The Institute of Rock Structure and Mechanics of Academy of Sciences of the Czech Republic, v.v.i

Studies on historical mortars

application of ^{27}Al MAS-NMR

T.Hanzlicek[1], I.Perna[1], Z.Ertl[2]

[1]Institute of Rock Structure and Mechanics of the Academy of Sciences of the Czech Republic

[2] Czech Development Agency O.P.S.

Introduction

- Historical mortars present various secrets:
- Durability,
- Hardness,
- Insolubility even in sea waters,
- Combination of components.

Taking into consideration the technology of limestone firing in simple kilns without any temperature control and difficulties with fuel (especially in the Middle East) we are surprised by the quality of this materials in many countries as Turkey, Israel, Spain, Portugal, etc.

Principal findings

- Historical mortars theoretically consist of calcium carbonates (calcite) and quartz sand and are complemented by small amount of mica, rutile and ferrous oxides – but by XRD analyses we found also portlandite and signal of amorphous component.
- In different countries and in different ages of building era the constructors used very often ceramic shreds as component of calcareous mortars.
- Identification of ceramic shreds in mortars by traditional analytic methods (XRD, GTA/DTA) does not resolve the problem why this material was chosen and added to the mortars :
- 1. We could exclude substitution of gravel or filler by ceramic shreds.
- 2. We could exclude the „green power organization" of forced recycling of ceramic fragments and broken pieces.
- 3. We state that ceramic shreds means enormous pottery production and excludes specially fabricated fired clay shatter.

Pottery

- Pottery is connected with many different knowledge, from clays extraction and preparation of appropriate mixtures to the creation of pieces, their drying and finally very costly firing. Basic technology does not consider knowledge of decoration techniques (glazes, colors, application, etc.).
- In that connection fired ceramic shard was a material with high value added. The use of this valuable material as admixture in calcareous mortars was commonly spread knowledge, experimentally proved and confirmed in many countries.
- Broken ceramics - means obtaining fragments and also receiving lot of powdered material !

Connections

- The use of pottery shreds should have some very important reason. The ancient and medieval ceramics are dominantly formatted on the pottery wheel – means from plastic clays and fired in primitive kilns hardly reaching temperature of 1000 °C.
- Similar or identical situation could be obtained if the ceramic shreds (low fired) are substituted by low fired clay and this so-called „activated" clay is added to the slaked lime.
- The thermally treated clays represented by kaolin, loss their reflections on X-ray diffraction patterns but chemical analyses confirm presence of alumina and silica.
- Presented study on historical mortars identified aluminum ions in connection with silicon and offers explication of the long term stability of these mortars.

Results of study on historical mortars

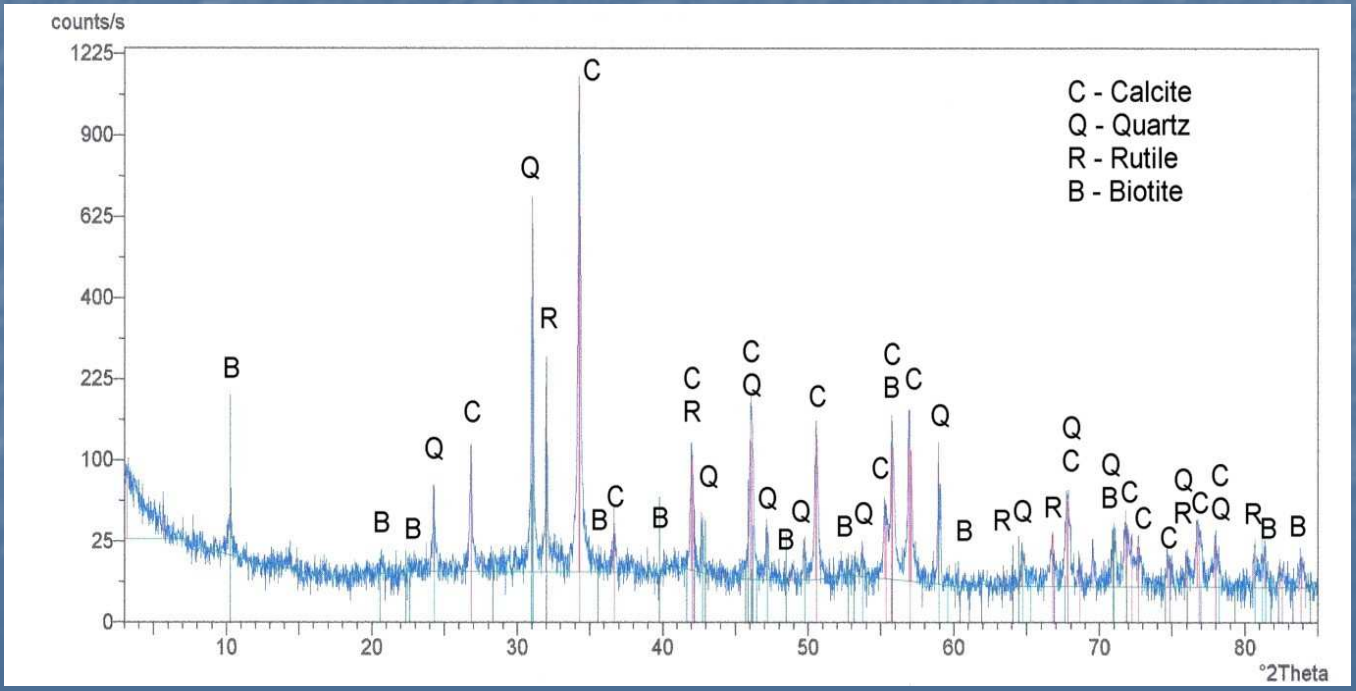
- Three samples of historical mortars from Czech republic (11.century at South Moravia and 12.century at Central Bohemia regions) were analyzed by XRF method, recalculating elements into oxides and later applying ^{27}Al MAS-NMR in solid state on prepared samples.

- Table shows principal oxides of historical mortars

Oxides/ samples	L.O.I.	Al_2O_3	SiO_2	CaO	Fe_2O_3	MgO
Roudnice	13.80	6.28	50.66	22.02	2.38	1.66
Znojmo1	9.30	8.12	55.94	18.35	3.39	0.85
Znojmo3	16.20	6.08	34.83	35.83	2.92	1.28

XRD analysis

- Dominant calcite and quartz in all three samples is complemented by rutile and mica in all samples
- Presented Figure shows typical XRD pattern of Znojmo

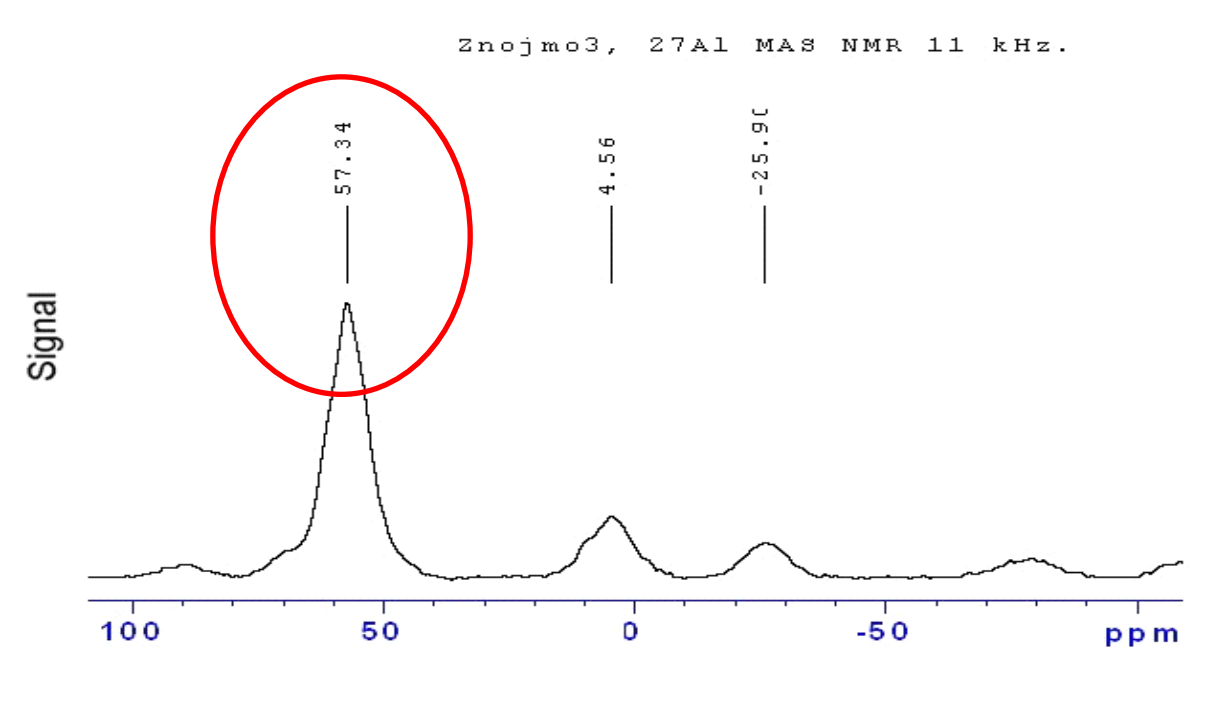


Aluminum, Alumina, Calcium-Aluminates

- Studied XRD analyses of all three historical samples do not present any diffraction peak corresponding to the aluminous component.
- Chemical analyses confirm from 6 to 8 wt.% of alumina and this oxide could not be present as such, but commonly and naturally in connection with silica. The state and form of aluminum ions was studied by ^{27}Al MAS-NMR.
- First explication of aluminum ion coordination was published in 1988 by Sanz et al. and transformation of aluminum ions was related to the temperature.
- Later experiments based on this new information described affinity of four (five)-coordinated aluminum ion to form, together with silicon, the poly-condensed netting when negatively charged [4] Al^{3+} is balanced by positive alkali ion.

^{27}Al MAS-NMR

- The state of naturally positioned aluminum ion in kaolinitic clay is presented together with change of its position obtained from the sample of historical mortar.



Hypothesis

- The clay mineral (theoretically kaolin) was included as an inseparable part of fired calcite and during the temperature treatment the coordination level of aluminum ions changed. (Common calcareous sediment always contains clays and quartz sand).
- During the lime slaking all requirement for aluminum-silicon chaining were fulfilled:

1/ alkali aqueous condition,

2/ hydration of both main participants (only [5] Al^{3+} and [4] Al^{3+} could be hydrated),

3/ calcium ion is balancing negative charges of two aluminum ions.

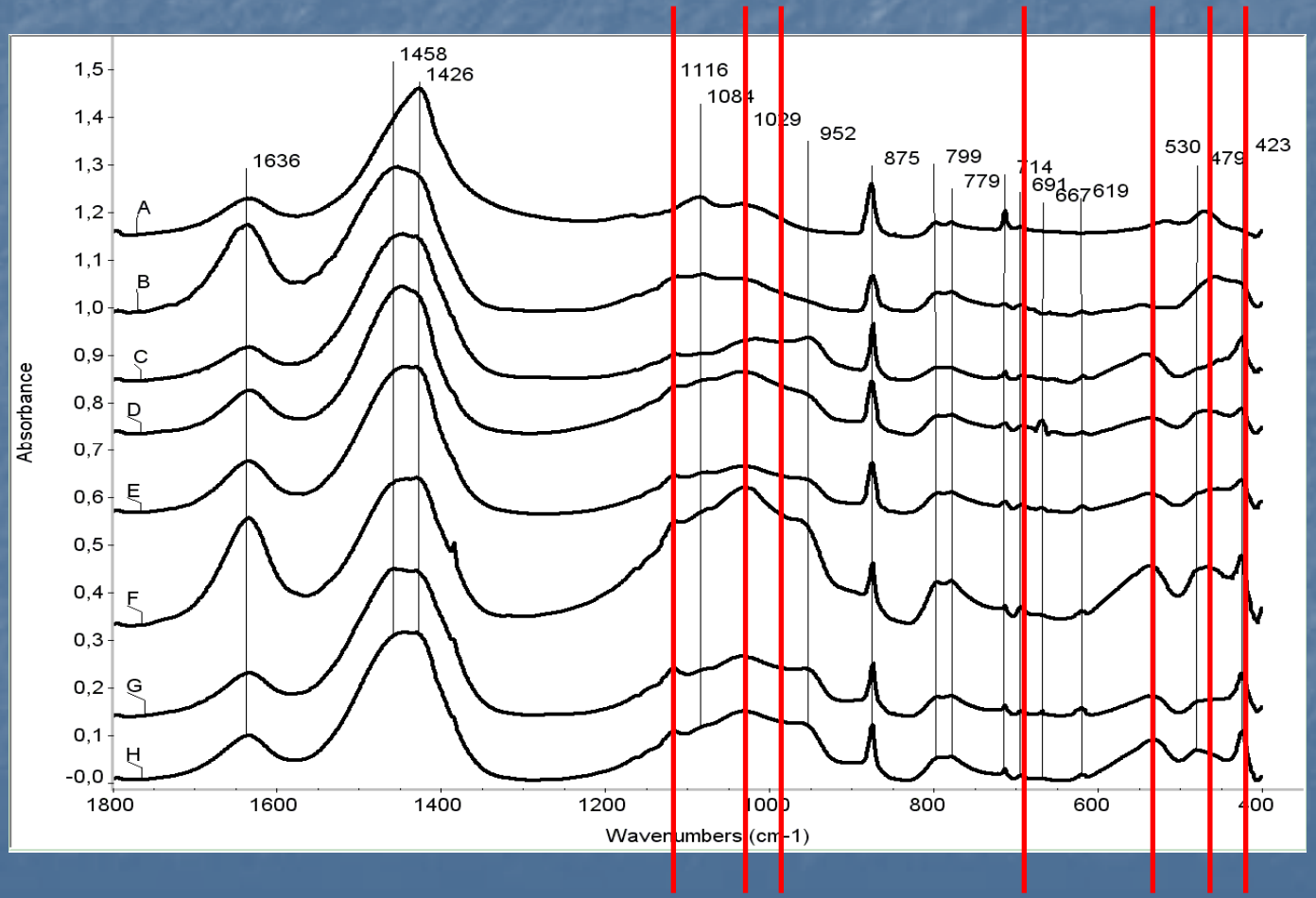
Formatted longer or shorter chains of -Al-O-Si- with -OH terminal groups are spread in dominantly calcareous surroundings.

Ceramics or activated clay

- Addition of ceramic shreds is complementing calcareous matter with defined proportion of alumina-silicates in state of „activation". This is considered as a base for poly-condensation of Al-O-Si chains.
- Powdered particles are dissolved in aqueous alkali conditions, forming XRD invisible, amorphous binding agent. The chained formation of amorphous alumina-silicates improves the quality of mortars.
- Modeled experiments of calcite/clay/quartz sand mixtures fired separately and also together show the same results – in all cases the FTIR analyses confirms chained Al-O-Si formations. (recently published in Int. Journal of Architectural Heritage – 2011)

FTIR analyses on modeled mortars

The bands codified by Lee, Phair and Van Deventer (2003)



1147, 1080,1030 cm^{-1} 713, 548, 467, 423 cm^{-1}

Simplified calculations

- Commonly used equation of lime hydraulic module

$$M_h = CaO / (SiO_2 + Al_2O_3 + Fe_2O_3)$$

distinguishes mortars as highly, medium and low hydraulic limes (1.7 – 9) respectively, but do not say nothing about stability and durability (e.g. Znojmo1 = 0,817).

- With a specification of aluminum ion coordination we could offer new possibility of mortars recognition, based on ^{27}Al MAS-NMR analysis.
- 75 wt. % of aluminum ions are in four coordination and in state of predictable hydration in alkali aqueous conditions. Negative aluminum charges are balanced by positive calcium ion (e.g. sample Znojmo1).

6.08 * 0.75 = 4.56

4.56*120/102 = 5.36 (molar rate of SiO_2/Al_2O_3= 120/102)

4.56* 56/102 = 2.50 (two Al are balanced by one Ca – 56/102)

A_c =12.42 % of amorphous component

Maintenance of historical mortars

- Defined **A_c** in calcareous mortars quantifies chained alumina-silica structures and could help to formulate substitutes for repairs and maintenance of historical monuments.
- The use modern materials as pure slaked lime with addition of calculated amount of "activated" kaolinitic clay and this admixture with gravel or quartz sand results in similar or identical material as used in historical time.
- Porosity, color, proportion of calcareous substances and alumina- silicates are easily calculable.
- Many restoration works were done by mortars based on Portland cement with results in incorrigible damages on original structures.

Conclusion

- The limestone fabrication works with current temperature of 1000°C and in historical times these temperatures were hardly reached due to the poor firing technology.
- Natural clayed participant in calcareous sediment influenced by calcinations temperature or addition of more or less powdered ceramic have had the same reason:
- The addition of alumina-silicates improves the final quality of calcareous mortar.
- We offer the idea of chained alumina-silicate structures, which explains long-term stability and corresponds to the behavior of poly--condensed alumina-silicates.
- Replacement or repair of historical mortar could be formulated by the application of A_c factor.

Thank you for your attention