitive to hydrogen and

therefore to moisture as well. Hence, the moisture profiles can be nondestructively measured with a high spatial resolution on the order of 2–3 mm. In this study, we use the same experimental setup to investigate the moisture and temperature profiles as a function of position for a variety of castables based on different material formulation inputs. By measuring the moisture distribution over time, we can quantify the position of the drying front, where the moisture removal is dependent on internal transport processes, as well as the temperature and vapor pressure at the front position.

2 | FIRST-DRYING THEORY: A FIRST-ORDER APPROXIMATION

During a one-sided first-drying experiment, the total moisture loss of castables can be described by two general stages: (i) externally limited and (ii) internally limited drying. In the former case (i), the mass-loss rate is governed by externally controlled boundary conditions, such as humidity, temperature, or heat flux at the surface. In this regime, liquid transport will be the dominant process, which is furthermore reflected in the homogeneous moisture profiles. Hence, for stage (i) drying, the environment is the limiting factor.

However, after the moisture content drops below a certain threshold, that is, the so-called critical moisture content, the liquid network connectivity is no longer maintained. Consequently, the locally distributed moisture can only escape as vapor. This release occurs in the form of a liquid-vapor boiling front developing and entering the pores of the material, corresponding to stage (ii) drying. Depending on the material of choice, this transition can occur at temperatures in the range of 100°C–200°C. From this moment on, the vapor flux is pressure-driven by ebullition where the transport process is limited by internal properties of the pore structure, that is, the permeability of the material. Therefore,

FIGURE 1 Schematic representation of the conceptual model describing one-dimensional moisture and vapor transport during heating. The variables P , T , and S correspond to the pressure, temperature, and saturation (moisture content), respectively. A uniform heat flux is directed toward the surface of the sample, at $x = 0$. The back end of the sample ($x = L$) is closed and insulated. At the boiling front ($x = u(t)$) the moisture evaporates and is pushed out at the drying surface

for stage (ii) drying, the internal vapor transport is the limiting factor.

Once the drying front has entered the material we can model vapor transport on the basis of a sharp front approximation, which is schematically shown in Figure 1.¹¹ Here, we assume that the moisture and heat transport can be described in 1D, where x is the distance toward the heated surface of a sample with length L . At the position $x = u(t)$, the sharp boiling front of the sample divides the material into a wet part and a dry part. In this model, we introduce two simplifying assumptions. Firstly, we assume that the liquid saturation content in the wet region of the sample remains constant, that is, $S(x, t) = S$; here S corresponds to the moisture level where a drying front appears. Therefore, liquid transport over time in the wet zone can be neglected. At the same time, we assume that vapor transport is the dominant process in the dry part. Secondly, while we are close to the temperatures of dehydration in the range of 200°C–300°C, physically free water (ie, nonchemically bound water) is the quantity which is mostly released from 100°C to 300°C.

Driven by the boiling of moisture, the drying front will recede into the material. Assuming the pore liquid volume per unit area $nS du$ is transformed into vapor over time dt , the boiling front enters the material with speed du/dt ; here n corresponds to porosity. Accordingly, a vapor mass-flux J_V is established. This mass flux is determined by the product of the volumetric flux q and the liquid density ρ . The density is defined by the molar volume V_m and molecular weight M_w . Based on this relationship, liquid water is boiling at the front and evacuates from the pores by escaping toward the surface as vapor:

$$J_V = q\rho = -\frac{nS}{V_m} \frac{\partial u}{\partial t} M_w \quad (1)$$

In our system, the pore length scale is much greater than the mean free path of a water molecule, therefore the continuum approximation of vapor transport is valid. Hence the vapor flow can be calculated from Darcy's law, where the vapor flux is determined by the pressure distribution, reaching a maximum value at the boiling front position. The surface pressure is fixed by external boundary conditions, that is, atmospheric pressure of 101 kPa. Finally, the vapor phase itself can be modeled as an ideal gas and hence the vapor flux is given by¹¹:

$$J_V = q\rho = \left(-\frac{k}{\mu} \frac{\partial P_V}{\partial x}\right) \left(\frac{P_V M_w}{RT}\right) \quad (2)$$

where k is the permeability, V_m the molar volume, μ the viscosity of vapor, R the universal gas constant, and T the temperature. (Here we have used $P = \rho RT/M_w$).

The pressure at the boiling front is determined from the Antoine equation, assuming a local thermodynamic equilibrium exists between liquid and vapor,

$$\log_{10}(P_V) = A - \frac{B}{C+T}, \quad (3)$$

where $A = 8.14$, $B = 1810$ and $C = 244$ are constants.¹²¹³

As a first-order approximation, we may assume that $\partial P/\partial x \approx \Delta P/u$ and hence by combining Equations (1) and (2), we get the following expression for the boiling front position as a function of time:

$$\frac{\partial u}{\partial t} = \frac{kV_m}{2\mu RTnS} \frac{\Delta P_V^2}{u} \quad (4)$$

The input for temperature can be taken directly from the experimental data, that is, the measured temperature profiles which will be presented later on. Hence, by combining Equations (1) and (2), we arrive at Equation (4), a first-order differential equation that relates the velocity of the boiling front with the other properties of the material. The numerical solutions to Equation (4) are presented in the subsequent sections and compared with the experimental results. In this simplified transport model, the only free parameter is the permeability which allows us to quantitatively assess the difference in drying behavior for various materials.

3 | EXPERIMENTAL SETUP

A home-built NMR setup was used for conducting nonisothermal one-sided heating on freshly cured castables in the temperature range of 100°C–300°C. A schematic view of the setup is presented in Figure 2. The experiments were conducted inside a whole-body 1.5 T magnet (Intera, Philips). In order to send the RF pulses and receive the NMR signal for measuring moisture profiles, a home-built, low-pass Birdcage coil was constructed and tested. With this configuration we achieved pulse times as short as 50 μ s. The birdcage coil is secured around a ceramic aluminum oxide tube, which is capable of withstanding temperatures beyond 1000°C. Therefore, the setup can be exposed to high temperatures without risking damage to the equipment. For providing the magnetic field gradient we use two larger coils, oriented in an anti-Helmholtz configuration. With a calibrated strength of 80 mT/m, this gradient allows performing one-dimensional slice imaging without moving the sample. With such a gradient and applied pulse, we achieved a spatial resolution on the order of 2–3 mm. Situated around the birdcage is a diametrically adjustable Faraday cage for tuning/matching of the Birdcage coil. In addition, this Faraday cage should also protect the superconducting magnet of the whole-body MRI in case explosive spalling will occur.

FIGURE 2 Schematic representation of the experimental setup for measuring the moisture profiles during heating up. The sample is placed inside the birdcage coil, secured by an aluminum oxide ceramic tube. Thermocouples are placed inside the holes of the sample. The insert is enclosed by a Faraday cage for tuning/matching. A pair of anti-Helmholtz coils is used to generate the magnetic field gradient. An array of 100 W halogen lamps is used to provide the heat, with a typical heat flux of 3.5 kW/m^2

Special attention has been given to ensure the NMR signal can be measured quantitatively. This was achieved by placing an additional shielding coil between the sample and the birdcage coil in order to minimize the effects of changes in the dielectric constant.^{14,15}

The cylindrical samples, 74 mm in diameter by 74 mm in length, were isolated with rock wool and Teflon, thus preventing heat and moisture loss, respectively, and exposing only one surface toward external heating. In this way, we can create a one-dimensional heat and moisture flow experiment. For measuring temperature profiles, each sample is equipped with 6 K-type thermocouples that are plugged in airtight with Teflon tape. The heating source is an array of gold-coated 100 W halogen lamps capable of heating the surface up to temperatures above 200°C . The maximum heat flux and heating rate is 3.5 kW/m^2 and 2°C/min , respectively. The lamps were gold coated, because gold has a high infrared reflectivity of 0.98. For comparison purposes, the final measured moisture and temperature profiles should be aligned in time; to this end, both datasets were linearly interpolated to the same points in time, without significantly shifting the data beyond a threshold that would impact our conclusions.

4 | SAMPLE PREPARATION

The materials for this study were selected for comparison according to different formulation parameters: water demand, binder content, fillers, and additives. On this basis, the

materials are grouped into three different families: regular castables (RC); low-cement castables (LCC); and noncement castables (NCC). By adjusting these material inputs, we can map the influence of specifically chosen material parameters on the drying behavior, in particular the speed and temperature of drying.

The different samples were prepared according to a formulation recipe list as shown in Table 1. The castable components (total batch weight 5 kg) were dry mixed for 1 minute and then wet mixed for 4 minutes in an A 200 Hobart mixer at speed 1 before being mechanically vibrated at an amplitude of 0.5 mm. NCC required a longer wet mixing time of 6 minutes, in order to achieve optimum dispersion of the solid components. The dry components consist of the aggregates, which are broadly sized tabular alumina grains ranging from tens of micrometers to millimeters, as well as fine filler: for example, reactive alumina or microsilica addition,¹⁶ and chemical binder, that is, calcium aluminate or hydratable alumina. Additives are used for controlling rheology, reaction kinetics and/or dry-out behavior, that is, accelerators, dispersing agents, and permeability-enhancing fibers. The commercial label for these components is provided in Table 1.

The samples are cast into cylindrical Teflon beakers, with dimensions of 74 mm in diameter by 74 mm in length. A template scale and Teflon needles are used for positioning the thermocouples for temperature profile measurements: 7, 27, 44, 56, 64, and 71 mm from top to bottom. During the wet phase of casting, the Teflon needles are inserted into

TABLE 1 Recipe list of the different castables considered in this study

Component	Commercial label	RC (% Dry)	LCC (% Dry)	LCC fume A (% Dry)	LCC fume B (% Dry)	NCC (% Dry)
Tabular Alumina T60/64	≤6 mm	80	82	82	82	84
Alumina	CL 370	—	13	—	10	13
	CT 9 FG	—	—	10	—	—
Microsilica	Elkem U971	—	—	3	3	—
Binder	Secar 71	20	5	5	5	—
	Alphabond 300	—	—	—	—	3
Additives	ADS 3/ADW 1 (LCC/NCC)	—	1	—	—	1
	M-ADS 1/M-ADW 1 (LCC Fume)	—	—	1	1	—
	PP Fibers	0.08	0.08	0.08	0.08	0.08
Water Demand (% dry basis)	Dry Basis (excluding additives)	9	4.7	4.7	4.5	4.6

Note: The mixing components consist of the aggregate, fine filler, binder, additive, and water demand along with the associated commercial description. The dry components (aggregate, fines and binder) add up to 100%; the water demand is taken with respect to the dry components. The tabular alumina component is a broad grain size distribution for which only the upper bound is provided in the table.

TABLE 2 Typical values for the initial free moisture content, permeability, density, and boiling front speed of the different materials considered in this study

Material properties	RC	LCC	LCC fume B	NCC ³
Initial free moisture content ($\text{m}^3 \text{m}^{-3}$)	0.05	0.12	0.10	0.20
Permeability (m^2)	1.33×10^{-16}	4×10^{-17}	7.30×10^{-17}	3.8×10^{-17}
Density (kg/m^3)	2850	3191	3157	3248
Front speed (mm/min)	0.60	0.22	0.35	0.08 (48 h)/0.17 (24 h)
Time front appears (min)	50	100	100	170

predrilled 2.5-mm diameter holes and left there as the sample cures overnight. Immediately after casting, the samples are completely covered, so as to prevent evaporation, and cured for 24 and 48 hours at 20°C. The curing times were chosen in order to assess the effect of changes in the hydration state, which is reflected in the pore structure, on drying behavior. In Table 2, typical values for the initial moisture content, permeability and density are provided for materials cured for 48 hours. The initial free moisture content is calculated according to the total amount of moisture loss, that is, of free water, after an experiment. The permeability measurements were performed at room temperature using the Air Permeability Test by passing gas through the specimen and then into a vacuum chamber.¹⁷ It was found that there was little difference in the permeability during 24–48 hours curing time, that is, within an experimental accuracy of 0.01 mD. It should be noted that the permeability value for NCC is taken from literature for samples cured at higher temperatures and characterized with different equipments. Therefore, it is only

provided as a reference and cannot be directly compared with the permeability results of the other materials.

4.1 | Measuring moisture loss during first-drying

As an example material, RC is used to discuss the one-dimensional, one-sided moisture loss throughout a first-drying experiment. Due to the relatively short sample length (74 mm), the timescale of an experiment is around 1.5 hours. In Figure 3B, the measured temperature profiles are shown, which demonstrate the standard techniques of evaluating moisture loss in a first-drying experiment. As can be seen, once the heat flux is applied, the temperature at the surface begins to rise and a temperature gradient develops. The sample average heating rate is 1.5°C/minute. The maximum surface temperature that reached the top of the sample is around 180°C–200°C. As soon as the temperature at the surface reaches values on the order of 110°C, a decrease in both

FIGURE 3 The measured saturation and temperature profiles for regular castables (RC) (A) and (B) and low-cement castables (LCC) fume (C) and (D) cured for 48 hours. The black markers indicate the position of the drying front as a function of time. The time in between each profile for RC is 3 minutes and LCC Fume is 6 minutes. The data from each experiment were normalized to an initial isothermal reference profile at room temperature, with a significantly high number of averages to correct for inhomogeneities in the sample. The dashed lines in the figures indicate the critical moisture content. The solid line at the bottom of the saturation profile figures corresponds to the residual moisture background level. Items I-III in (A-B) correspond to the three different drying stages of RC: (I) early dehydration, (II) externally limited drying, and (III) internally limited drying

the heating rate and temperature gradient is observed. This indicates that around 110°C a drying front should develop, however, no direct information can be taken from this temperature data.

In Figure 3A, the corresponding saturation profiles are shown demonstrating what additional information can be measured by NMR. Here we have plotted the saturation profiles, that is, each profile is obtained by dividing by a reference taken at the beginning of the experiment at room temperature, corresponding to a uniform saturation of 1. This allows for sample inhomogeneities to be eliminated from the measured quantitative moisture content. Depending on the number of averages, measuring each profile for RC takes on average 1 minute. The time-step in between subsequent measurements is 3 minutes.

Three drying stages are identified (I-III) from the saturation profiles in Figure 3A. Initially, as the temperature is increasing from room temperature up to about 70°C, we see that the total moisture content rises above the first profile, corresponding to a saturation level above 1. This initial rise (I) corresponds to the transforming pore structure upon initial heating. During this initial heating stage, of up to 70°C, dehydration will occur,^{2,9} where chemically combined water is released, resulting in an increase in the moisture content.

As soon as the temperature rises above 70°C-80°C a new drying stage has begun (II). From this moment on, the sample

is drying quite fast as the internal transport is dominated by liquid transport and the dewatering rate is determined by external boundary conditions, such as temperature and humidity, that is, the externally limited drying stage. At the same time this is a combined process of drying and moisture release as in this temperature range the metastable hydrate CAH_{10} also loses its water and converts to the stable crystalline AH_3 , and thereby transforms the pore structure, according to a multistep process: $6\text{CAH}_{10} (-27\text{H}) \rightarrow 3\text{C}_2\text{AH}_8 + 3\text{AH}_3 (-9\text{H}) \rightarrow 2\text{C}_3\text{AH}_6 + 4\text{AH}_3$.

However, these phases evolve as a function of time and temperature. Previous investigations suggest that CAH_{10} and C_2AH_8 will transform into the stable AH_3 and C_3AH_6 at 110°C-120°C or dehydrate entirely (C_2AH_8 at higher temperatures).^{2,5} It is also expected that the rapid transformation of C_2AH_8 to C_3AH_6 at 80°C-100°C, or its complete decomposition can occur which is consistent with the fast moisture increase we also observe in these temperature ranges.²

Also observed in Figure 3A is the onset of a new drying phase (III) at about 110°C. From this point on a drying front begins to develop and the drying rate slows down. This transition coincides with the critical saturation content of 0.4 in the sample, which is indicated by the dashed line. At and above 110°C, the dewatering process is internally limited, as drying is now dependent on the internal pore structure and transport processes governing moisture loss. At the same

time, the greater amount of energy required to remove large quantities of free water from the porous network results in a decreased sample heating rate. This latter effect is due to the high latent heat of evaporation of water.

We can identify the drying front position by taking the midpoint along the liquid-vapor boundary in the moisture distribution, as indicated by black markers in Figure 3A. The corresponding temperatures at the drying front are indicated by markers in the temperature profiles in Figure 3B.

The critical saturation content corresponds to the transition point in the drying rate, that is, from externally limited (fast) to internally limited (slow) drying. In Figure 4 we have demonstrated this by plotting the total average saturation content as a function of time for four different materials: RC, LCC, LCC Fume, and NCC. Again, we use RC (from Figure 3A) as the standard example and employ linear fitting of the data for the two different stages of drying. To a first-order approximation, the critical saturation content is quantitatively defined as the interception point of these two fitted lines (see small dashed line in Figure 4). For the other materials, the transition is less sharp due to their different characteristics.

For the purpose of comparing two materials with very different properties, we have also plotted the results of the measured temperature and moisture profiles for LCC Fume A as shown in Figure 3C,D, where the time-step between subsequent profiles is 6 minutes. The material recipe is listed in Table 1. As a first observation, we see that the moisture content does not rise above 1 for LCC Fume. The changing hydration kinetics seen with RC, once the sample heats up corresponding to the transformation of the high-solubility metastable hydrates as a function of temperature, is not observed with LCC Fume.

In Figure 5A,B, we have plotted the corresponding front position and the temperature at the front for RC as a function of time. Indeed, the measurement reveals that the temperature

FIGURE 4 A plot of the total average saturation content as a function of time for four different materials: RC, LCC, LCC Fume, and NCC. The plot of RC demonstrates the quantitative determination of the critical moisture (saturation) content by fitting two lines (solid lines) to the externally and internally limited drying stages. The intercept of these fits quantitatively defines the critical moisture content, which for RC is 0.4 (short dashed line)

at the drying front is increasing as the boiling front progresses deeper into the material. It is noted that both the front position and front temperature are linear functions of time. Furthermore, the drying front first emerges 50 minutes after the heat is turned on. And as the drying front is entering the material, the temperature at the front increases, thus indicating that the boiling pressure must also increase as required for the vapor to escape from the top of the sample. In Figure

FIGURE 5 The boiling front position as a function of time (A), the boiling front temperature as a function of time (B), and front temperature as a function of front position (C) for low-cement castables (LCC) fume A and regular castables (RC) cured 48 hours as determined from the measured moisture and temperatures profiles (see Figure 3). The simulations based on the best fitted permeabilities are indicated by the solid black lines (k_{fit}). The simulations based on the experimentally determined permeabilities at 20°C are indicated by the solid gray lines ($k_{20^\circ\text{C}}$). The dashed lines passing through the data are a linear fit to the boiling front speed

5C, the front temperature has been plotted as a function of the front position, where again a linear relation is observed. The maximum front temperature reached is 150°C, with a corresponding position of 40 mm from the hot face of the material. The vapor pressure can be calculated on the basis of the boiling front temperature (see Figure 5B). Hence, the saturated vapor pressure of the front starts at 0.1 MPa and rises up to 0.5 MPa (5 bars) during this experiment with RC.

In contrast to RC, we observe that as the surface temperature of LCC Fume A increases, the material immediately begins to dry uniformly until the saturation level is on the order of 0.6. From this moment on there is a transition, that is, the temperature slowly increases until 200°C after which a drying front begins to enter the material. This feature, again, corresponds to the transition in the temperature profiles where the heating rate decreases. It should be taken into account that LCC Fume A contains four times less hydraulic binding phases than RC. From the moment boiling occurs, we once again observe the development of a linear drying front position as a function of time. If we identify the front position and the corresponding temperature at the drying front, as we did before with RC, we observe that in this case the temperature at the boiling front increases up to 220°C. This increase in temperature at the boiling front implies that the vapor pressure will approach a maximum of 4 MPa (40 bars), that is, 15–40 times as high as RC.

As can be seen in Figure 3A for RC, at the end of the drying process there is still some residually distributed moisture on the order of 10% in the sample. This moisture content is, however, well above the noise level, which is just under 1%. This is likely due to the fact that free moisture remains in the small pores over increasing time and increasing temperature. If we look at the average moisture content at the surface of the RC sample, that is, the averaged moisture content over 7–25 mm, which is shown in Figure 6A, we see that the moisture level stagnates toward the end of the experiment.

One possible explanation for the source of this feature is that since we are approaching 200°C, chemically bonded water is becoming released from the solid matrix thereby contributing to the signal as free moisture.² In Table 3 we have provided the various temperature regimes where hydrate decomposition occurs.^{2,3} Accordingly, the stable components AH_3 and C_2AH_8 are expected to release water through a mineralogical phase transformation from 170°C onward. This process will continue for temperatures above 200°C where the energy of dehydration is on the order of 10 000–20 000 kJ/mol.¹⁸ Since we are within the starting temperature range of the dehydration process, it is likely that water still remains inside the small, isolated pores. Indeed, taking an RC sample after drying in an NMR experiment and placing it in a 1000°C furnace reveals that more than twice as much previously liberated water will continue to be released over higher temperatures.

FIGURE 6 The averaged moisture content over 7–25 mm of the sample as a function of time (A). The dashed line illustrates the stagnating background moisture level. The average moisture content over the whole sample as a function of time (B). After 400 minutes have passed, the heat is turned off and the sample cools. The final moisture content here is 0.02 and is indicated by the dashed line

TABLE 3 List of hydrate phases and their corresponding dehydration temperatures^{2,3}

Hydrate phases ^a	Decomposition temperature (°C)
CAH_{10}	120
C_2AH_8	170–195
C_3AH_6	240–370
AH_3 - gibbsite	210–300
Alumina gel	100

^aC = CaO, A = Al_2O_3 , H = H_2O .

To further test the hypothesis that free water is trapped in the small pores, the experiment was repeated over a longer time, where at the end of the experiment the heating was turned off and the results are shown in Figure 6B. Here, we have again plotted the average moisture content as a function of time. As can be seen, the moisture content slowly decreases with time as the heat is turned off, which is likely due to rehydration with the cementitious phases. After the sample sits for 1–2 days at room temperature, following the end of the experiment, the

total signal decreased to 2%. Therefore, there is still free moisture trapped inside the small pores, which has not rehydrated.

4.2 | Comparing experimental results with the conceptual model

In order to validate the observed drying behavior of RC and LCC Fume we need to identify the limiting process governing moisture transport in our experiments, that is, heat transfer or vapor transfer. On one hand, the combined effect of heat capacity and thermal conductivity, that is, thermal diffusivity, will influence the temperature distribution. That is because more energy must be supplied to evaporate the moisture at the boiling front. Consequently, this will limit the maximum boilable moisture/moisture loss and therefore the dewatering rate. On the other hand, vapor transport as determined by the high-temperature permeability can also be the limiting factor, therefore restricting the dewatering rate.

In order to determine the limiting process, a first-order estimation is made of the characteristic time-scales corresponding to the vapor mass flux and thermal diffusivity, t_J and t_D , respectively. The characteristic time-scale for the vapor mass-flux is given by;

$$t_J = \frac{L^2 \mu}{k \hat{P}} \quad (5)$$

where L is the length-scale, μ the dynamic viscosity of vapor, $\hat{P}$ the typical vapor pressure. On the other hand, the characteristic time-scale for the thermal diffusivity is given by;

$$t_D = \frac{L^2 \rho C}{\lambda} \quad (6)$$

where λ is the thermal conductivity and ρ and C the density and specific heat capacity, respectively. A list of the values for these parameters is provided in Table 4, for both RC and LCC Fume. Here we apply the same characteristic heat capacity $C = 900$ J/kg K for both materials, for which values have been previously determined by the Hot Wire

Method.^{19,20} The values of thermal conductivity in Table 4 are determined for each material on the basis of the established relationship between bulk density and thermal conductivity of partially dried dense, insulating castables.²⁰ A plot of the ratio of time-scales corresponding to thermal diffusivity and vapor transport as a function of vapor pressure is given in Figure 7 for RC and LCC Fume. The typical pressure corresponds to the range of values calculated according to the boiling front temperature in Figure 5B for the two different materials. The boiling pressure of RC is in the range of 0.1-0.5 MPa and for LCC Fume the pressures are 1-4 MPa. Based on these values, the time-scale of thermal diffusivity for RC is 2-3 times slower than that of the mass flux; for LCC Fume, the ratio is 9-10 times. It is only for pressures above 0.1 MPa that $t_D > t_J$, as indicated by the dashed line in Figure 7. Hence, on the basis of these characteristic time-scales, we observe that thermal transport is too slow, compared to mass transport, to have any significance on the physical interpretation of the data. Thus, for the purpose of validating the experimental data, permeability is the limiting factor affecting vapor transport, and we can thus apply our simplified model.

We will use the experimentally determined temperature distribution as an input for the simplified model. Combining this with the experimentally determined permeability at room temperature (see Table 2), we can now simulate the front positions as a function of time using this model. The results of these simulations for both RC and LCC Fume are given in Figure 5A,C by a gray solid line. As can be seen, only in the case of LCC Fume is the simulation able to reasonably describe the experimental data. This is most probably due to the fact that we have used the permeability as determined at room temperature.

Therefore, we chose to use the high-temperature permeability k as a fitting parameter to our experimental data. The simulations based on the best fitted permeabilities are indicated by the black solid lines in Figure 5A,C. As can be observed in this case, the simplified model is able to describe

FIGURE 7 A plot of the ratio of the characteristic time-scales of thermal diffusivity and vapor mass flux as a function of the typical boiling front vapor pressure for regular castables (RC) and low-cement castable (LCC) fume

TABLE 4 Material properties for regular castables (RC) and low-cement castables (LCC) Fume used to calculate the transport time-scales of thermal diffusivity and vapor mass-flux

Material properties	RC	LCC fume A
Permeability (m ²)	1.33×10 ⁻¹⁶	7.30×10 ⁻¹⁷
Density (kg/m ³)	2850	3157
Thermal conductivity (W/m•K)	2.77	4
Vapor pressure range (MPa)	0.1-0.5	1-4
Specific heat capacity (J/kg•K)	900	900

FIGURE 8 The measured moisture and temperature profiles for the different materials considered cured for 24 and 48 hours: (A) LCC (B) LCC Fume A (C) LCC Fume B and (D) NCC. The dashed line in the middle of the figures corresponds to the critical moisture content and the solid line at the bottom indicates the moisture background level. For each material the time between the measurement of two subsequent profiles is indicated

the drying behavior more accurately than before, that is, using the room temperature-based permeability.

By comparing the permeability as determined by fitting the simplified model to the data with the permeability determined at room temperature, we observe that there is a twofold difference ($k_{2,\text{fit}} = 3.5 \times 10^{-17} \text{ m}^2$, $k_{2,20^\circ\text{C}} = 7.3 \times 10^{-17} \text{ m}^2$) for LCC Fume and a 15-fold difference ($k_{1,\text{fit}} = 2 \times 10^{-15} \text{ m}^2$, $k_{1,20^\circ\text{C}} = 1.33 \times 10^{-16} \text{ m}^2$) for RC. This permeability is a direct reflection of the boiling front speeds of both materials where RC travels through the sample 50%-70% faster than the LCC Fume A.

The most plausible explanation for this discrepancy in the experimental and fitted values of the permeability is that the materials were dried at 110°C for 24 hours before the measurements were carried out at room temperature via the Air Permeability Test. As already reported in a previous study,⁹ the pore system of RC undergoes structural transformation

from 20°C to 110°C . This means that over the course of 24 hours the pore network has changed. In fact, after 110°C the sample mass has slightly decreased as a result of the 24-hour thermal treatment process, indicating moisture loss. Finally, the permeability is measured at room temperature which therefore cannot capture the high-temperature effects taking place throughout an actual first-drying experiment.^{21,22} In this sense, the simplified model results more accurately capture the reality of the pore structure than room temperature measurements. As such, the experimentally determined permeability at room temperature should be taken with caution.

It should be mentioned that the pore size distribution of castables is expected to change, thereby transforming the permeability as a function of time and temperature. However, assuming a constant permeability over the narrow temperature range of 100°C - 200°C still yields a quantitatively reasonable

FIGURE 9 The boiling front position as determined from the measured moisture profiles as a function of time (A) and the boiling front temperature as determined from the measured temperature and moisture profiles as a function of time (B) for all the materials from Figure 8 (A-D). The solid lines running through (B) are the fitted permeabilities of different material families, with associated fitted values of k_1 , k_2 , k_3 , and k_4

fit of the model to our data for different materials. Therefore, in a first-order approximation, the effects of a dynamic permeability are insignificant to the validation of our experimental data in this temperature range.

5 | DRYING BEHAVIOUR OF CASTABLES: RESULTS AND DISCUSSION

The measured moisture and temperature profiles of all other materials tested, that is, LCC and NCC (also see Table 1), subjected to the same heating program are shown in Figure 8.

The time-scale of these experiments is 2-3 hours. Regardless of material choice, the saturation profiles display similar behavior to RC at the end of the experiment, where a small, residual moisture quantity remains indicating that moisture is still trapped in the small pores.

In the case of LCC/NCC, we observe that the drying front does not emerge until 100 minutes in the experiment have passed. At this point of time (see Figure 9), the temperature at the drying front is on the order of 150°C and continues until 200°C (and above that for NCC) corresponding to a vapor pressure of 0.5-1.5 MPa. For LCC Fume A and B, the starting and maximum front temperatures reached are close to 200°C and 250°C corresponding to a vapor pressure of 1.5-4.0 MPa, respectively. Furthermore, the drying front does not appear until about 100 minutes have passed. These maximum saturated vapor pressures of the front are almost eight times higher than that of RC.

The slowest drying behavior is observed for NCC cured for 48 hours. For this material, it takes 5 full hours before the sample completely dries out, in comparison to the RC, NCC 24 hours and LCC systems. It should be mentioned that the heating for NCC 48 hours was not switched on for the first hour of the experiment. Furthermore, while the drying of the other NCC/LCC materials does not generate an initial moisture content that rises above 1, as we saw in the case of RC, it is seen with NCC cured 48 hours that the initial moisture content does indeed rise above 1 after the heat is turned on. As a note of consideration, this particular material is unique in the sense that it uses a noncementitious alaphabond binder, which has entirely different bonding phases than CAC.

Finally with LCC/NCC, it is also observed that the moisture is decreasing at the back of the sample, which is not seen in the case of RC. This moisture decrease at the back of the sample correlates with the low-permeability, high-front temperature matrix systems, that is, all except RC. Since a low permeability is related to the higher front temperature, it means that the vapor pressure will also be higher. It must be emphasized that the no-flux boundary condition at the back of the sample still remains unviolated and the decreasing moisture content does not corrupt our analysis of quantitative differences in the drying behavior between different materials.

However, although differences can be observed from one material to another, it is difficult to compare all the drying experiments for the various materials. But, as shown in Figure 9, the drying behavior can be characterized by considering both the front positions and the front temperatures as a function of time. As can be seen, there are some common features displayed by the drying behavior of most materials. Firstly, the drying front speed is approximately linear, regardless of material choice. The slope of this front is related to the high-temperature vapor permeability, as already discussed in the previous section according to the simple model. Secondly, it is seen that

all materials (with exception to NCC cured for 48 hours) have similar drying front speeds to the first-order approximation (also see Table 2). Thirdly, if the front temperatures for various materials are combined into one figure, thereby reflecting the vapor pressure as a function of temperature, the materials can be grouped into roughly three families in order of increasing starting front temperature: (A) RC at 120°C (B) LCC/NCC at 150°C and (C) LCC Fume A and B at 170°C–200°C.

By again employing the simplified vapor transport model, the drying behavior of these families of materials can be related with the high-temperature vapor permeability. The four solid lines given in Figure 9B provide the fitted permeability for these three families of materials, indicating similar drying behavior for that group independent of the material in consideration. In the first case of family A (k_1), RC displays the lowest drying front temperature, 120°C corresponding to the highest permeability on the order of 10^{-15} m^2 . In the second case of family B (k_2), the materials LCC (24 and 48 hours) and NCC (24 hours) display intermediate drying front temperatures of 150°C with all permeabilities on the order of 10^{-16} m^2 . Finally, for family C (k_3) Fume-containing LCC materials (24 and 48 hours) display the highest drying front temperature, 170°C–200°C, in comparison to families A and B, with a permeability on the order of 10^{-17} m^2 . While NCC cured for 48 hours has a similar starting front temperature as NCC cured 24 hours, it, however, has two times slower front speed and thus a permeability on the order of 10^{-18} m^2 . Therefore, it is the only outlier case (k_4) that lies outside the permeability families A–C.

It can be gathered from the experimental results in Figure 9 that the drying front speed is approximately the same for all materials (except NCC cured 48 hours), as shown in Figure 9A. Looking further, each family of materials is characterized according to a common start of drying front temperature. Furthermore, while each family has a characteristic fitted permeability, it is observed that there can be an exceptional case in which a material within a family has a unique permeability that is uncommon to the other materials of the same family, that is, NCC cured for 48 hours. In terms of pressure this means that NCC cured for 48 hours will have the same front temperature and vapor pressure as the materials from family set B, but a lower permeability. Therefore, release of pressurized steam toward the surface will be a relatively slower process than for other materials in the same family. With family C (LCC Fume), it has the second lowest permeability of all materials and displays the highest front temperature and pressure, that is, on the order of 4 MPa.

6 | CONCLUSION

In this study, the results for an experimental investigation into the drying behavior of different calcium aluminate cement and

hydratable alumina-bonded castables have been presented. It has been shown that a specialized high-temperature NMR setup is capable of directly and nondestructively measuring the moisture profiles along with temperature profiles during a first-drying experiment, where the samples can reach temperatures as high as 250°C–300°C. The measured moisture profiles gathered from the NMR data, in conjunction with the temperature profiles for different materials, provide direct information on the drying front speed and front temperature.

Two primary features are gathered from the analysis of the profiles. First, all materials display a linear drying front speed, regardless of differences in drying behavior for various material compositions. The linear functional form of this drying behavior can possibly be related to the evolution of the moisture diffusivity parameter that appears in analytic models for the nonlinear drying problem.^{23,24}

In order to further interpret this drying front behavior, a simple vapor transport model demonstrates that the boiling front behavior is closely related to the high-temperature vapor permeability; the high permeability corresponds with a low front temperature, where low permeability materials display high front temperatures. The assumption in this simple model is that pressure-driven flow is the main transport mechanism for vapor.

Based on the drying front temperatures, the materials can be grouped into different families. Additionally, on the basis of the simple model a fitted permeability can be assigned to these different families of materials: (A) RC at 120°C (B) LCC/NCC at 150°C and (C) LCC Fume A and B at 170°C–200°C, with A–C in increasing order of front temperature and decreasing order of permeability, with exception to NCC cured for 48 hours which has the lowest fitted permeability of all materials. Therefore, the LCC Fume family displays the highest front temperature and vapor pressure. This simple model is unique in the sense that only one free parameter is required, with k being the permeability. Here it is found that the fitted results justify the simple model, where the first-order approximation is quite valid in the regime of vapor transport.

However, there is still one outlier case which does not depend on the fitted permeability alone, that is the exceptionally slow drying of NCC 48 hours. This material has a boiling front temperature range which is within the 150°C family of materials, even though the fitted permeability is more reflective of the 200°C family. Here it has to be taken into account that curing NCC for 48 hours will slow the progression of the boiling front position. Therefore, everything else being equal, adjusting both k and du/dt will determine the correct drying front temperature.

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ORCID

Ahmed J. Barakat <https://orcid.org/0000-0002-5921-9723>

REFERENCES

- Spink J. A review of explosive spalling of castable materials. *Refract Eng*. 2014;13–7.
- Cardoso FA, Innocentini MD, Akiyoshi MM, Pandolfelli VC. Effect of curing time on the properties of CAC bonded refractory castables. *J Eur Ceram Soc*. 2004;24(7):2073–8.
- Da Luz AP, Braulio M, Pandolfelli VC. Refractory castable engineering. Baden-Baden & Karlsruhe: Federation for International Refractory Research and Education & Goller Verlag. 2015;320–73.
- Cardoso FA, Innocentini MD, Miranda MF, Valenzuela FA, Pandolfelli VC. Drying behavior of hydratable alumina-bonded refractory castables. *J Eur Ceram Soc*. 2004;24(5):797–802.
- Lee W, Vieira W, Zhang S, Ahari K, Sarpoolaky H, Parr C. Castable refractory concretes. *Int Mater Rev*. 2001;46(3):145–67.
- Valentin O, Nazaret F. Industrial simulation for pore pressure prediction during the first drying of refractory castables. In: 57th International Colloquium on Refractories. Aachen, Germany: European Center for Refractories, Höhr-Grenzhausen; 2014:58–62.
- Gawin D, Pesavento F, Schrefler BA. What physical phenomena can be neglected when modelling concrete at high temperature? A comparative study. Part 1: Physical phenomena and mathematical model. *Int J Solids Struct*. 2011;48(13):1927–44.
- Schrefler BA, Majorana CE, Khoury GA, Gawin D. Thermo-hydro-mechanical modelling of high performance concrete at high temperatures. *Eng Comput*. 2002;19(7):787–819.
- Barakat AJ, Pel L, Adan O. One-dimensional NMR imaging of high-temperature first-drying in monolithics. *Appl Magn Reson*. 2018;49(7):739–53.
- van der Heijden G, Huinink HP, Pel L, Kopinga K. One-dimensional scanning of moisture in heated porous building materials with NMR. *J Magn Reson*. 2011;208(2):235–42.
- van der Heijden G, van Bijnen R, Pel L, Huinink HP. Moisture transport in heated concrete, as studied by NMR, and its consequences for fire spalling. *Cement and Concrete Res*. 2007;37(6):894–901.
- Reid RC, Prausnitz JM, Poling BE. The properties of gases and liquids. 4th ed. In McGraw-Hill Inc., 1987:208–9.
- Speight JG. Formulas and Calculations for Drilling Operations. 2nd ed. Beverly, MA: Scrivener Publishing LLC, 2018; 1–72.
- Kopinga K, Pel L. One-dimensional scanning of moisture in porous materials with NMR. *Review of Scientific Instrum*. 1994;65(12):3673–81.
- Pel L, Donkers P, Kopinga K, Noijen JJ. ¹H, ²³Na and ³⁵Cl imaging in cementitious materials with NMR. *Appl Magn Reson*. 2016;47(3):265–76.
- Kockeey-Lorenz R, Buhr A, Zacherl D, Long B, Hayashi S, Dutton J. Review of matrix aluminas for refractory formulations. Kyoto: UNITECR. 2011.
- Canon J, Sander T. New test method for evaluating permeability of refractory castables. *Refract Appl*. 1997;2(1):6–7.
- Schmitt N, Hernandez JF, Lamour V, Berthaud Y, Meunier P, Poirier J. Coupling between kinetics of dehydration, physical and mechanical behaviour for high alumina castable. *Cement and Concrete Res*. 2000;30(10):1597–607.
- dos Santos W. Effect of moisture and porosity on the thermal properties of a conventional refractory concrete. *J Eur Ceram Soc*. 2003;23(5):745–55.
- Routschka G. Thermal conductivity of refractory castables. *Interceram*. 1988;37:1–6.
- Ribeiro C, Innocentini M, Pandolfelli VC. Dynamic permeability behavior during drying of refractory castables based on calcium-free alumina binders. *J Am Ceram Soc*. 2001;84(1):248–50.
- Innocentini MDM, Silva MG, Menegazzo BA, Pandolfelli VC. Permeability of refractory castables at high temperatures. *J Am Ceram Soc*. 2001;84(3):645–7.
- Landman KA, Pel L, Kaasschieter EF. Analytic modelling of drying of porous materials. *Math Eng Industry*. 2001;8(2):89–122.
- Pel L, Landman KA, Kaasschieter EF. Analytic solution for the non-linear drying problem. *Int J Heat Mass Transfer*. 2002;45(15):3173–80.

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