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Historical mortars

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Review of the 19.Century experiences

- Vicat: Annale de chimie et de physique (1820) Vol.XV. Page 365
- *"Since the quality of natural hydraulic lime, depends solely* ***on the presence of a certain quantity of clay, combined by fire with the calcareous matter****, it was natural to think that by mixing clay in suitable proportions with fat lime, slaked, no matter how, and then* ***submitting the mixture to calcinations****, a similar result would be obtained: experiments made on a large scale, and in many places, have confirmed this idea in a manner so complete, that it is possible* ***to fabricate anywhere, and at a very moderate price****, artificial lime superior to the natural analogous lime"*

Review of the 19.Century experiences

- Extract of Moniteur of January 22nd, **1823** : Mr. Sganzin reports on page 31 *" They prepared in Amsterdam an artificial trass: it is clay taken from the bottom of the sea, which they burn highly as they do bricks. These bricks-like pieces are broken by pestles worked by horses: the substance is then put under millstones, where it acquires the fineness necessary to be converted into mortar by mixture with lime. Bergman analysed this artificial trass, which bears the name of Privileges cement of Holland: he found that it contained in about 100 parts* ***silex from 55-60, alumine 19-20 lime 5-6, iron 15 to 20.*** *There is no doubt, considering the composition of this clay, and the degree of heat to which it is subjected, that it must give very good artificial trass."*

Review of the 19.Century experiences

- Journal of the Franklin Institute of the State of Pennsylvania,**March 1838**
- **On Concrete**
- By General Treussart (France)
- Page 154: " The best process for converting fat lime into hydraulic lime, is to burn it with a small quantity of crude clay, the proportion of 1/5 of a clay, seems the most suitable, and appears that the best clay is that which contains **as much silex as alumine**."
- Page 156
- "All clays calcined to the proper degree are reduced to powder, are susceptible of giving factitious puzzollanas – better or worse according to the composition. The clay most proper to make good puzzollanas are those which are greasy to the touch – such as commonly used for making Dutch ware , stone ware, earthen ware and tobacco pipes. Clays which contain **one fourth of alumine are greasy** to the touch, those which **contain from third to one half give** very good result."

Review of the 19.Century experiences

- Page 159
- " Concrete is nothing else than masonry made of hydraulic mortar and small stones."
- Experiments of Mr. Thomas P. Jones, M.D. proves that much better results are given when used with **little burned tiles and bricks (using their dust)** than with well burned ceramic items. **(Low red heat for six hours – see date of edition, 1838).** The experiments of the author agree with the opinion of Mr.Vicat, who says: *"that clay should be submitted to a feeble heat only".*
- *Vicat: " …. That all the mystery of puzzalona resides, not in the presence of iron or lime, but in particular state of combination of silex and alumine."*

Understanding of the pozzolanas

- Vitruvius Polio mentions this material in his famous opus „X. Books of architecture“, year 57 b.J.CH. He describes the cementitious quality of a powdered material which was extracted by Romans from the slope of volcano Vesuvius close to the village Puteolo.

- „Pozzolan“ and „pozzolanic quality“ is defined, (see e.g. Wikipedia) like a material which forms with slaked lime cementitous matter.

- Let us contribute to the understanding why and how this materials forms solids. The review of 19.Century experience shows experimental works without the explanation, our own laboratory studies of an old and very old mortars offer solution.

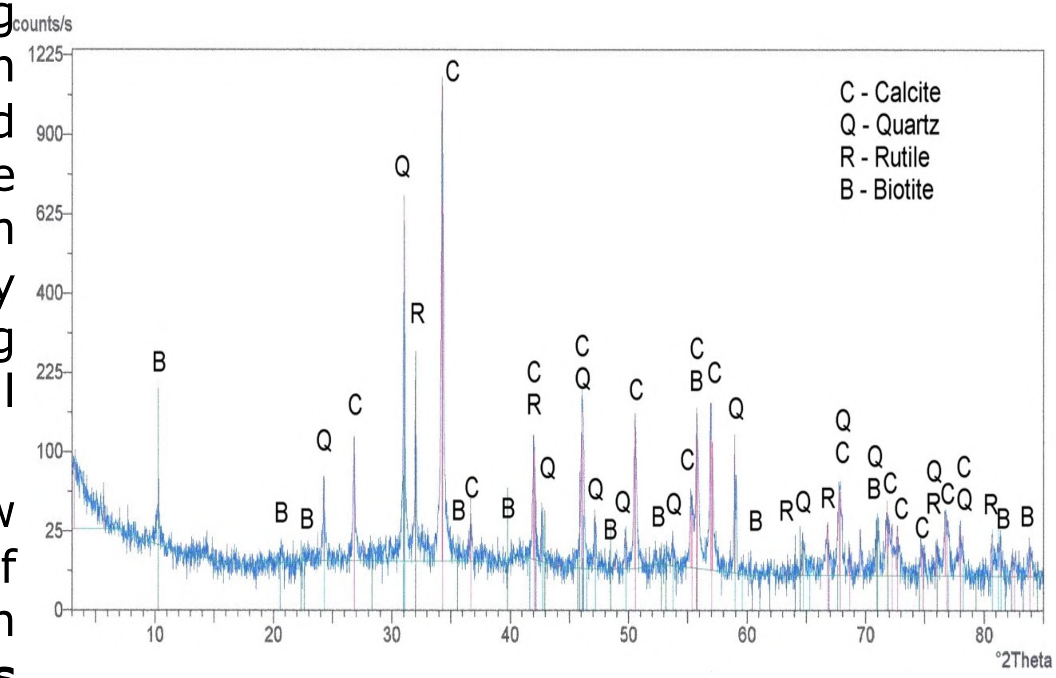
Mortars from 11.Century (Central Europe)

- Three samples of historical mortars from the 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

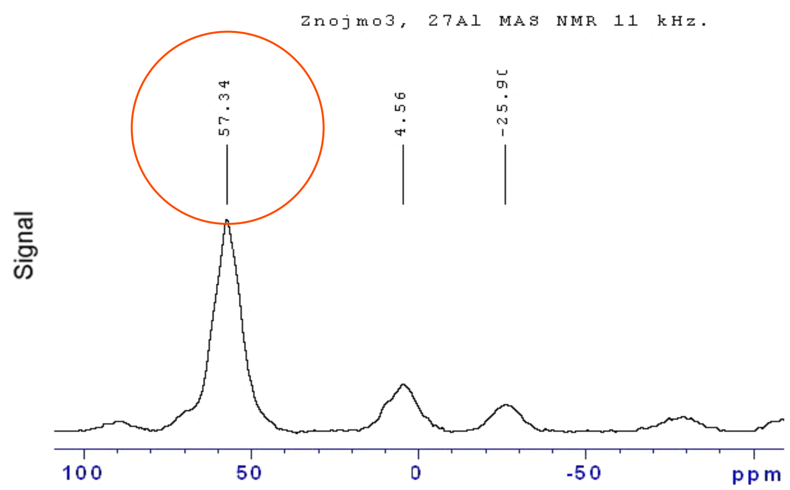
XRD pattern

- The sample of historical mortar (Znojmo) does not present the clay reflection and does not show any aluminum containing matter excluding its content in biotite traces. From biotite and also from rutile content we could pretend that both of them were impurities originally complementing clay, resulting from the weathering of original rock.
- If the chemical analyses show 6, respectively 8 wt. % of aluminum oxide, the question is: **Could we identify its content?**



^{27}Al MAS-NMR of the 11.Century mortars

- The sample of mortar from Znojmo (1 and 3) historical building was studied by nuclear magnetic resonance. This method answers the state of aluminum ions. Indicated ppm location appoints the four coordinated alumina ion.



Simple calculation

- With the respect to the experience to the 19.century literary resources we could contribute:
- A) The ideal stechiometric rate between silica and alumina is done by this formula: $Al_2O_3.2SiO_2.2H_2O$ or after calcination $Al_2O_2.Si_2O_5$ – considering the aluminum ion shift form hexa-coordination to the penta and four coordination to the oxygen.
- Than: using the atomic mass, the kaolinit equals to 102 + 120 + 36 = 258 and in case of our samples 8.12* 120/102 = 9.55 and 8.12* 36/102 = 2.86 we suppose that original clay substance was
- = 8.12 + 9.55 + 2.86 = 20.53 wt. %

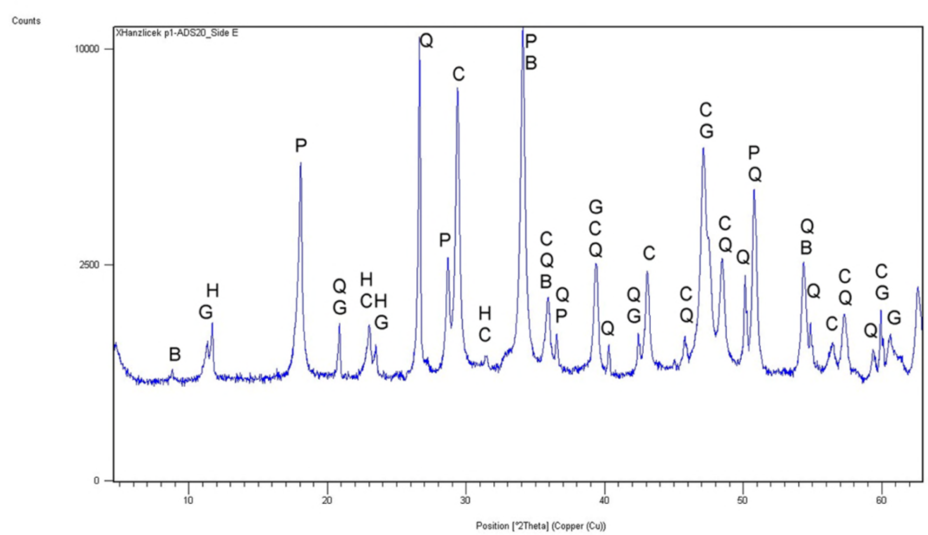
If we go back to the fifth slide – General Treussart expression: *„The proportion of 1/5 of a clay, seems be the most suitable*". I would say, the result of calculation is matching with later experience. The combination of clay substances with lime is much older and was probably spread in whole Europe.

Mortar from historical town SIDE (Turkey)

Town of Side (founded in the 7th century B.C.,) , sampled at 2010. (Observation: white-gray matrix with fine sand and red particles of ceramics shards).

The main components: **Portlandite**-$Ca(OH)_2$,quartz-SiO_2 and calcite-$CaCO_3$, recognized by the XRD analysis.

- P-portlandite, C-calcite, Q – quartz, G- gypsum, traces of B-biotite and H-hydrocalumite,



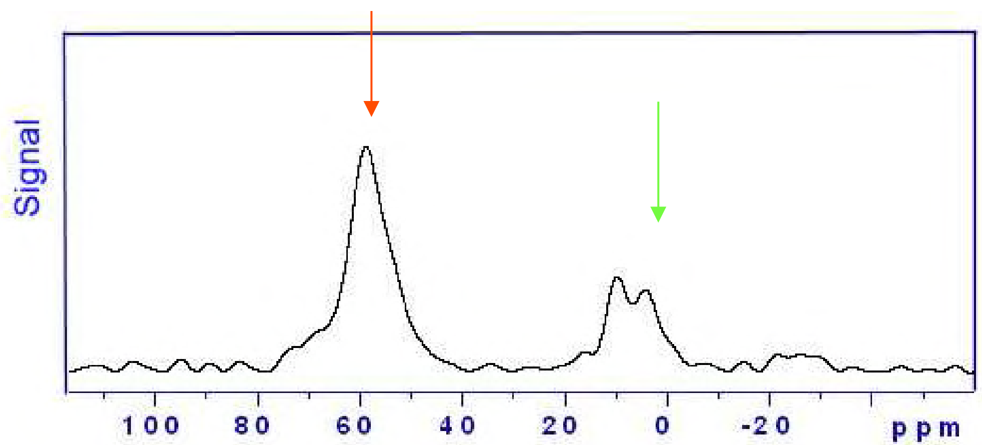
Chemical analysis of the Side mortar

- Portlandite and calcite are confirmed by high LOI data, obvious is the content of quartz but alumina content does not take part of any crystal phases.
- If the mass components, detected by XRD, do not include alumina we could identify its XRD „hidden“ form by ^{27}Al MAS-NMR and calculate the composition of eventual substitute.

Side mortar	CaO	$Si0_2$	Al_2O_3	Na_2O	K_2O	MgO	Fe_2O_3	LOI
wt. %	37.26	22.68	4.18	≤ 0.11	0.34	2.87	1.95	29.80

The ^{27}Al MAS-NMR of mortar from Side

- The typical shift as was presented before on ppm scale, where the main peak (cca 57-58 ppm) corresponds to the four coordinated aluminum ion.
- Comparing the aluminum ions amount in position close to „0" (six aluminum coordination) with the peak on 58 ppm, we estimate the rate 25 : 75.
- We pretend the presence of formatted chains of alumino-silicates.



Ceramics or activated clay

- Addition of ceramic shards (low fired) was a possibility how to complemented calcareous matter with defined proportion of alumino-silicates. We experimentally proved that the same effect as addition of shards was obtained by the addition of thermally activated clay.
- Ceramic powdered particles were dissolved in aqueous alkali conditions (achieved by calcium), forming XRD „invisible", amorphous binding agent. The chained formation of amorphous alumino-silicates improves the quality of mortars.
- All experiments of modeled calcite/clay/quartz sand combinations: Fired separately and in variations and also fired together **show the same results** (Vicat 1820 !!). In all cases the FTIR analyses confirms chained Al-O-Si formations. (Two articles describing these experiments were recently (2012) published in International Journal of Architectonic Heritage).

Hypothesis

- The clay mineral (theoretically kaolinit) was included as an inseparable part in a fired calcite. The coordination level of aluminum ions changed during the calcination. (Common calcareous sediment always contains clays and quartz sand).
- Or the content of alumino-silicate were added in form of ceramic shards.
- During the lime slaking all requirement for alumino-silicate 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- groups are spread in dominantly calcareous surroundings.

Hydraulic module

- 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 (range from 1.7 – 9) respectively, but does not say nothing about the stability and durability of the mortars (e.g. Znojmo1 = 0.817).
- With a specification of aluminum ion coordination we could offer new possibility of mortars recognition, based on MAS-NMR analysis.
- 75 wt. % of aluminum ions are in four coordination to oxygen. The negative aluminum charges were balanced by positive calcium ion (e.g. sample Znojmo 3).

  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 $Ca^{(2+)}$)

Amorphous component, A_c =12.42 %

The form of alumino*-silicate

- If the XDR analysis does not identify the **aluminum ion (oxide)** participating in the found crystal substances (including its proportion in micas, feldspar, etc.), but its presence is evident from the chemical analysis, we suppose:
- The content of Al_2O_3 detected by chemical analysis is connected by corresponding part of SiO_2 and forms together the amorphous base of chained $(Al_2O_2.Si_2O_5)^*$.
- The calculation of $\mathbf{A_c}$ could help to formulate the combination of clay and calcareous substances which together will form the cementitious part of the mortar.

Maintenance of historical mortars

- Defined $\mathbf{A_c}$ in calcareous mortars quantifies chained alumino-silicate structures and could help to formulate substitutes for the repairs and maintenance of historical monuments.
- The use of contemporaneous materials as pure slaked lime with addition of calculated amount of “activated” kaolinitic clay and their admixture with gravel or quartz sand results in similar material as used in historical time.
- Porosity, color, proportion of calcareous substances and alumino-silicates are easily calculable.
- Many restoration works were done by mortars based on Portland cement with results in incorrigible damages on original structures.

Conclusion

- We state, that real hydraulic mortar could be prepared by the combination of thermally activated kaolinitic clay and slaked lime.
- Hydraulic properties (e.g. hardening under the water) is done by a slow and **partial polymerization** of thermally treated clayed substances in aqueous calcareous conditions.
- We suppose the distribution of shorter or longer chains formed by two alumino-silicates balanced by one atom of calcium spread in calcareous surrounding.

Thank you for your attention