

INVESTIGATIONS OF SOME ANCIENT MORTARS

Herki HELVES, Lindy PIIRI, Kalju UTSAL, Kaja KÕRGE, and
Tullio ILOMETS

Tartu Ülikooli orgaanilise keemia instituut (Institute of Organic Chemistry, University of Tartu),
Jakobi 2, EE-2400 Tartu, Eesti (Estonia)

Received 2 May 1996, revised version received 30 August 1996, accepted 8 September 1996

Abstract. A set of ancient mortars was analysed by several chemical and instrumental methods. In most cases assessing the mortar composition without thermographic methods that reveal the presence of some X-ray amorphous mineral phases was found to be very difficult. The applicability of some analytical methods to lime mortars is discussed. The best method for correct estimation of calcite content was the determination of the ignition loss between 500 and 1000°C. The addition of Mg compounds to the binder is justified only for brucite because of the lack of its carbonation under North-European climatic conditions. There was no evidence of the use of hydraulic additives in ancient mortars.

Key words: ancient mortars, analytical methods, thermal analysis.

INTRODUCTION

Ancient mortars are defined as mortars used before the beginning of the “cement age”. Systematic examinations of ancient mortars have been performed all over the world. Interest in and need for the analytical investigation has grown especially from the 1980s [1]. The reasons for such studies are both theoretical and practical. The composition, properties, and possible age of the ancient mortars, old building technologies, and sources of raw materials are of theoretical interest. From the practical aspect information on mortar composition is needed for correct and authentic restoration work and wider use of lime mortars, which have some better properties than concrete [2–4].

Since 1993, an investigation of ancient mortars has been carried out in the laboratory of conservation chemistry of the Institute of Organic Chemistry, University of Tartu. Mortar samples were taken mostly from Jaani (St. John’s) church (14th century) in Tartu, but also from several other historic buildings, sites, and archaeological excavations from the

cities of Tartu, Tallinn, and Viljandi. The total number of mortar samples analysed reaches one hundred. The aim of the investigations reported here was to find out possibilities and suitable methods for lime mortar analysis.

EXPERIMENTAL

Applying chemical methods, the amount of the fraction soluble in water, the acid insoluble portion, the solubilized Ca and Mg, and eliminated CO_2 were estimated. For the determination of proteinic additives in mortar, ninhydrin tests were performed. Water soluble salts were specified by chemical tests and ion chromatography. Acid insoluble fractions were examined by sieve analysis and also the fraction easily soluble in alkali (saturated solution of Na_2CO_3) was established. Thermal analysis (TA) was performed stepwise, and by differential thermographic methods with Netzsch STA 409 (50 mg samples in Pt crucibles, 10 K/min, 20–1000°C, O_2 75 cm^3/min). X-ray diffraction (XRD) spectra, SEM micrographs, and X-ray microanalysis were applied. Water absorption, porosity, and density were also estimated.

Mortar samples were dried at room temperature for at least one week. Crushing was done carefully in iron mortar, not disrupting the original aggregate size distribution. Rarely present particles bigger than 3 mm were excluded by sieving. From the crushed sample about 20 g was taken for the determination of acid (HCl 1 : 2) insoluble part. From the aliquot of the solution, Ca and Mg were complexometrically titrated [5, 6]. The insoluble residue was washed, dried, weighed, and sieved with a set of sieves. The remaining part of the sample was crushed to particles smaller than 1 mm and was used in further experiments. Mortar strength was evaluated subjectively while crushing the sample for analysis.

Water absorption, porosity, and density were estimated by keeping a suitable piece of mortar sample under water in vacuum for 24 h and weighing it before and after diving. The volume of the test sample was calculated by weight loss in water.

Ninhydrin solution in ethanol was 0.1%. About 1 cm^3 of the sample and 1–2 cm^3 of the solution were heated in a closed test tube near boiling and left to cool down. After 24 h the colour of the solution was evaluated. The test was counted positive if there occurred some colour from red to blue.

The water soluble part (salts) was evaluated by extracting a few grams of the prepared sample powder many times with hot water. The filtrate was evaporated to dryness, dried at 105°C, weighed, dissolved in a few millilitres of water, and chemical tests for Cl^- , NO_3^- , and SO_4^{2-} were performed. The same ions were determined quantitatively from a parallel water extract by anion chromatography on Anieks N column with indirect UV detection.

The ignition loss was determined with 5 g samples. First the adsorption water was eliminated by drying at 105°C, then the crucibles with samples were heated in a muffle oven at 650°C and finally at 1000°C. The weight loss during heating at 1000°C corresponds to decarbonation and therefore the CaCO₃ content was calculated from the evolved CO₂.

CO₂ was determined also directly with the Mohr apparatus, where a few grams of the sample react with HCl and the formed gases exit through concentrated SO₄²⁻. Mass difference is calculated to CaCO₃ in the same way as in the case of the ignition method.

Preliminary results of the analyses of some mortar samples from different parts of Jaani church are given in Table 1. By running parallel determinations, the confidence limits of the applied methods were evaluated for sample JK-112 (*n* = 5 for most analyses). The precision of the titrimetric analysis was checked with known mixtures of reagents (Merck) in similar proportions of Ca and Mg to lime mortars. The deviation from the calculated values was 0.1% for Ca and 0.6% for Mg.

Table 1

Basic results of the analysis of mortar samples from Jaani church

Parameter	Sample				
	JK-51	JK-52	JK-54	JK-74	JK-112
Strength	very strong	strong	strong	strong	very strong
Water absorption, m%	15	21	14	16	28±3
Porosity, v%	27	32	26	29	40±2
Density, g/cm ³	1.8	1.5	1.8	1.8	1.4±0.1
Ninhydrin reaction, +/-	+	+	-	-	-
Water soluble, %	1.1	1.6	1.2	1.6	1.57±0.08
HCl (1 : 2) soluble, %	36	43	37	33	41.8±0.7
Ignition loss 105–650°C, %	7.7	10.6	7.5	3.6	8.3±0.2
Ignition loss 650–1000°C, %	10.1	10.8	10.0	11.8	6.0±0.1
CO ₂ %, directly	14.5	17.1	13.1	13.6	6.5
Ca %, titration	8.8	10.4	10.4	11.2	10.0±0.2
Mg %, titration	2.9	4.3	1.2	1.2	5.4±0.1
SO ₄ ²⁻ %, precipitation	-	0.67	0.99	0.78	-
Alkali soluble part of the sand residue, % from the sample	2.9	1.6	5.4	1.4	2.3±0.3
Size distribution of the sand residue, %					
1–3 mm	7	9	6	12	0.26±0.06
0.25–1 mm	67	75	68	42	81±1
<0.25 mm	26	16	25	46	19±1

RESULTS

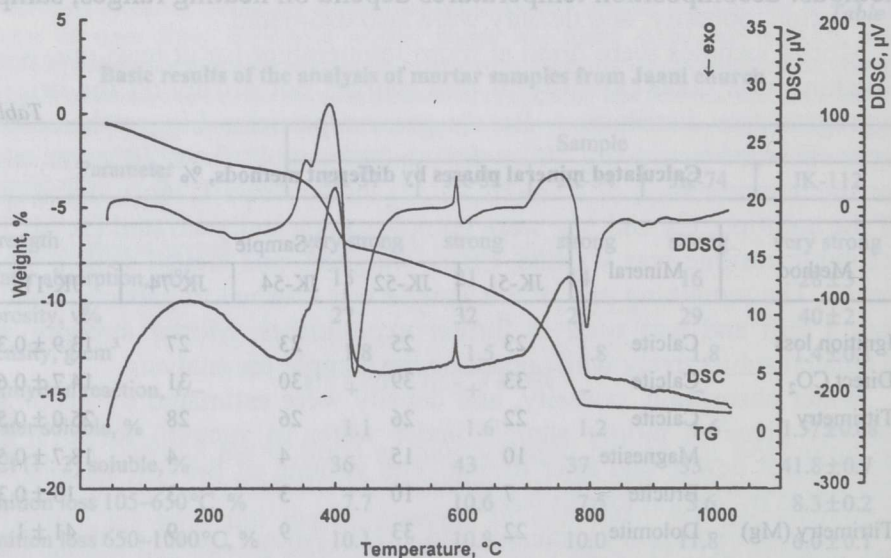
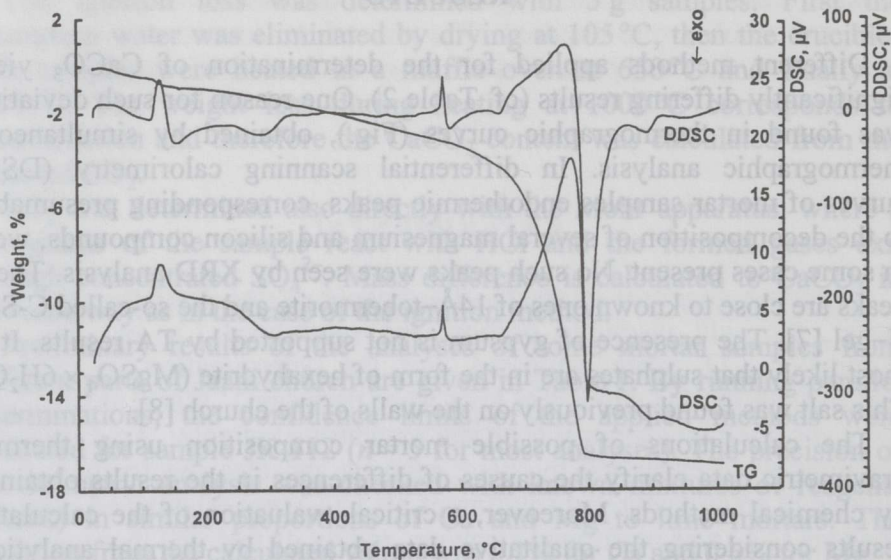
Different methods applied for the determination of CaCO_3 yield significantly differing results (cf. Table 2). One reason for such deviation was found in thermographic curves (Fig.), obtained by simultaneous thermographic analysis. In differential scanning calorimetry (DSC) curves of mortar samples endothermic peaks, corresponding presumably to the decomposition of several magnesium and silicon compounds, were in some cases present. No such peaks were seen by XRD analysis. These peaks are close to known ones of 14\AA -tobermorite and the so-called C-S-H II-gel [7]. The presence of gypsum is not supported by TA results. It is most likely that sulphates are in the form of hexahydrate ($\text{MgSO}_4 \times 6\text{H}_2\text{O}$). This salt was found previously on the walls of the church [8].

The calculations of possible mortar composition using thermogravimetric data clarify the causes of differences in the results obtained by chemical methods. Moreover, a critical evaluation of the calculated results considering the qualitative data obtained by thermal analytical methods shows them to be in agreement with the results gained by chemical methods. Nevertheless, there are problems with thermographic methods: decomposition temperatures depend on heating ranges, sample

Table 2

Calculated mineral phases by different methods, %

Method	Mineral	Sample				
		JK-51	JK-52	JK-54	JK-74	JK-112
Ignition loss	Calcite	23	25	23	27	13.9 ± 0.3
Direct CO_2	Calcite	33	39	30	31	14.7 ± 0.6
Titrimetry	Calcite	22	26	26	28	25.0 ± 0.5
	Magnesite	10	15	4	4	18.7 ± 0.5
	Brucite	7	10	3	3	13 ± 0.3
Titrimetry (Mg)	Dolomite	22	33	9	9	41 ± 1
Gravimetry	Gypsum	-	1.2	1.8	1.4	-
DSC						
340-480°C	Brucite	3	12	8	-	13
420-560°C	Magnesite	6	6	-	-	-
580-800°C	Calcite	25	27	26	36	14
XRD	Quartz	59.7	56.8	56.6	58.7	65.3
	Feldspar	8.7	6.4	9.7	7.8	4.9
	Calcite	27.5	30.7	28.7	27.6	19.4
	Dolomite	4.0	6.1	5.1	5.9	-
	Brucite	-	-	-	-	10.5



Thermogravimetric curves of samples JK-74 (above) and JK-112 (below).

masses and compositions [7, 9]. Therefore, additional evidence from other methods is needed to be sure of the identification of DSC peaks. Still, these curves may be considered as characterizing and illustrative patterns, we may call them even “fingerprints” of mortars.

XRD analysis is important for differentiating carbonates of lime and sand origin and for verifying the presence of some minerals. The lack of carbonation of $Mg(OH)_2$ shows the dolomite found in mortar to be terrigenous. The results of XRD analysis sometimes differed significantly from data obtained by other methods. This might be due to the occurrence of non-crystal or distorted mineral phases. The XRD results show usually higher contents of main minerals.

X-ray microanalysis indicated different distribution of Ca and Mg in mortars. On the SEM images different crystal structures on the mortar surface were also seen.

The investigation of the granulometric composition of acid insoluble residue (sand contains sometimes minerals soluble in acid) allows us to evaluate the quality of the sand used. Good building sand is supposed to be fine, with a uniform size distribution [10, 11].

Mortars are rather inhomogeneous and that is probably the biggest obstacle in assessing their exact composition. For that reason the precision of analytical methods (e.g. Ca and Mg titration) is not crucial for the analysis. Ancient mortar samples are usually available in rather small quantities and so the evaluation of confidence limits is impossible. However, for sample JK-112 it was done. For lime mortar analysis the highest precision for main constituents seems to be about $\pm 1\%$. The best method for the determination of calcite percentage is the ignition loss in the range 500–1000°C, because in this case there is no influence from other minerals, notable in other methods. The necessity to add to calcite also Mg minerals for the calculation of the binder content exists only if brucite has been detected. The addition of the alkali-soluble portion of the residue sand as the indicator of possible hydraulic additives to the binder percentage becomes important when it exceeds certain limits (although these limits are not sharply defined).

It is interesting to note that the most porous mortar sample JK-112 is on the other hand one of the strongest, and brucite makes up about one third of its binder.

CONCLUSIONS

The analysis of mortars is reported to be very complicated [12]. This is supported by our experience. A number of analyses are needed to get a correct picture about mortar composition. The application of thermal analytical methods is advisable. They are informative for evaluating the real mineral composition of mortars as they show the presence of some amorphous phases, some Mg, and Si compounds. The most correct method for the determination of calcite could be the estimation of weight loss during ignition between 500 and 1000°C. XRD analysis does not show all components in mortar mixtures but it is important for differentiating carbonates of lime and sand origin. Because of the lack of

carbonation of brucite, dolomite found in mortars is terrigenous and originates from sand.

Our data indicate a possible use of "fat" lime mortars as their binder content is relatively low. Some samples from lower brick layers contain a considerable amount of brucite. It may have been done on purpose to make the mortar more water-resistant as the solubility of calcite in CO₂-rich water is about 140 times bigger than that of brucite.

ACKNOWLEDGEMENTS

The financial support by the Volkswagen-Stiftung is gratefully acknowledged. The authors are thankful to Dr Gabriele Grassegger, Forschungs- und Materialprüfungsanstalt Baden Württemberg, Otto-Graf Institut, Stuttgart.

REFERENCES

1. Nöller, R. *Schäden an Ziegelbauten und ihre Behebung; Baupraxis+Dokumentation*, 4. Expert-Verlag, Ehningen bei Böblingen, 1992.
2. Doglioni, F. The importance of the plaster for the authenticity of conservation in architectural restoration. In *Conservation of Architectural Surfaces*. Il Cardo editore, Venice, 1993, 37-42.
3. Zappia, G., Sabbioni, C. & Pauri, M. G. Damage induced by atmospheric aerosol on ancient building materials. *J. Aerosol Sci.*, 1992, 23, suppl. 1, S917-S920.
4. Lindqvist, J. E., Schouenborg, B., Sandstroem, M., Sandstroem, H., Sandin, K. & Sidmar, E. Comprehensive studies of old mortars from three medieval churches in Southern Sweden. In *Proc. 16th Int. Conf. Cem. Microsc.*, 1994, 306-322.
5. Nerchik, F. I. Uskorenyj analiz silikata s primeneniem trilona B. *Izv. Kievsk. politekhn. instituta*, 1960, XXIX, 1, 119-121.
6. Knöfel, D. & Schubert, P. (eds.). *Mörtel und Steineränzungsstoffe in der Denkmalpflege*. Verlag Ernst & Sohn, Berlin, 1993.
7. Mackenzie, R. C. (ed.). *Differential Thermal Analysis*, vol 2. Academic Press, London, 1972.
8. Piiri, L., Utsal, K., Helves, H., Kõrge, K. & Ilomets, T. Tartu Jaani kiriku terrakotamaterjalide kahjustused soolade toimel. *XXVII Eesti keemiapäevade teaduskonverentsi ettekannete referaadid*, Tartu, 1996.
9. Vecchio, S., La Ginestra, A., Frezza, A. & Ferragina, C. The use of thermoanalytical techniques in the characterisation of ancient mortars. *Thermochim. Acta*, 1993, 227, 215-223.
10. Bache, H. H. Model for strength of brittle materials built up of particles joined at points. *J. Am. Ceram. Soc.*, 1970, 53, 12, 654-658.
11. Adams, J., Dollimore, D. & Griffiths, D. L. Thermal analytical investigation of ancient mortars from Gothic churches. *J. Therm. Anal.*, 1993, 40, 1, 275-284.
12. Deloye, F.-X. Le calcul minéralogique. Application aux monuments anciens. *Bull. Liaison Lab. Ponts Chaussées*, 1991, 175, 59-65.

MÕNEDE AJALOOLISTE LUBIMÖRTIDE UURIMINE

Herki HELVES, Lindy PIIRI, Kalju UTSAL, Kaja KÕRGE,
Tullio ILOMETS

Ajalooliste lubimörtide analüüsil kasutati mitmeid keemilisi ja instrumentaalseid meetodeid. Leiti, et mördi täpse koostise selgitamine on üsna töömahukas ja röntgenamorfsete mineraalsete faaside identifitseerimiseks on vaja rakendada termilist analüüsi. Mitmed mördi analüüsil kasutatavad meetodid annavad ebakorrektsed tulemused, kui ei arvestata mineraalsete faaside paljust. Uuriti kasutatud meetodite rakendatavust ja täpsust lubimördi analüüsil.

Parim kaltsiidi määramise meetod on kuumutuskaos selgitamine temperatuurivahemikus 500–1000 °C. Mg liitmine sideaine hulka on mõeldav vaid juhul, kui see esineb brusiidina, sest viimane ei karboneeru Eesti kliimas. Oletatavasti on seda mineraali veekindluse tõstmiseks teadlikult lisatud maapinnalähedastesse mördikihtidesse. Hüdraulilisi lisandeid uuritud mörtides arvestataval hulgal ei leitud.