Development of a Small-Scale Lime Kiln and Experimental Assessment of the Produced Quicklime

Jan Válek, O. Skružná, V. Petráňová, D. Frankeová and J. Jiroušek

Abstract A small-scale lime kiln was designed and built in order to evaluate lime binders produced in the past. The design does not copy any specific historic model but it is made to replicate two main historic procedures: intermittent wood and mixed-feed burnings. The prototype is equipped with sensors and the burning process is monitored by a set of thermocouples in three height levels, an air flow gauge on the primary air inlet and a gas analyser of fumes (CO, CO_2 and O_2) passing through a chimney. The obtained data are used for an assessment of the whole burning process and its optimisation. The paper presents data about four experimental wood burnings of air lime and summaries the newly gained experience regarding the operation of the kiln. In order to assess the quality of the produced lime several samples of quicklime were taken from three main positions according to heat distribution in the kiln. These samples were analysed and compared with samples obtained from five different modern industrial shaft kilns which use oil, gas and coal as fuel. The micro-structure of quicklimes was evaluated focusing on the influence of calcination temperature and its duration. SEM, MIP and BET analyses were used to evaluate the morphology, size of crystallites, porosity, pore size distribution and surface area of the produced quicklimes. The obtained characteristics were compared to the reactivity of lime and the quality of the products was discussed.

J. Válek (✉) · O. Skružná · V. Petráňová · D. Frankeová · J. Jiroušek
The Czech Academy of Sciences, Institute of Theoretical and Applied Mechanics, Prosecká 76, 190 00 Prague 9, Czech Republic
e-mail: valek@itam.cas.cz

O. Skružná
e-mail: skuzna@itam.cas.cz

V. Petráňová
e-mail: petranova@itam.cas.cz

D. Frankeová
e-mail: frankeova@itam.cas.cz

J. Jiroušek
e-mail: jjirousek@itam.cas.cz

1   Introduction

Traditional lime burning is not a uniform technology and many historic methods exist. A typical example of traditional lime production is burning in a flare kiln. A common construction method for burning in a flare kiln is that a rough vaulted dome is built from larger pieces of limestone creating a combustion chamber. Smaller fragments of limestone are placed above the dome in sizes respecting assumed heat distribution within the kiln space. This way of lime burning is known since the Roman period (Adam 1994) and is technologically connected with the use of long flame burning fuels; the most widespread being wood. Wood-fired kilns were originally used for lime burning in many European countries and in less populated and developed regions with sufficiency of wood they survived up to the mid-19th century. About this time lime production technology started to become industrialised and only exceptional cases of traditional lime burning in flare kilns survived until today. In some places with a lack of firewood, other fuels had to be used. Olive kernels, bushes, dried grass and pine cones were utilised in Greece, Italy and Tunisia (Adam 1994). In some areas technological progress was faster, and as lime consumption increased so did the demands on its production, which required an ever-increasing quantity of fuel. Wood soon became scarce in these areas and the lime industry had to adapt to the use of coal, which impacted on the established technologies. Lime kilns using coal as fuel had to be adapted to the different operation modes and over time they gradually developed further and transformed from periodic to continuous operations. The use of coal or charcoal for lime burning is known from London, where the nuisance of smoke from coal burning was already noted as a problem in the early 14th century (Bowyer 1973).

Traditional lime burning is supposed to affect the final product. Hughes et al. (2002) concludes that lime burnt in an experimental mixed feed vertical shaft kiln is a different product in comparison with commercial product from the same raw material. Advantage of burning in a flare kiln is the separation of fuel from the charge. Wingate (1985) suggests that wood firing could produce some of the best quality lime. Also Eckel (2005) mentions, that lime is more evenly burnt and whiter when burnt separated from the charge. This suggests that lime burnt in a traditional flare kiln has a potential to be a high quality product. On contrary, there are some drawbacks when lime is burnt in a flare kiln. Eckel (2005) points out that stone nearest to the dome is liable to be overburnt (hard burnt and sintered).

Quicklime is divided into three categories according to the degree of burning: soft, medium and hard burnt. The bulk density of lime increases from approximately 1.5 g/cm^3 (soft) to over 2.1 g/cm^3 (hard) and reactivity (t_{60}) decreases from

<3 min for soft lime to >9 min for hard burnt lime (Oates 1998). Sintering of lime starts on its surface and is caused by calcination at high temperatures and prolonged residence time. Sintering of quicklime has a negative effect on its reactivity. In the case of large pieces in the dome it is a question whether sintering takes place on the sides even though the core is not fully dissociated or not. A complementary question is about the relation of the size of stone and the progress of the sintering. The liability to sintering also depends on limestone parameters and composition. Limestone with an extremely small portion of impurities exhibits high hard burn potential, i.e. is liable to sintering (Hogewoning 2008a). According to Hogewoning (2008b), sintering potential of limestone can be divided in three groups on the basis of Lime Saturation Factor (LSFII), expressed as the ratio of CaO to the amount of CaO that can be combined with impurities present in limestone, see formula (1).

$$LSFII = \frac{CaO \times 100}{(2.8 \times SiO_2) + (1.18 \times Al_2O_3) + (0.65 \times Fe_2O_3)} \tag{1}$$

Tests on quicklime are usually carried out as a quality control assessing the suitability of a product and monitoring its compliance with a specification, e.g. European standard EN 459. For building limes fineness, reactivity, yield and bulk density are the typical tests. Very important part of testing and interpretation of the test results is sampling process. The quality of quicklime is influenced by the composition of the raw material and the production process as mentioned before. Obtaining a representative sample is therefore important when two different products are to be compared. In addition to this, storing and handling quicklime can also affect the test results. Negative effects of absorption of water (air slaking) and CO_2 (carbonation) on reactivity of lime are known (Oates 1998) and these two parameters should be determined and checked when samples of quicklime are tested.

2 Design and Development of a Small Scale Lime Kiln

The experimental lime kiln, shown on Fig. 1, was built to investigate the influences of traditional burning on the quality of lime and for the production and subsequent research of lime binders made with historically used raw materials (Válek 2015). In addition to the research reasons, it was constructed as a prototype enabling small-scale production of lime binders by traditional methods. A single batch wood-fired burning of limestone can be replicated in the kiln—this is what it was designed for—but the kiln can also be used to burn limestone in a mixture with fuel, known as mixed feed burning. Other elements of the design satisfied requirements for the durability of the kiln and ease and safety of operation.

Fig. 1 Prototype of a lime kiln

2.1 Construction

The actual kiln design is shown in Fig. 2. It consists of a cylindrical shaft with an inner diameter of 0.8 m and a height of 1.3 m above a cast-iron grate. The inner walling is made of refractory circle bricks on clay mortar. The brick cylinder is sheathed in a 50 mm layer of heat-resistant mineral wool insulation. On the outside, the kiln is enclosed by vertical timber boarding. The space between the exterior wooden shell and the insulation is filled with crushed limestone grit with grains fraction 0/4 mm. Air is fed into the kiln primarily through an inlet measuring 20×20 cm and passing through the ash pit and the grate. A secondary air inlet is situated in the burning chamber door. The crown of the kiln is formed of a 60 mm thick cast-concrete slab made of natural cement and gravel. The slab is cut into segments allowing its thermal expansion and the segments can be removed for inspection of the backfilling. A conical hood with flue can be optionally fitted onto the kiln to monitor combustion products and regulate the draught. The draught can be also regulated by opening or closing two main air inlets.

Fig. 2 Cross section of the lime kiln prototype
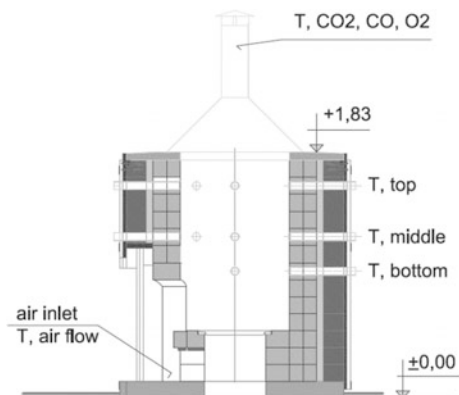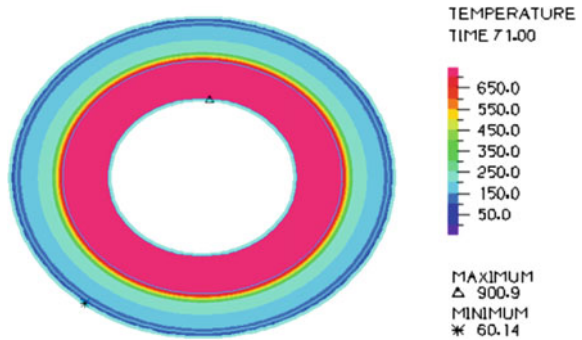
Fig. 3 Model of a
temperature transport through
a kiln wall

The kiln is designed and constructed using materials and technologies that can be regarded as generally available and which copy the traditional design in some points, e.g. bricks are laid on clay mortar, backfill is used as an elastic layer allowing expansion and movements of the inner walling. In order to decide about the insertion of a thermal insulation a model of temperature distribution in a kiln wall after 50 h of heating to 950 °C was computed, see Fig. 3. The effect of thermal insulation is clearly visible reducing the temperature by 200 °C. The model also predicted the maximum temperature on the external surface of the kiln. This confirmed the possibility to use timber boarding and provided information regarding the safety during operation. In practice, the burning lasts shorter time and the external surface does not reach temperatures higher than 35 °C.

2.2 Monitoring

Monitoring of the burning process was introduced for the evaluation of the kiln design and its operational modes. Heat distribution in the kiln can be monitored during the whole process with the aid of S-type thermocouples that are inserted into the built-in protection sleeves in three horizontal profiles and three vertical cross-sectional axes, see Fig. 4. The temperatures are usually monitored around the perimeter of the shaft, but the temperature profile from the middle to the perimeter can also be determined in three selected sleeve positions. This is enabled by insertion of an additional protection sleeve made of heat resistant steel (DIN X10CrAlSi25, grade 1.4762) with openings (four 12 mm holes drilled across diameter and placed 100 mm apart). Moving a thermocouple inside this sleeve allows measurements of temperatures in a horizontal profile within the kilns space in 100 mm steps. Emission gasses and the calcination process is monitored by an
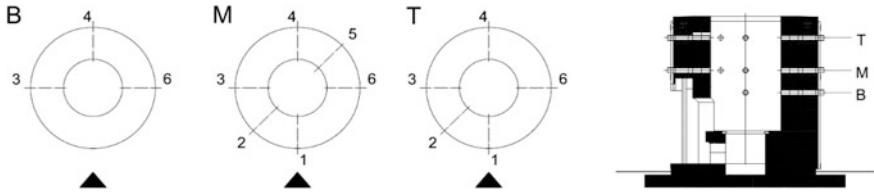
Fig. 4 Positions of kiln wall bushings for thermocouples' placements. Three horizontal levels are coded B—bottom, M—medium, T—top, the vertical profiles are numbered

MRU gas analyser Optima 7 with IR CO_2 sensor and O_2 and CO electrochemical sensors. In addition, the airflow velocity at the primary air inlet and the temperature, relative humidity and atmospheric pressure of the surrounding environment can be monitored. This relatively extensive monitoring is undertaken in order to describe the calcination processes and allow a subsequent optimisation of this process using known traditional measures, e.g. covering the top of the kiln with daub, draught regulation, insertion of stakes, etc.).

2.3 Filling the Kiln for Wood-Fired Burning

The first step is to build a vaulted dome. The internal space under the dome is the burning chamber and the dome holds all limestone feedstock above it. In many ways its proper construction is key for the successful burning. It is typically built from relatively large angular sharp-edged limestone pieces that have a good grip and also irregular surface that allows air, fumes and flames passing through the voids it creates. The stones are arranged in the vault vertically, with the narrower end at the bottom. After ensuring that the dome structure is well built and stable the rest of the kiln can be filled up with limestone to its upper rim. Altogether, just under one tonne of limestone fits in this experimental kiln. The size of the dome stones ranges from 100 to 250 mm. Then stones measuring around 80–125 mm are placed in the kiln, with fractions measuring around 20–40 mm placed in the 'cooler' areas. For this kind of calcination it is very important that the fuel burns with a long flame that passes through the entire limestone batch. When filling the kiln it is essential to know or predict areas where the heat does not spread easily by natural draught. These are usually at the base of the vault in the bottom part of the kiln, around the perimeter of the kiln and above the stoke-hole. Therefore, the batch is placed in the kiln in various sizes in a manner that corresponds to the expected spatial temperature distribution, ensuring that the burning efficiency is as high as possible. The stone should get gradually smaller from halfway up the kiln and to the sides.

2.4 Wood-Fired Burning Procedure and Variability of the Progress

The burning process follows four main stages: drying, heating, limestone decomposition and cooling. Duration of the drying stage is based on estimation and is typically a relatively short. During this first stage, the fire is kept low in order to avoid a shock heating and cracking of limestone. The aim of the second stage is to reach 900 °C within the kiln space. In average ambient conditions and stoking rate of 16 kg/h these two stages together span from 12 to 20 h (considering the kiln is fully loaded). Duration of the following decomposition stage depends on the size of charged limestone. For the stone sizes presented above minimal 12 h are allowed to ensure full decomposition of limestone. This residence time is estimated based on known tabulated values (e.g. Oates 1998). When the limestone decomposition is finished, no more fuel is added and the kiln is let to cool down. The final stage lasts approximately 24 h and lump quicklime is drawn from the kiln when temperature is below 60 °C.

Table 1 presents selected characteristics regarding the fuel consumption and environmental conditions of four experimental burnings. In order to be able to compare the burnings the following two parameters were selected: time to reach 900 °C on any of the thermocouples and fuel consumption from the beginning to the point of reaching 900 °C. A high scatter of these two parameters points at the fact that the burning process was dependent on some influential factors. Amongst them were environmental conditions and some other parameters. The ambient environment was partially monitored; other parameters like the type of wood and its moisture content were noted; but there were also other factors that were more difficult to be determined, like the way the stone pieces were placed in the kiln, or to be controlled, like the effect of wind and climatic changes.

In practice, the burning process is often related to the draught in the kiln. The higher the draught is the more intensively fuel burns and thus the calcination process progresses faster. The draught depends on the air pressure difference between the bottom (air inlet) and top (fume outlet) parts of kiln, which exists due to temperature differences and other factors. The complexity of the factors that affect the burning is illustrated by the following examples noted during the trial burnings. In the case of the second burning, the wood burnt very slowly and the draught was minimal for the first 24 h. This was possibly due to the passing thunderstorms and rapid changes in climatic conditions, like descending air currents, which affected the duration of the whole burning process and the corresponding fuel consumption per hour. On contrary, the best draught occurred during the fourth burning and that led to the intensification of burning and calcination.

For each burning the fuel consumption was driven mainly by the draught and thus the amount of oxygen which was let in by the primary and secondary inlets. For each burning condition a certain stoking pattern was established; usually 8–15 kg in a 30 min span. Figure 5 shows the fuel stoking rate during the third burning.

Table 1 Fuel consumption up to reaching 900 °C and environmental conditions of experimental burnings (*n.m.* not measured; *VT* Vitošov limestone; *CS* Koněprusy limestone)

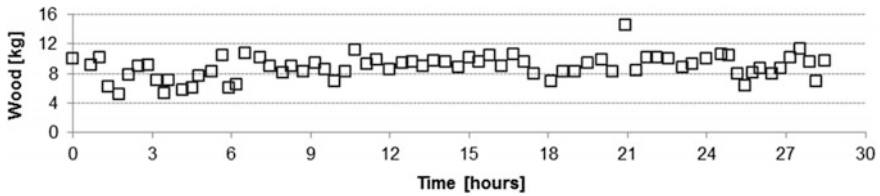| Burning | Stone | Heating to 900 °C | | | | Environmental conditions | | | | | | |
		Position	Time (h)	Wood (kg)	Wood (kg/h)	p_{atm} (Pa) @ 320 m AMSL		T (°C)		rh (%)	
						Min	Max	Min	Max	Min	Max
I	VT	M2 wall	12.7	284	22.4	97,182	97,379	11	28	27	53
II	VT	M2 wall	30	528	17.6	96,630	97,130	10	28	30	71
III	CS	T4 centre	16.8	368	22.0	n.m.	n.m.	4	22	52	72
IV	CS	M4 centre	8.8	237	26.9	98,025	98,796	6	14	66	77

Fig. 5 Fuel stoking during the third burning

The highest temperatures were reached in the centre of kiln right above the firing space. Hotter zones were also established in draught channels within the stone. These channels were typically in the centre of kiln but their position was also influenced by the wind direction, the way stone was placed in kiln and its sizes, and the way the kiln top was covered. The fume hood with a 1.5 m tall chimney was placed on the top of kiln to measure emissions and to unify the burning conditions during the experiments. The distribution of temperatures recorded during the third burning is shown in Fig. 6. All thermocouples but one (T4) were placed so that they protruded about 5 mm inwards to the kiln space. T4 was recording in the centre of the kiln and was placed in the sleeve number 4 at the top level. It should be noted that thermocouples recorded the temperature of air, not the stone, in a certain spot. The recorded value was affected by the temperature of passing air and gases, conduction of heat by the surrounding solids and radiation. The thermocouples that responded to the wood stocking by dropping and rising temperature usually showed the higher temperatures. They were influenced by passing air. On contrary, the more stable ones typically showed the lower temperatures. The thermocouples placed at the periphery of the feedstock showed the lowest temperatures within the kiln. Temperatures identified within the stone by moving thermocouples from the sides about 10 cm inwards were about 150–200 °C higher during the calcination phase. That is why almost 90% of limestone was fully calcined even though the most of the thermocouples placed on the perimeter did not reach 900 °C by the time the burring was stopped. This estimation of burning efficiency was based on weighing the stone charge before and after calcination and was also confirmed by the amount of material left on a sieve after slaking. It was also interesting to note that the highest temperature during this third burning was almost reaching 1200 °C. During the fourth burning the highest temperature reached even 1270 °C. Considering the relatively small scale of this operation, low capacity of the burning chamber and short burning times it can be suggested that in traditional wood-fired kilns temperatures around 1300 °C and possibly higher were commonly reached; although only locally in the hottest zones.

Figure 7 shows the level of oxygen, temperature of fumes and air flow velocity. All three values fluctuated due to stoking. The fumes temperature measured in the
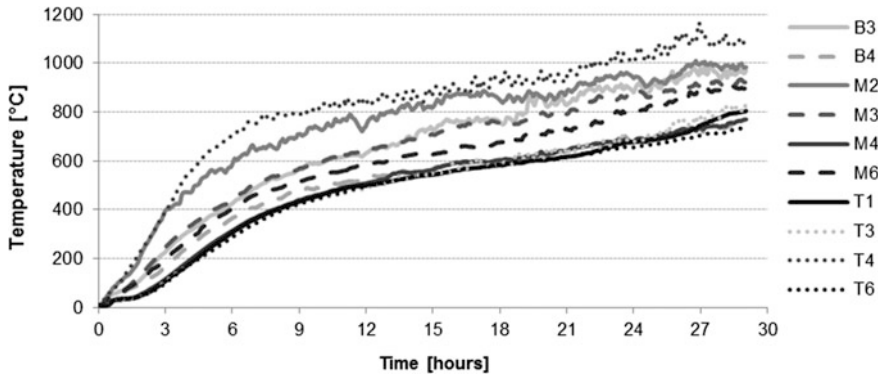
Fig. 6 Example of temperature distribution in the experimental kiln during the third burning

chimney at app. 1 m above the kiln top gradually increased and after approximately 15 h flames started to reach the thermocouple after stoking. There are visible small peaks on the temperature chart due to this effect. The level of oxygen (O_2) in the chimney also corresponded to the stoking regime. When a new fuel was added burning of released combustible gases consumed almost all oxygen. However, the monitored values demonstrate that overall wood burnt in the atmosphere with oxygen surplus. A certain balance between the primary and secondary air inlets had to be maintained to optimise the process of wood burning. The air flow values, shown in Fig. 7, were determined in the primary air inlet only and in average the flow velocity there was about 0.8 m/s through an area of 0.04 m^2. The temperature in the burning chamber as of the whole kiln also gradually increased with time and this affected the dynamics of burning.
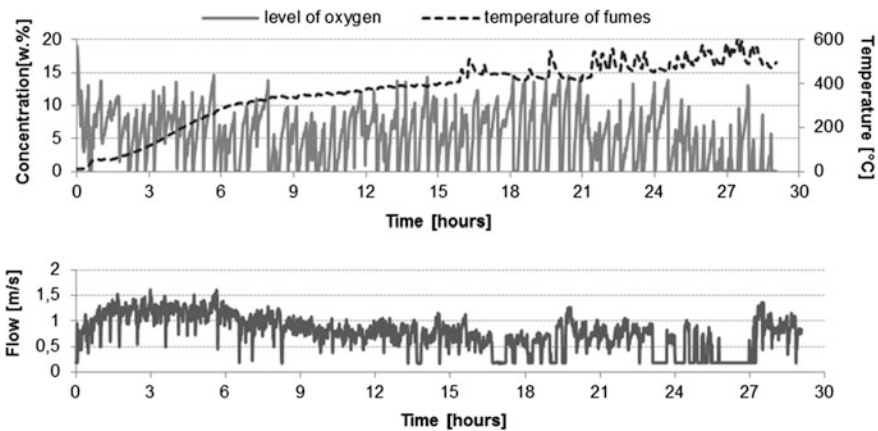

Fig. 7 Third burning. Examples of characteristics monitored during the third burning

2.5 Kiln Efficiency

Kiln efficiency and fuel cost have been always important issues for lime production. The kiln efficiency can be calculated based on formula (2) used by Practical Action (1997) advice adopted from Boynton (1980). The formula expresses the ratio between the theoretical heat required to decompose limestone and the heat provided in relation to the final quicklime (CaO) gain. The L_s value in the numerator considers chemical composition and variety of imperfections of the burning process (recarbonation, underburning etc.). In the denominator there is the total heat provided by the fuel burning.

$$E = \frac{H_c \times L_s}{C_f \times M_f} \tag{2}$$

where E is kiln efficiency; H_c is theoretical heat of calcination per tonne for pure quicklime (CaO), in this case taken as 3200 MJ/t; L_s is available CaO content in produced quicklime; C_f is calorific value of fuel (MJ/kg); and M_f is mass of fuel per tonne of quicklime (kg/t). The calorific value of wood was considered as 16.6 MJ/kg for both pine and oak, both having moisture content around 7%.

The kiln efficiency E calculated for the selected four burnings is expressed in Table 2. Available CaO content in lime was calculated from the chemical content of limestone multiplied by the burning efficiency, which was determined as a percentage ratio of achieved and expected theoretical weight losses due to calcination. Regarding the burning process, it should be mentioned that the first burning was not completely finished due to problems with the stability of the dome. The second burning was strongly affected by the adverse environmental conditions (thunderstorms). The third and fourth burnings can be considered as standard. Based on these trials the kiln efficiency ranges between 21 and 26%. A target efficiency, stated by the Practical Action Technical Brief (1997) for a forced draught vertical kiln, is 50%. The kiln efficiency value is low for single batch kilns as they operate on intermittent bases. During a traditional wood-fired periodic burning there are substantial heat losses due to the heating of the air, of which there is always an excess amount, and heating the kiln itself. Moreover, the batch burning does not allow any pre-heating of stone as is common in kilns operating in continuous modes. The calculated kiln efficiency is suitable for comparing calcinations performed in this specific kiln and can be also used for comparisons with equivalent facilities.

Table 2 Heat provided and kiln efficiency of four experimental burnings

Burning	Stone	Heat provided					Heat required to decompose $CaCO_3$						Efficiency
		Total fuel (kg)	Total duration (h)	Rate (kg/h)	Heat (MJ)		Limestone (kg)	CaO (%)	Burning efficiency (%)	Available CaO (%)	Heat (MJ)	E (%)
I	VT	397	18	22.1	6590		856	97	65	63.2	1732	26
II	VT	664	36	18.4	11,022		941	97	80	77.8	2344	21
III	CS	635	28.5	22.3	10,541		894	99	90	89.1	2549	24
IV	CS	720	27	26.7	11,952		917	99	90	89.1	2615	22

3 Experimental Assessment of Traditionally Produced Quicklime

The experimental replication of lime production in a wood-fired flare kiln was carried out at the above mentioned facility. The aim was to characterise the produced quicklime and a special focus was given to the degree of burning. The replication of traditional burning process also aimed at understanding of influences of production technology on the final product. The traditionally produced quicklimes were compared with industrially produced quicklimes. Two types of raw materials were used in the experiment and both were calcined in the traditional and industrial kilns. Each raw material calcined in the traditional and industrial kiln came from a single bench blast.

3.1 Raw Materials

Two type of high-calcium limestones were selected for the experiment. Vitošov (Vit) was a finely (0.05–0.25 mm) crystalline limestone with homogenous structure, see Fig. 8. Koněprusy (CS) was a well compacted micritic limestone with bioclasts and extraclasts, see Fig. 9. The average size of its particles was about 0.8 mm. Open porosity of both limestones was below 1%. Average chemical composition of the limestones, based on XRF analysis of powder samples drilled during bench blast preparation, and calculated Lime Saturation Factor (LSF II, see formula 1) are presented in Table 3. Koněprusy limestone had the LSFII factor in order of 10^4 and thus should be more liable to sintering than the Vitošov limestone.

Fig. 8 Microphotograph of limestone from Vitošov (Vit), XPL. The fissure in the middle is secondarily filled with quartz. Field of view 2 mm across
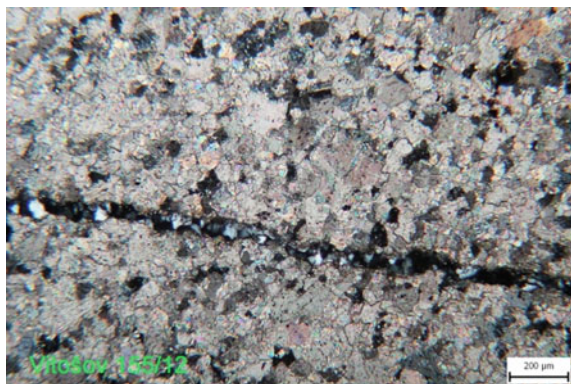
Fig. 9 Microphotograph of Koněprusy limestone (CS) showing larger (300–1000 μm) micritic extraclasts and bioclasts XPL. Field of view 5 mm across
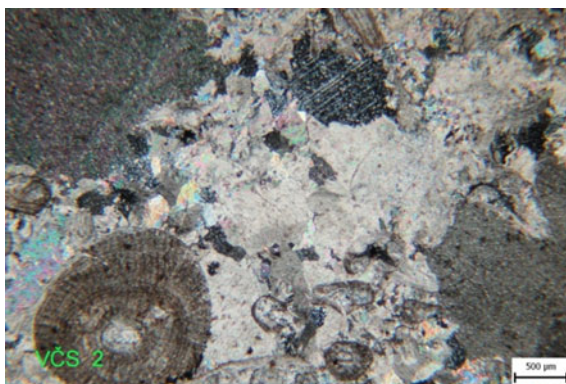

Table 3 Composition of limestone (in wt%) determined by XRF, loss on ignition (LOI) and LSFII

	Origin	CaO	MgO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	LOI	LSF II
Vit	Vitošov	54.5	0.2	0.63	0.17	0.17	0.02	40	2626
CS	Koněprusy	55.5	0.33	0.04	0.04	0.03	0.006	42.9	31,058

3.2 Lime Production and Sampling

Altogether, thirteen 20 kg samples of quicklime were collected and initially evaluated. The overview of the collected samples is presented in Table 4. There were five samples from five different commercial kilns operating in continuous regime and nine samples from the traditional flare kiln obtained during four batch burnings. Samples are characterised by their way of production (first letter **C**-commercial, **T**-traditional) followed by the type of limestone (Vit-Vitošov, CS-Koněprusy), by a number referring to kiln/burning and in the case of traditional quicklime also the position in kiln is distinguished by additional number where 1 denotes a sample from the bottom part of the vaulted dome, 2 denotes a spot sample from the middle of the kiln and 3 denotes a sample from the top part of the kiln, app. 20 cm under the top feedstock surface.

Samples of quicklime (CVit 1-3 and CCS 1) were obtained from four different continuous vertical shaft kilns of two different lime producers. These kilns operate on the same principle using parallel flow of hot gasses and altering burning and non-burning shafts during operation. They apply regenerative preheating of all combustion air. Sample CCS2 was obtained from a production using classical mix-feed shaft kiln. Traditional samples of quicklime (TVit and TCS) were obtained during the experimental calcinations. Production-related characteristics of the collected samples are presented in Table 4. The temperature range and residence time are approximated to characterise the main calcination conditions. Typical temperature profile of the Maerz kilns and other production details are published by the producer.

Table 4 Denomination of samples and their production-related characteristics

	Calcination temperature (°C)	Residence time (h)	Fuel	Feedstock stone size (mm)	Spot sample acquisition
CVit1	~1150	10.5	Recycled oil/gas	40–70	Continuous production
CVit2	~1250	10.5	Recycled oil	20–40	Continuous production
CVit3	1050–1150	12	Coal/gas	20–80	Continuous production
TVit I-2	900–1000	6	Wood	30–120	Flare kiln—middle
TVit II-1	900–1050	8.5	Wood	150	Flare kiln—vault
TVit II-2	900–950	7.5	Wood	30–120	Flare kiln—middle
CCS 1	900–1000	12	Liquid fuel	40–100	Continuous production
CCS 2	900–1300	24	Solid fuel	60–100	Continuous production
TCS I-1	900–1150	16	Wood	150	Flare kiln—vault
TCS I-2	900–1150	14	Wood	30–120	Flare kiln—middle
TCS I-3	900–1150	13	Wood	30–50	Flare kiln—top
TCS II-1	900–1250	18	Wood	150	Flare kiln—vault
TCS II-3	900–1200	11	Wood	30–50	Flare kiln—top

3.3 Comparative Analysis of Samples

Interpretation of analytical results of quicklime samples is challenging due to several reasons. The first one is the representativeness of a sample to the produced batch. Lime kilns in general do not have uniform distribution of temperature during calcination process, raw material is naturally heterogeneous and the process of limestone decomposition is a function of burning temperature and stone physical size. Due to the above mentioned points and some additional influences the parameters of quicklime can differ significantly even so the samples are from the same calcined batch. In addition, quicklime typically reacts fast with air humidity and thus samples should be protected immediately after sampling and stored in conditions that do not allow hydration and subsequent carbonation. Last point to mention is that when comparing physical properties of quicklimes only fully calcined samples are comparable.

Some of the obtained samples were not fully calcined; some contained high portion of calcium hydroxide (they were partly hydrated). These samples were excluded from the detailed analytical studies described below that aimed to focus on the comparative assessment of well-burnt lime.

3.4   Analytical Techniques

Acquired samples of about 20 kg of quicklime were stored in plastic buckets closed with a lid and wrapped with a cling foil. Powdered CaO was prepared from app. 1 kg of lump lime with a pestle and mortar and passed through 2 mm sieve immediately before the further testing. The homogenised powder was used for reactivity test carried out according to EN 459-2. The presented values are average of two measurements. The composition was evaluated by thermogravimetric analysis (TGA/DTG) in the 20–1000 °C temperature range with a heating rate of 10 °C/min in a nitrogen atmosphere with SDT Q600 (TA Instruments).

Lump samples were used to study the CaO structure in low and high temperature zones (e.g. samples from the top and vault positions). Pore size distribution, surface area and skeletal density of lump samples were characterised by mercury intrusion porosimetry (MIP) by AutoPore IV with maximum pressure 33,000 psi; nitrogen gas adsorption (BET) at 77.5°K by ASAP 2020; and helium gas pycnometry (GP) by Accupyc II 1340, respectively. Morphology and structure of lump samples were qualitatively described in scanning electron microscope (SEM), Mira II LMU (Tescan) equipped with secondary electron (SE), back scattered electron (BSE) and energy dispersive X-ray (EDX) detector (Bruker). The samples were coated with a thin gold layer (app. 15 nm) to obtain better conductivity necessary for scanning in a high vacuum mode. The SEM set up was: 15 kV high voltage and 15 mm working distance in case of EDX analysis. The absorbed current reached the value 1.4 nA and the time of collecting of X-rays was 60 s. For quantification of elements was used a standard-less elemental analysis.

4   Results

The experimental study focused on properties of well-burnt quicklime samples and the results are summarised in Table 5.

4.1   Thermal Analysis (TA)

Thermal analysis identified that all quicklimes were partially hydrated (4–8%) and also partially carbonated (around 1%). The DTG peak of calcium carbonate

Table 5 Properties of analysed quicklime samples

	TA		MIP	BET	GP		Reactivity	
	Ca(OH)$_2$ (%)	CaCO$_3$ (%)	Porosity (%)	Surface area (m^2/g)	Density (g/cc)	Bulk density (g/cc)	t$_{60°C}$ (min)	T'_{max} (°C)
CVit 3	4.3	1.0	50.9	2.89	3.19	1.57	0.3	78.0
TVit II-1	7.1	1.0	50.9	1.65	3.15	1.55	5.3	72.7
CCS 1	3.0	1.0	54.5	2.08	3.30	1.50	0.4	79.1
TCS I-1	5.9	0.9	49.2	1.55	3.23	1.64	2.4	79.5
TCS I-2	7.4	1.1	49.9	1.36	3.18	1.59	2.5	78.9
TCS II-1	5.8	1.1	52.2	1.41	3.20	1.53	3.0	78.7

Fig. 10 Derived weight changes of selected lime samples when heated from 20 to 1000 °C. Ca(OH)$_2$ peak is about 400 °C, CaCO$_3$ peak is just above 600 °C
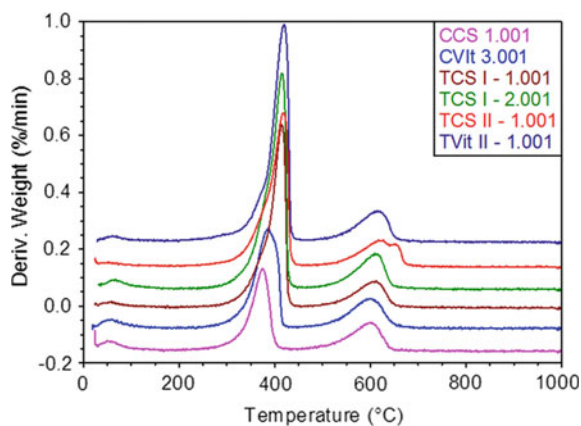
dissociation was accounted to re-carbonation as it appears in a relatively low dissociation temperature, just above 600 °C, see Fig. 10. All limes were thus assumed to be well burnt. The level of hydration was relatively high and might affect the reactivity and also other structure related properties. However a certain level of hydration and re-carbonation has to be expected due to the production processes and this is especially the case of traditional production when quicklime is left in kiln to cool down in natural conditions. A certain contribution of sample handling and storing to the elevated hydration of quicklime cannot be excluded.
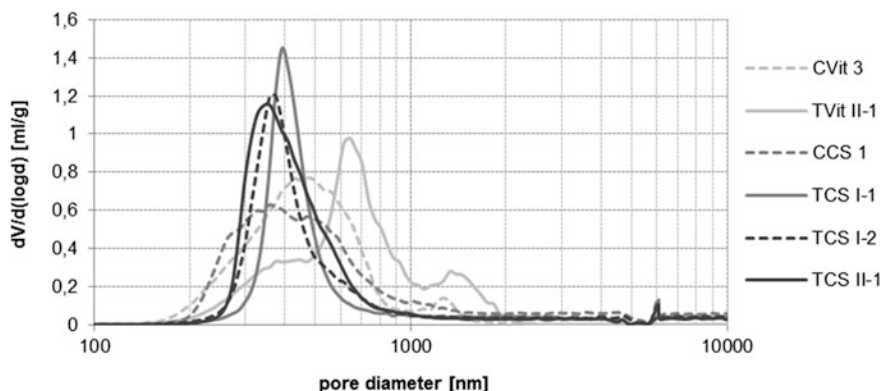
Fig. 11 Pore size distribution of lime samples determined by MIP

4.2 Mercury Intrusion Porosimetry (MIP)

Open porosity of quicklime samples was from 49 to 54.5%, see Table 5. This values indicate that all the tested samples fit to a category of soft burnt, which according to Oates (1998) ranges between 45 and 55%. Figure 11 presents pore size distributions and for most of the samples the main pore size was within the range of 200–600 nm. The exception was sample **T**Vit II–1 which was taken directly from the surface of stone placed in the vaulted dome. This could indicate lime sintering effect on the surface. The effect of quicklime hydration on the pore size distribution was not significant enough to be determined.

4.3 Gas Adsorption and Density

Density, bulk density and specific surface area (BET) of quicklimes are compared in Table 5. The two commercially produced limes had higher surface area values which also corresponded to a more rapid reactivity. The density values were similar for all six samples and according to Oates (1998), the analysed samples could be classified as soft burnt by their density.

4.4 Reactivity

Reactivity of the selected quicklimes is presented in Fig. 12. The commercial quicklimes were the most reactive and in general the samples from the dome had slower reaction. However, only the sample **T**Vit II-1 from the dome was classified
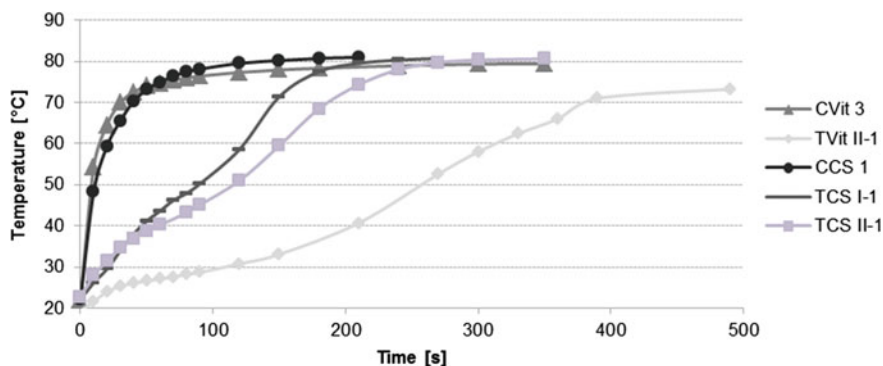
Fig. 12 Reactivity of quicklime samples

Table 6 Typical reactivity of commercial limes and production targets

	CVit 1	**C**Vit 2	**C**Vit 3	**C**CS 1	**C**CS 2
t_{60} (min)	3–4 min	6–8 min	<1 min	0–1 min	5–15 min
Production	Soft burnt lime	Hard burnt lime	Soft burnt lime	High react. low CO_2 content	Slow react. low CO_2 content

as a medium burnt lime based on the reactivity test. The rest was soft burnt according to the criteria of Oates (t_{60} of a medium burnt lime is 3–9 min). The industrial production targets certain degree of burning, see Table 6. The reactivity, degree of burning and further processing, depends on technological requirements of final customers. Both commercial samples involved in the experiment were produced with the intention to be fast reactive reaching temperature of 60 °C in less than 60 s.

4.5 SEM Observations

Samples of quicklime observed in SEM were all evaluated in three positions; region of surface exposed during the calcination in kiln, region 2–3 mm below the surface and region about 5 mm below the surface. These positions were all on the same line perpendicular to the surface. Images presented in Fig. 13 are all from the surface region. There were differences in the size of crystallites and interspatial voids but in principle the structure was very similar for all evaluated samples. Just comparing the set of the six samples, the smallest particles of CaO were about 400 nm and the largest ones were about 2000–3000 nm. One should note, that this quantification is
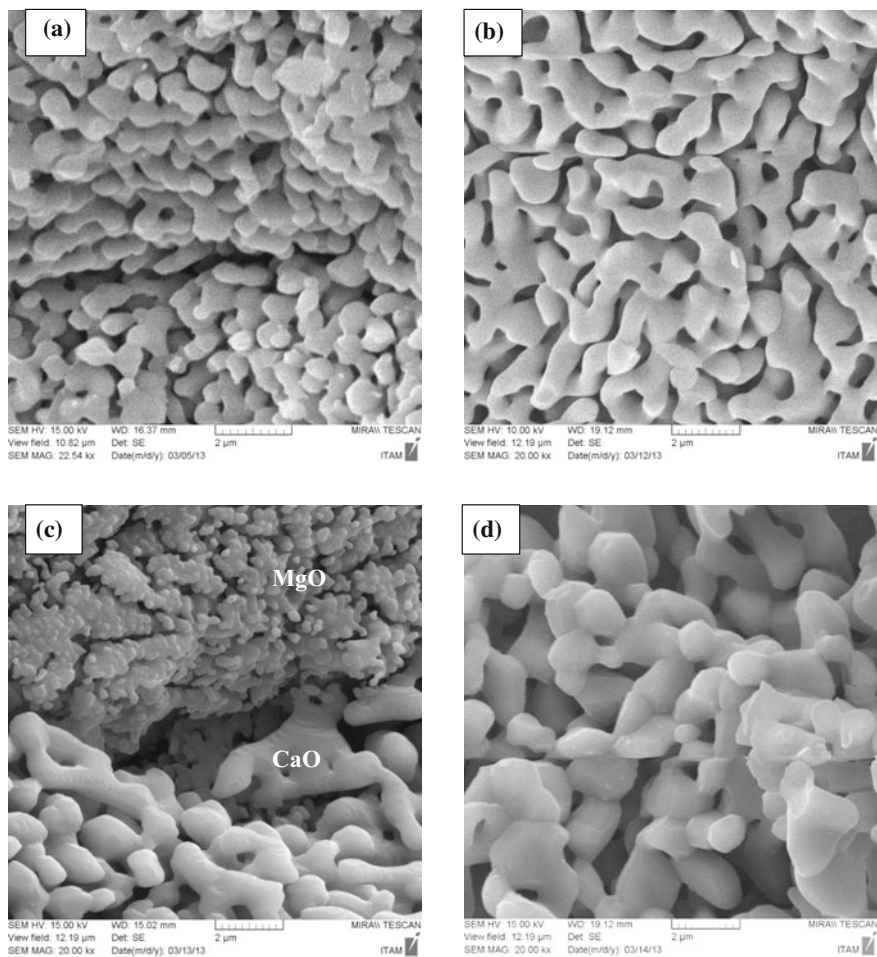
Fig. 13 Images from SEM (**a C**Vit 3, **b T**Vit II-1, **c C**CS 1, **d T**CS II-1); all images in the same scale; field of view 12.19 μm across

valid only for the six samples and it describes a very small area. On Fig. 13c there is also visible an MgO structure with much finer particles. Figure 14 left shows morphology of quicklime sample **T**CS I-1 that was obtained from the vaulted dome where larger crystallites of CaO (5–10 μm) were identified in the surface region. Just a few mm below are particles about 5x smaller than that of those observed on the surface, see Fig. 14 right.
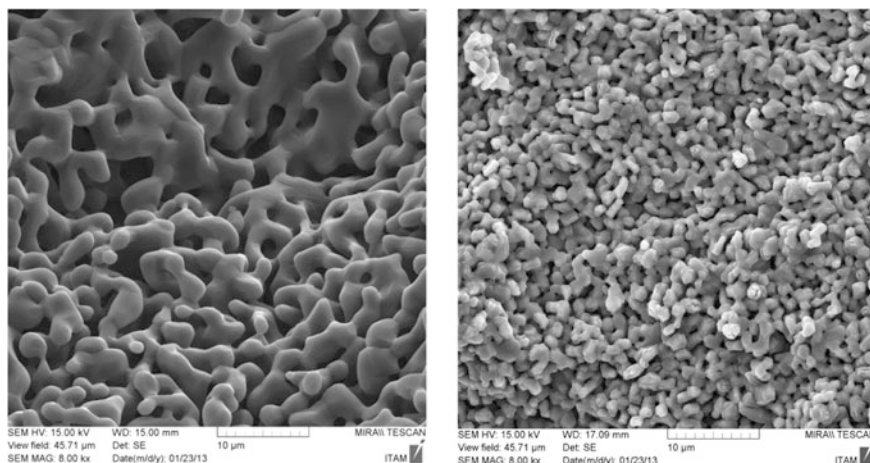
Fig. 14 Sample **T**CS I-1. Image of CaO crystallites near surface showing partially sintered particles (5–10 µm) on the left. Image from the same sample but just 3 mm below the surface showing CaO crystallites in the range of 1–2 µm, on the right. Field of view 45.7 µm across

5   Discussion

Lime was burnt in a way that replicated the traditional calcination process in a wood-fired flare kiln. Due to the experiment, it was possible to identify the key technological points which are significant for this traditional burning process: building the vaulted dome, distributing the stone within the kiln, optimal wood stoking and burning regime. The burning process was extensively monitored and described by quantitative values. In addition, some qualitative observations were noted. For example: colour of flames, relation of draught and rate of wood burning, temperature increase and its relation to the moment when flames appear at the top of kiln etc. The influence of environmental conditions on the burning process was noted, however, it was not possible to conclusively relate the monitored parameters, selected to describe the ambient environmental conditions, to the effects observed during burnings. A practical recommendation could be that certain climatic conditions should be avoided. For example rapid unpredictable changes in air currents due to thunder storms. The rate of burning depended on draught conditions in the kiln. With a good draught one tonne of limestone could be successfully calcined within 24 h in a kiln of this type. This time span also corresponds to known one day lime kilns that operated at the end of the 19th century in Moravia (Vápenice) and Slovakia (Skýcov). It is interesting to note that temperatures above 1250 °C, i.e. cement clinkering temperature, were reached by wood burning in this relatively small kiln. This means that mineral phases that are formed in this high temperature region, like C_3S, could have been produced in the past depending on limestone composition. Their proportion was probably negligible due to the facts that such

high temperatures were localised, high calcium limestones were historically preferred and particles that did not slake required additional treatment.

The temperature differences in the experimental kiln show that the same batch of lime is burnt in a very nonhomogeneous temperature field with a difference of 500 °C between the hottest and coolest zones. Considering the heat concentration to the central zone of the vaulted dome and also fact that typical historic flare kilns were much larger and thus probably reaching even higher temperatures in and above the combustion chamber leads to questions regarding the quality of lime from the hottest zones. It is known that the goal of every burning was to reach maximum burning efficiency in terms of converting limestone to lime. Longer residential times and relatively high temperatures suggest a possibility that lime from the vaulted dome could have been often hard burnt.

The laboratory assessment of the traditionally produced quicklimes attempted to answer two main questions; (i) was the quicklime produced in a wood fired flare kiln comparable with the modern commercial production and (ii) was the lime exposed to the high temperatures in the vaulted dome hard burnt? The evaluation of quicklime contributed to the assessment of the calcination procedure in the designed kiln. The results indicated that the chosen size of stone and the selected calcination regime was appropriate in terms of the reached temperatures. It also pointed out at some deficiencies in terms of heat distribution in the kiln.

The preliminary assessment of quicklime samples from commercial and traditional production led to a further selection and only well-burnt samples were analysed. It was interesting to note that a certain portion of underburnt, re-carbonated and hydrated parts was present in samples from the traditional kiln as well as from the modern industrial kilns. The complete process of lime production is the largest difference between the current industrial and traditional productions. Both, the modern and traditional processes have their own ways how to sort quicklime according to its quality. Modern processes allow a better control of the calcination conditions and quicklime can be sorted based on analytical results. Traditional processes relied on skills, experience and manual handling. The evolved knowledge and crafts of lime burning was linked to a further processing of lime and its application. The way lime was slaked and processed further in a traditional way allowed for selection of a good quality product in relation to its application.

The well-burnt traditionally produced quicklimes were not significantly different from the commercially produced ones in their main physical characteristics. There were two parameters, surface area and reactivity, that pointed at the difference between the commercial and traditional limes. The reactivity of the selected commercial limes was higher as it was a special intention of the producers; they also produce limes with lower reactivity. The traditionally produced limes could be regarded as soft burnt and the selected limes had reactivity between 2 and 5 min. In fact a very fast reactivity could be a problem for slaking lime in a traditional way. If the reaction is too fast, access of water to particles of CaO may not be sufficient (hand mixing is not fast and efficient enough) and the temperature can, due to the exothermic reaction, locally exceedingly rise and the slaked lime particles consequently aggregate together.

Temperature in the kiln reached over 1200 °C in the space above the combustion chamber when the sample **T**CS I-1 was calcined and the stone there was exposed to temperatures above 900 °C for 16 h. Some sintering effect was identified on the surface of stones placed directly above the combustion chamber however, given the size of stone, the sintered layer was relatively thin and the spot sample from this location could still be classified as a soft burnt lime. The sintering effect progressed from the surface inwards. These are interesting facts suggesting that the sintering (hard burning) was in practice dependent also on the size of calcined stone. The proportion of surface to total volume is decreasing with increasing diameter and thus a sintered surface into the depth of few µm has a relatively low effect on a decimetre large stone block.

A quantitative comparison of characteristics of quicklimes produced in industrial and traditional kilns is difficult as there are too many variables like natural variability of limestone, temperature variation and calcination conditions, re-carbonation, hydration etc. that cannot be determined. A statistically significant amount of data on representative samples would have to be analysed to relate the quicklime properties with influences of a specific kiln and production technology. In addition studying properties of lump quicklime is difficult as the pore structure related properties change across the particle. Particles of the same material but different sizes calcined in the same conditions thus have different pore structure.

6 Conclusions

The study demonstrated that a small-scale custom made lime production is in principle possible. The designed prototype was proved to be functional and lime was successfully produced. The experimental burnings and their monitoring allowed to describe the temperature distribution in the kiln including also the effect of formation of draught channels within the feedstock. The temperature difference within the kiln space was reaching 500 °C. The data obtained by monitoring confirmed the importance of placement of stone to the kiln in terms of their size and inter-particle voids. The size should correspond to the expected heat spread and should be in relation to the temperature reached during calcination and its duration. The inter-particle voids are important for the transfer of heat by hot air and fumes. The positioning of stones affected permeability and formation of draught channels. The experimental burning confirmed the importance of placement of stone within the kiln known from historic and ethnographic studies dealing with traditional lime burning. The practical experiment demonstrated that the environmental conditions significantly influence the burning process. However, the established monitoring of atmospheric pressure and ambient air humidity and temperature could not be fully related to the observed effects. Other, more influential factors existed that were not monitored. These were probably air currents and local wind conditions. The experimental burning demonstrated that the burning efficiency, i.e. the rate of converted quicklime, could under standard conditions reach 90% or possibly even

higher. The process was however energy demanding and the kiln efficiency was about 25%. High fuel consumption is typical for the traditional burning in open-top kilns without any heat recuperation. A practical conclusion is that the higher production costs would have to be justified by other reasons, like production of unique materials for conservation and restoration projects.

Based on the assessment of the produced quicklime the following conclusions can be drawn:

- According to the evaluated lime samples, the lime produced in the experimental wood-fired kiln could be classified as a soft burnt lime.
- Well-burnt quicklime produced in the experimental lime kiln was of a good quality and similar in properties to some currently produced commercial soft burnt limes.
- In the region of the vaulted dome, where the stone was exposed to temperatures reaching over 1200 °C, a sintering of quicklime occurred. The study indicates that in the case of the four experimental burnings, this effect was quite localised and mostly affected only a relatively thin surface layer.
- Wood-fired lime differs from the modern one in characteristics which relate to their technology of calcination and subsequent processing. The product is affected by specific conditions in the kiln that can differ based on external influences. In order to compare lime produced in traditional and modern kilns a long-term statistical study would be required.

Future studies will focus on an improved quantification of the identified effects and also on the relation of the production technology to the quality of lime and its use.

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