

## Competition Between Hydration and Carbonation in Hydraulic Lime and Lime-Pozzolana Mortars

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**Abstract** A combined reaction of hydration and carbonation takes place in hydraulic lime and lime-pozzolana mortars. Hydration reactions are the first reaction and carbonation of lime is the complementary reaction in the strength gain. Competition between these two reactions can occur in lime-pozzolana mortars if the pozzolanic material has low reactivity with lime, leading to the consumption of lime by carbonation reaction. The degree and the order of these reactions are strongly influenced by the moisture content. Hydration reactions are enhanced under moist conditions while carbonation is delayed. Curing under dry conditions does not sufficiently increase their strength because the hydration reactions are slowed down or even terminated by the full carbonation of lime in lime-pozzolana mortars. The consequence of this on the mechanical properties of the mortars is remarkable while the same impact is not observed in their porosity. Such mortars require moist conditions to ensure sufficient strength development.

**Keywords:** Lime, hydraulic lime, pozzolana, carbonation, hydration

### Introduction

The use of hydraulic lime and lime-pozzolana mortars has a prominent status in restoration works and more recently in construction practices for sustainability reasons. Little information is available on their hardening reactions composed of a combined reaction mechanism of carbonation and hydration. It has been found that calcium silicate-calcium hydroxide blended compositions may lack long-term strength development due to the order of these two reactions influencing each other (Van Rickstal et al. 2003, Cizer et al. 2009). This can cause negative consequences for the long-term durability and safety of the structures. Therefore, special attention should be paid to the combined hardening process of carbonation and hydration for a better understanding of the hardened mortar properties.

Hardening of hydraulic lime occurs by hydration of calcium silicates (mainly belite) and calcium aluminates, which is very similar to cement hydration. If free calcium hydroxide is available in the composition, carbonation will take place as well as the secondary reaction. Hydration of hydraulic lime proceeds slower than the fast hydration of cement due to the slow reaction kinetics of belite phase. Therefore, hydraulic lime mortars take longer than cement mortars to achieve mechanical strength.

In lime-pozzolana blends, pozzolanic reaction between pozzolanic material and lime, and carbonation of lime will be responsible for the hardening reactions. The degree and the order of these two reactions will depend on the binder composition, pozzolanic reactivity of the material and curing conditions. Besides, the degree of pozzolanic reactions will be affected by the carbonation reaction because part of the lime will be consumed by this reaction. This may influence the mechanical properties and the porosity of the mortars. These issues will be highlighted in this article in which the hardening reactions of the hydraulic lime and lime-pozzolana mortars are studied under various curing conditions promoting either or both hydration and carbonation reactions. The results extracted from a dedicated work will be summarized and discussed (Cizer 2009).

## Research programme

**Mortar compositions and curing conditions** Commercial lime hydrate (LH), and metakaolin (MK) and Rheinisch trass (RT) as the pozzolanic materials were used to prepare lime-pozzolan mortars. Two types of natural hydraulic lime (HL1 and HL2) in class NHL2 having different mineral compositions were considered to produce hydraulic lime mortars. These mortars were prepared in 1:4 binder to sand ratio by mass using sand with maximum grain size of 2 mm. Lime to pozzolana ratio is 1:1 by mass. Similar flow table values (preEN 1015-3) were considered to achieve similar fresh mortar properties.

Three different curing conditions were adopted: dry curing (20°C, 60% RH), moist curing (20°C, ~93% RH) and competitive curing (5% [CO<sub>2</sub>] at ~25°C, ~92% RH). Dry curing is in favour of carbonation reaction while moist curing is to promote hydration reactions. Competitive curing conditions intend to create conditions under which both carbonation and hydration reactions are enhanced in a CO<sub>2</sub> incubator with CO<sub>2</sub> concentration at 5% by volume and with controlled relative humidity at 85-90% using saturated KCl solution.

*Table 1: Composition of hydraulic lime and lime-pozzolana mortars*

<i>Mortar ID</i>	<i>Mortar type</i>	<i>Binder/sand</i>	<i>Water/binder</i>	<i>Flow value (mm)</i>
HL1	Hydraulic lime	1:4	0.77	120
HL2	Hydraulic lime	1:4	0.56	120
L-MK	Lime-pozzolana	1:4	1.11	121
L-RT	Lime-pozzolana	1:4	0.70	122

**Testing and analytical methods** Hardening of the mortars was studied using standard mortar prisms (40×40×160mm) prepared in accordance with EN 196-1. Flexural strength tests were carried out using these mortar prisms at 14, 28, 60, 90 and 180 days of hardening. The progress of hardening was studied by means of thermal analysis. The mortar specimens were gently ground in order to separate sand grains from the binder fraction and then vacuum dried at 0.025 mbar for 2 hours. Subsequently, the sample was sieved through 112 µm sieve to obtain the finest fraction rich in binder. This fraction was further subjected to thermogravimetric analysis using a Netzsch STA 409 PC DSC-TGA system in static nitrogen atmosphere at a temperature range between 20-1000°C with a controlled heating rate 10°C/min. open porosity of the mortars was determined by hydrostatical weighing.

## Results and discussion

The first derivative of the thermogravimetric analysis (DTG) shows the progress of hydration and carbonation reactions qualitatively. Three major peak areas are observed in the thermographs (Fig. 1). The first one at 100-250°C originates from dehydration of the hydrated phases. The second peak observed at ~480°C indicates decomposition of calcium hydroxide. The third peak area at 600-800°C is due to decomposition of the calcium carbonate formed by carbonation reaction.

The degree of hydration and carbonation reactions is very much influenced by the moisture content. Mortars cured under dry conditions indicate lower degree of the hydration reactions due to low moisture content (60%). Such conditions are more in favour of carbonation reaction by creating an ideal situation where the pores are partly filled with water, making both diffusion and dissolution of carbon dioxide possible (Van Balen 1991, Saetta et al. 1995). Even so the carbonation reaction proceeds gradually from 28 days up to 180 days as seen with HL1 and L-RT mortars with a gradual decrease in the calcium hydroxide peak at ~455°C in time.

In L-MK mortar, pozzolanic reactions under dry and moist conditions have progressed markedly within 14 days. The formation of C-S-H and AFm phases is observed with sharp peaks at ~100°C and at ~150°C respectively. A shoulder at ~230°C indicates the presence of strätlingite. Traces of calcium hydroxide at 14 days are hardly seen with a small peak at ~430°C, indicating its rapid consumption by

pozzolanic reaction and therefore high reactivity of metakaolin with lime. Pozzolanic reactions in L-RT mortar proceed more gradually, indicating lower pozzolanic activity of trass.

A remarkable difference in the degree of the pozzolanic reactions and carbonation reaction under dry and moist conditions is established. Carbonation reaction is delayed and pozzolanic reactions are enhanced under moist conditions, as seen with an increase in the intensity of the peaks of the hydration products in L-MK and L-RT mortars. In particular the peak corresponding to strätlingite phase at  $\sim 230^\circ\text{C}$  is more pronounced in L-MK mortar. Long-term progress of phase formations in lime-metakaolin pastes has indicated that the formation of strätlingite is favoured at high moisture level after 3 days as a result of an interaction of the C-S-H with alumina remaining unreacted in the system (Fig. 3). This is in agreement with the results of Jambor (1963). This interaction, destroying the C-S-H phase, is assumed to be responsible for the strength reduction after 28 days as seen in Fig. 2. The formation of strätlingite in hydrated high-alumina cement with the addition of silica is known to be in favour of strength but the phenomenon taking place is completely different because strätlingite is formed due to an interaction of hydrogarnet phase with silica (Ding et al. 1995). Despite this reduction, the flexural strength of L-MK mortar is improved under moist conditions when compared to dry conditions (Table 2). The flexural strength values of the L-RT, HL1 and HL2 mortars are almost doubled under moist conditions despite no considerable difference in their porosity. This clearly shows that the role of the hydrated phases on the mechanical properties of these mortars is more pronounced than the calcium carbonate phases. Fast evaporation of the water in hydraulic lime and lime-pozzolana mortars should be avoided by keeping them moist at least during 28 days to improve the hydration reactions and to assure sufficient strength development (Cizer 2009).

Pozzolanic reactions in L-RT mortar are affected by the carbonation of lime due to the low pozzolanic reactivity of trass. Pozzolanic reactions prevail within 14 days under dry conditions and within 28 days under moist conditions while it is the carbonation of lime that prevails afterwards. This shows a competitive reaction order starting first with the pozzolanic reactions but prevailing with the carbonation reaction afterwards. Therefore, consumption of lime by carbonation reaction lowers the degree of the pozzolanic reactions in the L-RT mortar. Due to the high pozzolanic reactivity of metakaolin, pozzolanic reaction dominates carbonation reaction independent from curing conditions. Therefore, any competition between the pozzolanic reactions and carbonation reaction does not occur. In hydraulic lime mortars, hydration reactions and carbonation of lime occur independent from each other without causing a competitive reaction order.

The order of the hydration and carbonation reactions in the mortars is altered under competitive curing conditions. It is the hydration reactions occurring in the first place but the carbonation reaction prevails afterwards by attacking not only lime but also the hydrated phases leading to their decalcification (Fig. 1). This has induced significant modification of the microstructure of the mortars with the formation of calcium carbonate as calcite and aragonite (Cizer 2009). As a consequence, the strength of the mortars has markedly decreased even though their porosity is lowered with the precipitation of calcium carbonate crystals. Note that competitive curing conditions used here are not realistic due to the  $\text{CO}_2$  level which is extremely higher than the one in air ( $\sim 0.03\%$ ). Nevertheless, accelerated carbonation conditions are often used in lime mortar research.

*Table 2: Open porosity (%) of the mortars cured under dry and moist at 180 days, and under competitive conditions at 90 days*

	<i>HL1</i>	<i>HL2</i>	<i>L-MK</i>	<i>L-RT</i>
Dry curing	30.32	31.00	33.77	26.37
Moist curing	28.79	30.93	33.02	26.67
Competitive curing	26.11	28.66	30.01	21.01

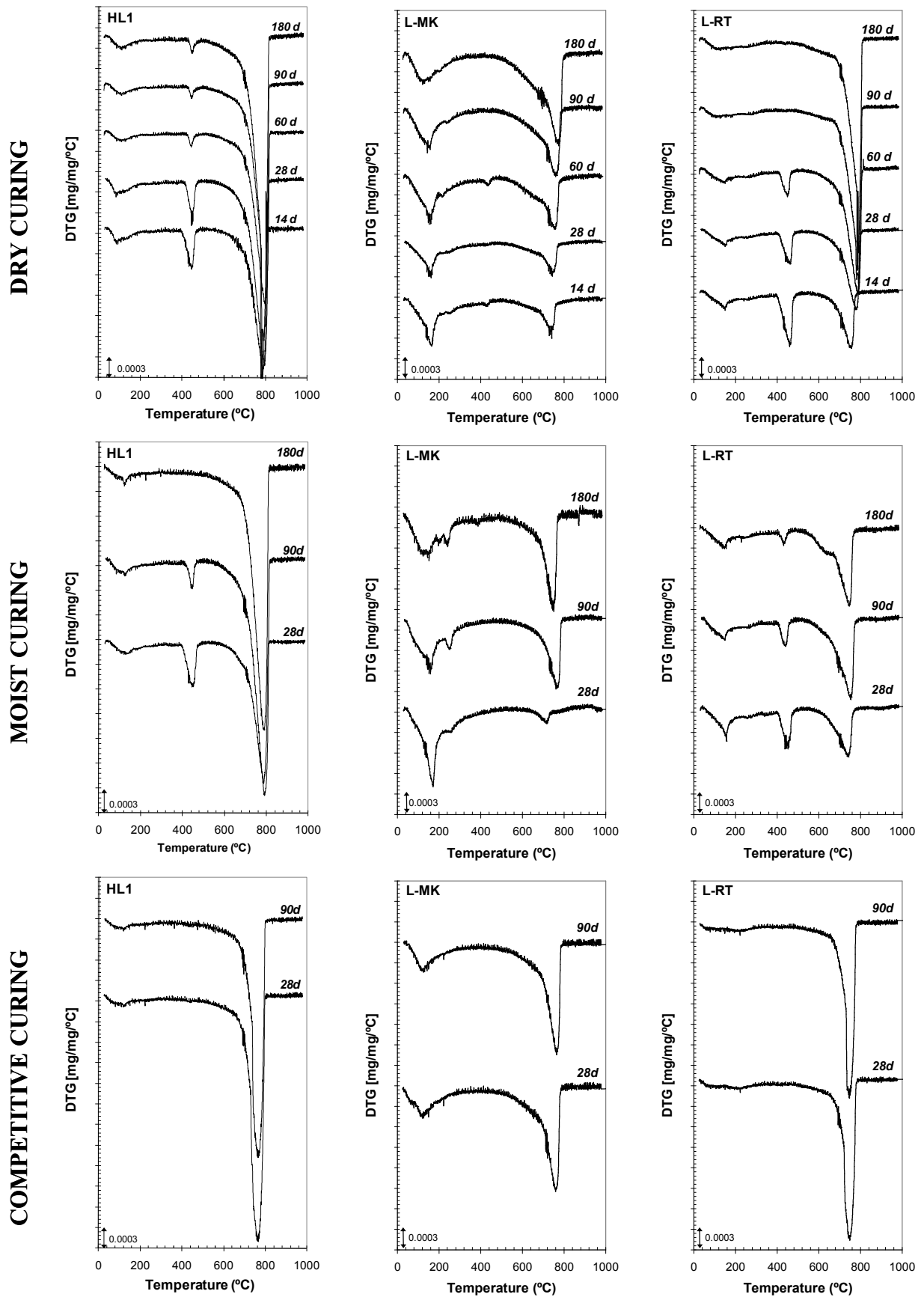


Figure 1: DTG graphs of lime mortars show the progress of hydration and carbonation reactions under dry, moist and competitive (in CO<sub>2</sub>) curing conditions

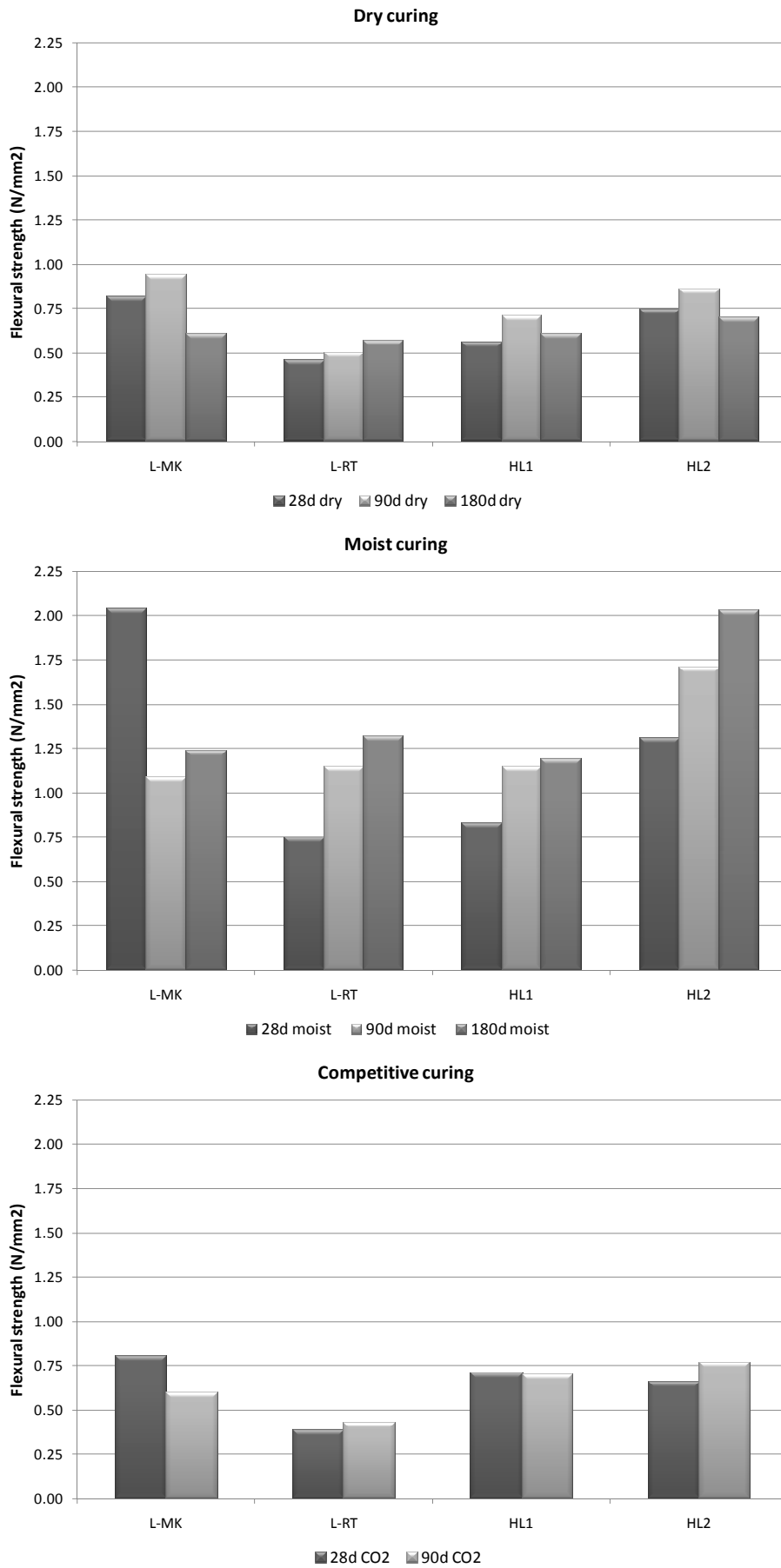


Figure 2: Flexural strength of the mortars under dry, moist and competitive conditions

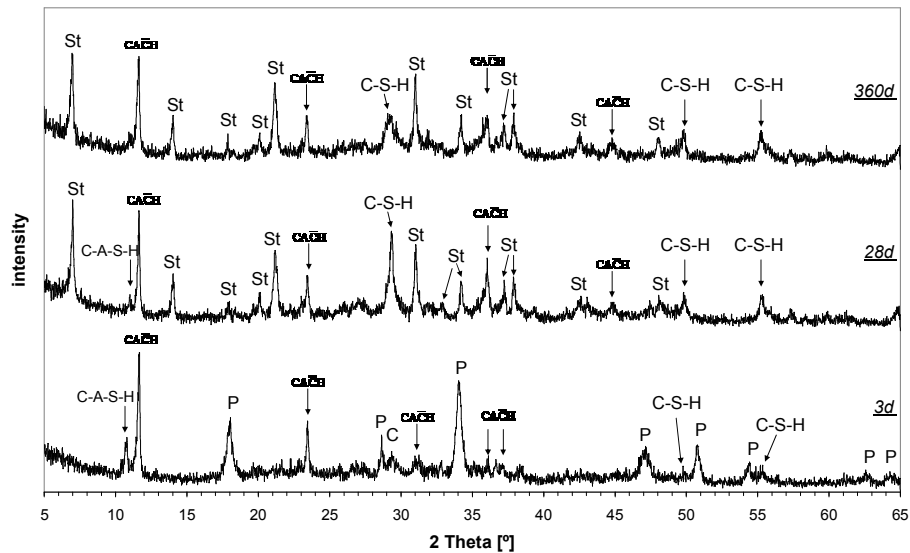


Figure 3: XRD patterns of the hydrated lime-metakaolin paste at 3, 28 and 360 days: C= calcite; P= portlandite; St= strätlingite; C-S-H= calcium silicate hydrate; CĀCH = calcium alumina carbonate hydrate

## Conclusions

Competition between carbonation and hydration can take place in lime-pozzolana mortars under atmospheric conditions if the pozzolanic material has low reactivity with lime. Highly reactive pozzolanic material like metakaolin may not provide sufficient strength development to the mortar due to phase modifications. It is the hydrated phases and their stability, which are crucial for the achievement of sufficient strength. The degree and the order of hydration and carbonation reactions are strongly influenced by the moisture content. Due to the gradual progress of the hydration reactions, hydraulic lime and lime-pozzolana mortars require moist conditions to ensure sufficient strength development. Curing under dry conditions does not sufficiently increase their strength because the hydration reactions are slowed down or even terminated by the full carbonation of lime in lime-pozzolana mortars. Therefore, hydraulic lime and lime-pozzolana mortars should be treated with moist curing during early stages to improve the hydration reactions.

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