CZECH TECHNICAL UNIVERSITY IN PRAGUE
Faculty of Civil Engineering
Thákurova 7, 166 29 Prague 6, Czech Republic

MASTER‘S THESIS PROPOSAL

study programme:	Civil Engineering
study branch:	Advanced Masters in Structural Analysis of Monuments and Historical Constructions
academic year:	2017/2018

Student’s name and surname:	Lavina jain
Department:	Department of Mechanics
Thesis supervisor:	Jan Válek
Thesis title:	Determination of component ratio in a historic lime-based mortar
Thesis title in English	see above

Framework content: The dissertation focuses on the study of binder to aggregate ratio of historic lime-based mortar. This work aims to study selected analytical methods used for the determination of binder to aggregate ratio to provide data about the reliability of these methods and evaluate their validity for conservation practice.

Assignment date:	9/04/2018	Submission date:	02/07/2018

If the student fails to submit the Master’s thesis on time, they are obliged to justify this fact in advance in writing, if this request (submitted through the Student Registrar) is granted by the Dean, the Dean will assign the student a substitute date for holding the final graduation examination (2 attempts for FGE remain). If this fact is not appropriately excused or if the request is not granted by the Dean, the Dean will assign the student a date for retaking the final graduation examination, FGE can be retaken only once. (Study and Examination Code, Art 22, Par 3, 4.)

The student takes notice of the obligation of working out the Master’s thesis on their own, without any outside help, except for consultation. The list of references, other sources and names of consultants must be included in the Master’s thesis.

Master’s thesis supervisor Head of department

Date of Master’s thesis proposal take over: July 2018

Student

This form must be completed in 3 copies – 1x department, 1x student, 1x Student Registrar (sent by department)

No later than by the end of the 2nd week of instruction in the semester, the department shall send one copy of BT Proposal to the Student Registrar and enter data into the faculty information system KOS. (Dean's Instruction for Implementation of Study Programmes and FGE at FCE CTU Art. 5, Par. 7)

DECLARATION

Name:	Lavina jain
Email:	gcad10114@gmail.com

Title of the MSc Dissertation:	Determination of component ratio in a historic lime-based mortar
Supervisor(s):	Jan Válek, PhD
Year:	2018

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

I hereby declare that the MSc Consortium responsible for the Advanced Masters in Structural Analysis of Monuments and Historical Constructions is allowed to store and make available electronically the present MSc Dissertation.

University:	Czech Technical University, Prague
Date:	2nd July, 2018
Signature:	

This page is left blank on purpose.

This dissertation work is dedicated to

my lovely parents Devender and Sarita,

my beloved fiancé Ashish,

my dearest brother and sister Sachin and sakshi

and my best friend sakshi.

This page is left blank on purpose.

ACKNOWLEDGEMENTS

I would first like to thank my thesis supervisor Jan Válek and ITAM (experimental centre for traditional lime technologies). The door to Jan Válek office was always open whenever I ran into a trouble spot or had a question about my research or writing. He consistently allowed this paper to be my own work, but steered me in the right direction whenever he thought I needed it.

I would also like to thank the experts who were involved in the validation study for this research work: Olga Skružná for chemical analysis, Petr Kozlovcev for optical microscopy and Dita Frankeova for thermal analysis. Without their passionate participation and input, the experiments could not have been successfully conducted. I am also thankful to civil engineering department of Czech technical university, prague for giving this opportunity. Amongst the team at the university, I would like thank coordinator Petr Kabele and secretariat Alexandra Kurfurstova.

I would also like to acknowledge my fiancé Ashish Shakuniya as the second reader of this thesis and I am gratefully indebted for his valuable comments and emotional support throughout this thesis. He was always been there whenever I needed him.

I would also like to express my very profound gratitude to my parents and my siblings for providing me with unfailing support and continuous encouragement throughout my study and writing this thesis. This accomplishment would not have been possible without them.

Last but not the least; I would like to thank my dear friends Sakshi Jain, Pratik Gajjar, Ali abbas, Omkar Adhikari and Carlo Alarcon for supporting me spiritually and emotionally throughout my study.

This page is left blank on purpose.

ABSTRACT

Lime-based mortar is the most commonly used material in restoring heritage structures by imitating the original one. Therefore, there has been a great number of research and practical attempts to replicate the historic lime-based mortars, but still many aspects of this subject are unexplored. Historic mortars are different from the modern ones and are more compatible with historical substrates. The limitations in the successful use in building conservation are the lost practical and theoretical information between the generation and minimum availability of technically oriented written records. In order to imitate the procedure, it is necessary to understand the character of binder and aggregate that is governed mainly by the type of binder, type and grain size distribution of aggregates and their mix proportions. The use of characterisation testing is considered in the context of data needed to have a successful formulation of a repair mortar for conservation practice.

The dissertation is centralised on the determination of binder to aggregate ratio of historic lime-based mortar including analysing the properties of binder matrix. Four analytical methods were selected to carry out the study and their outputs were analysed to check the reliability of these methods for conservation practice. The methods are laboratory based chemical analysis, optical microscopy, thermal analysis and scanning electron microscopy with energy dispersed spectrometric analyser. Mortar samples were collected from five different types of flooring, which had been recreated for conservation purposes. The examination of binder to aggregate ratio was discussed in comparison with the reference of original mortar mixing ratios and the results from the analytical methods were reviewed.

Keywords: Characterisation of lime mortars, mixing ratio, lime mortar, NHL, air lime, lime-pozzolana binder, historic lime floors.

This page is left blank on purpose.

ABSTRAKT

Vápenná malta je nejčastěji používaným materiálem při obnově památek, kdy je využíváno napodobení původního složení. Pokusů o napodobení historické vápenné malty tak bylo již mnoho, ale stále ještě mnoho aspektů tohoto tématu zůstává neprobádáno. Historické malty se od moderních malt liší a jsou s historickými materiály kompatibilnější. Omezeními pro zdárné využití v památkové péči jsou mezigenerační ztráta teoretických i praktických znalostí a nedostatek technicky zaměřených archivních pramenů. Za účelem napodobení postupu je nutné pochopit charakter pojiva a plniva, který je daný zejména druhem pojiva, druhem a velikostním rozložením zrn kameniva a jejich poměrem mísení. Použití testů charakterizace je hodnoceno v kontextu informací potřebných pro úspěšnou formulaci opravné malty pro konzervační praxi.

Diplomová práce se soustředí na určení poměru pojiva ku kamenivu historické vápenné malty včetně analýz vlastností pojivové matrice. Pro provedení této studie byly vybrány čtyři analytické metody a jejich výstupy byly analyzovány s cílem ověřit spolehlivost těchto metod pro konzervační praxi. Metody jsou založeny na laboratorní chemické analýze, optické mikroskopii, termické analýze a skenovací elektronové mikroskopii vybavené energiově disperzním spektrometrem. Vzorky malty byly odebrány z pěti různých typů podlah, které byly vytvořeny jako kopie pro účely památkové ochrany. Zkoumání poměru pojiva ku kamenivu bylo diskutováno ve srovnání s původním poměrem míseni a výsledky z analytických metod byly detailně zhodnoceny.

Klíčová slova: analýza vápenných malt, poměr mísení, vápenná malta, NHL, vzdušné vápno, vápeno-pucolánové pojivo, historická vápenná podlaha

This page is left blank on purpose.

सार

चूना-आधारित मोर्टार मूल रूप से अनुकरण करके विरासत संरचनाओं को बहाल करने में सबसे अधिक उपयोग की जाने वाली सामग्री है। इसलिए, ऐतिहासिक चूने-आधारित मोर्टार को दोहराने के लिए अनुसंधान और व्यावहारिक प्रयासों की एक बड़ी संख्या रही है, लेकिन इस विषय के कई पहलुओं को अनदेखा किया गया है। ऐतिहासिक मोर्टार आधुनिक मोर्टार से अलग हैं और ऐतिहासिक सबस्ट्रेट्स के साथ अधिक संगत हैं। संरक्षण के निर्माण में सफल उपयोग की सीमाएं तकनीकी रूप से उन्मुख लिखित अभिलेखों की पीढ़ी और न्यूनतम उपलब्धता के बीच खोए व्यावहारिक और सैद्धांतिक जानकारी हैं। प्रक्रिया की नकल करने के लिए, बांधने वाले और कुल योग के चरित्र को समझना जरूरी है जो मुख्य रूप से बांधने वाले प्रकार, प्रकार और अनाज के आकार के वितरण और उनके मिश्रण अनुपात के प्रकार से शासित होता है। संरक्षण अभ्यास के लिए मरम्मत मोर्टार के सफल फॉर्मूलेशन के लिए आवश्यक डेटा के संदर्भ में विशेषता परीक्षण का उपयोग माना जाता है।

शोध प्रबंध को बाइंडर मैट्रिक्स के गुणों का विश्लेषण करने सहित ऐतिहासिक चूने-आधारित मोर्टार के कुल अनुपात के लिए बाइंडर के निर्धारण पर केंद्रीकृत किया जाता है। अध्ययन करने के लिए चार विश्लेषणात्मक तरीकों का चयन किया गया था और संरक्षण अभ्यास के लिए इन विधियों की विश्वसनीयता की जांच के लिए उनके आउटपुट का विश्लेषण किया गया था। विधियां प्रयोगशाला आधारित रासायनिक विश्लेषण, ऑप्टिकल माइक्रोस्कोपी, थर्मल विश्लेषण और स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी ऊर्जा फैलाने वाले स्पेक्ट्रोमेट्रिक विश्लेषक के साथ हैं। मोर्टार नमूने पांच अलग-अलग प्रकार के फर्श से एकत्र किए गए थे, जिन्हें संरक्षण उद्देश्यों के लिए बनाया गया था। मूल मोर्टार मिश्रण अनुपात के संदर्भ के मुकाबले कुल अनुपात में बाइंडर की जांच पर चर्चा की गई और विश्लेषणात्मक तरीकों के परिणामों की समीक्षा की गई।

कीवर्ड: चूना मोर्टार, मिश्रण अनुपात, नींबू मोर्टार, एनएचएल, वायु चूना, नींबू-पॉज़ज़ोलाना बांधने की मशीन, ऐतिहासिक चूने के फर्श का वर्गीकरण।

This page is left blank on purpose.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

'Lime is a calcium-containing inorganic mineral in which oxides and hydroxides predominate'

'Mortar is a paste used to bind the building blocks'

Since the period of earliest civilizations, lime mortar has been considered as a major binder in construction and repair works of historic buildings around the globe. The earliest discovery of lime mortar was dated approximately 6000-7000 BC (John J Hughes, 2003), when limestone burnt and mixed with water and sand was used to produce material that would harden with age. The initiation of the use of lime mortar is not well documented. However, air lime mortar was used by Egyptians and Romans used hydraulic lime mortar with pozzolans in construction extensively. They also provided the guidelines for different mixes with higher strength and durability (Graymount, 2016). Whereas, over the period of time, numerous methods evolved to enhance the strength and durability of lime mortar. By adding different additives, for instance, Romans used to add blood, milk, and fats (A. Moropoulou *, 2005) likewise Indians used organics namely curd, jaggery, cactus extract, bel pulp, lentils and oil of margosa (R. Ravia, 2018).

Historic lime based binders can be divided into air lime, natural hydraulic lime, and a pozzolanic material.

Air lime

Air lime is also referred as non-hydraulic lime, high calcium lime, pure lime or fat lime. By nature, it is softest and most porous but when used then it is highly durable. Air lime is made up from chalk or limestone (calcium carbonate), and it hardens very gradually over the time to achieve full strength. The available form of air lime is either in dry powder or as lime putty but both are chemically identical. Dry powder is made up under the controlled condition where there should be no excess water once slaking is complete, whereas lime putty contains more water than needed for completion of slaking, resulting in a sticky wet paste. After slaking, lime putty should be matured in a pit or container, which allows excess water to drain away before it is ready to use. The longer it is matured, the better it will work. Today, air lime is widely used for conservation work, as it is suitable for the traditional building made up from stone, clay brick, and many other ancient materials. (Ashurst, 1983) (Cowper) (Modena, 2005)

Natural hydraulic lime

Natural hydraulic lime is different from air lime as it is made up of impure limestone. The impurities are particularly clay minerals such as silica and alumina, which become reactive when burned in the kiln and combine with quicklime to form hydraulic compounds. It can be slaked with water like air lime but the hardening process starts as soon as mixed with water. As a result, hydraulic lime needs to be used soon after slaking and difficult to store for a longer period. Nowadays, hydraulic lime is supplied in the form of powder in an airtight container to keep it for long. Comparatively, natural hydraulic lime reacts faster with water to form solid compounds than air lime and start gaining strength. Hydraulic lime also

contains variable proportions of calcium hydroxide, which carbonates slowly, in exactly the same way as non-hydraulic lime, and results in a gradual increase in strength of the lime, following the initial comparatively rapid hydraulic set. This lime is used for rough rendering shortly after mixing, but for fine work air lime is the best option because there is a risk of unslaked lime particles due to in situ slaking. The unslaked lime particle can cause disruption in the finished surface, for such work usually mature air lime putty is used. (Ashurst, 1983) (Cowper) (Modena, 2005)

Lime pozzolana hydraulic binder

Roman architect and engineer Vitruvius, described in his work about proportions and uses of pozzolanic mortars in all manner, not only on land but exceptionally under the sea. The knowledge allowed the Roman builders to create the structures in the sea or along the shorelines that previously would have been impossible. This technique revolutionized the design of harbour and other maritime structures – the use of a hydraulic lime-pozzolan binder. By some means, Romans found that when volcanic ash sand from quarries around the bay of Pozzuoli was mixed with lime, it made a stiff mortar that could be laid and cured underwater. Contained within formwork and laid in layers with large lumps of stone or tuff aggregate, it would set into a solid mass that has proved to resist the current of the sea for 2000 years. (C.J Brandan, 2014)

The pozzolanic mortar was made up with a highly reactive aluminosilicate component (pumice and volcanic ash) that when mixed with lime it led to the formation of strong reaction products. Vitruvius strongly recommended that it was necessary to use pozzolana from the Naples region in Italy to make a hydraulic binder that could set underwater. There were many Roman harbours investigated by the expert team by collecting samples from the remains of the mortar moles. In result, experts (C.J Brandan, 2014) found the uniformities among the samples: (a) The selection of raw materials were similar which include lime, pumiceous volcanic ash, and volcanic tuff or limestone rock rubble; (b) All the studied samples showed similar lime pumiceous volcanic ash mortar mix; (c) Similar binder components: a rare mineral, Al-tobermorite crystallized in all the mortars, calcium-aluminum-silicate-hydrate (C-A-S-H) is the principal binder throughout; (d) All the samples showed hydration of the mortar mix in sea-water and sulphate and chloride ions were sequestered in distinct crystalline microstructures; (e) All the samples had roughly similar mechanical properties where compressive strength was low, overall, but the structures were highly resistant to erosion by wave action and the force of impact of large waves. (C.J Brandan, 2014).

Vitruvius precisely states that the lime should be slaked before adding to the mortar mix (J.P.Oleson, 2014). The mortar should be mixed according to his suggestion: '*in case of quarry sand, mix three portions of sand to one portion of lime. The formula is for a hydraulic mix for the structures constructed on land and for marine structures ratio is two to one by volume*.' Moreover, Vitruvius specified that the slaked lime and pozzolana must be mixed in the trough immediately before use (J.P.Oleson, 2014). He

also mentioned the use of pozzolana soon after it is dug from the pit because weathering makes it earthy and incapable of bonding with the aggregate.

Aggregate

The choice of aggregates played a vital role in determining the appearance and performance of lime mortar. They added weight and strength to the lime, acting as a filler which allows reducing shrinkage of the lime as it dries out. Technically, this can be achieved with well graded and washed aggregates. This means that there is a range of particles, incorporating both fine and coarser particles, and that very fine clay and organic matter has been removed by washing. This kind of aggregates will interlock well, the smaller grains filling the spaces between the larger ones. Aggregates, where the fraction size is same, will not interlock properly and form less cohesive mortars. Limestone aggregate exhibit higher strength due to the growth of the calcite in the mortar which develops strength enhancing the binder aggregate interface. (Lanas, 2004) Angular aggregate increases the strength of the mortar than round aggregate. The use of round-shaped aggregate increases the large pores due to low cohesion between the binder and aggregate, causing strength reduction. Angular aggregates form a better-stiffed structure, less pore, and high strength. (Lanas, 2004)

Present conservation practice

Today, in the repair and restoration work of ancient structures, it is always preferable to imitate the original lime mortar (centre, 2003). To follow the same lines, it is important to understand the type of lime binder (chemical and mineralogical composition); type of aggregate, its composition and granulometry; additives and binder to aggregate ratio. A very important aspect is also the way the binder was produced and processed to make mortar and the ways mortar was applied. The first group of characteristics can be answered by a detailed material analysis, However, the later has to be deduced from the knowledge of construction technology of the particular period. One of the crucial aspects the analysis can answer is the binder to aggregate ratio, which affects the performance and workability of mortar in both ways mechanically and physically.

It is more important or recommended to use traditional lime mortar mix because they are more permeable and more flexible than cement mortars, they are less likely to decay in stone joints and are more environmentally friendly. Lime binder enhance the mechanical properties of the mortar and improve the binding strength between two consecutive lime particles and filler minimalize the percentage of porosity. (R. Ravia, 2018)

1.1 AIM

There has been a great number of research and practical attempts to imitate the historic lime-based mortar but still many aspects of this subject are unexplored. Historic mortars differ from the modern ones prepared from the readily available materials even though they are prepared according to similar recipes. Written records are limited and practical information have been lost between generations. The dissertation focuses on the study of binder to the aggregate ratio of historic lime-based mortar. This work aims to study selected analytical methods used for the determination of binder to aggregate ratio to provide some data about the reliability of these methods and evaluate their validity for conservation practice.

Finally, the dissertation aim are as follows:

- carry out experimental analysis of mortars of known composition in order to assess the established analytical procedures
- critically evaluate the analytical results in order to suggest practical approaches for conservation practice

1.2 OBJECTIVE

1. Understand the traditional lime production and processing technologies.
2. Study analytical methods in relation to the mortar composition.
3. Select the procedure of different analytical methods and assess their suitability and determine their limits.
4. Study mineralogical characterization of components of binder and aggregate based on various lime-based binders types (air lime, natural hydraulic lime, lime-pozzolana binders).
5. Analyse the results of all the tests and compare them with the known composition of mortars that were previously produced while making the floor panels.

2. STUDY MATERIAL: FLOOR PANEL

The experimental work was carried out on mortar samples taken from a running experiment regarding the historic lime mortar flooring technologies. This experiment started in 2016 when replicas of three mortar floors were made, two according to the description of Vitruvius and one according to the traditional technique of the Venetian terrazzo that is based on the surviving knowledge of the ancient times. There were two more floor panels added in the following year that replicated three common flooring systems found in historic structures of the Czech Republic.

The five-floor panels are categorized as follows: Greek floor (Vitruvius), Roman floor (Vitruvius), Venetian terrazzo floor, lime cast floor, a three-layer system with tiles.

2.1 VITRUVIUS DESCRIPTIONS

Book of Vitruvius: The Ten books on architecture.

Book VII, Chapter I (Morris hicky morgan, 1914)

Vitruvius explained firstly pozzolanic mortar based flooring which is considered to be most important in polished finishing's, which needs utmost precaution to ensure the durability of the flooring. Starting with leveling the ground for pozzolanic mortar based flooring and making sure that soil is solid everywhere. In the case of wholly or partly filling, the ground must be rammed with care. Wooden framework is used for the flooring with the certain procedure described by Vitruvius in the book which needs to be followed for the better workability of flooring (Morris hicky morgan, 1914). Then, "*firstly, lay the bedding composed of stones but not too small that can fill the hand, then lay the broken stone layer not less than three-quarters of a foot in the proportion of 3:1 with lime, if the stone is new otherwise 5:2. Beat the broken stone layer, repeatedly until it acts like a solid mass. Next, lay the nucleus consists of crushed tile with lime in the proportion 3:1 with the thickness not less than 6". Over nucleus layer, the floor, whether it is made up of cut slips or cubes, should be organised and laid by rule and level. Rubbed the top layer after setting the floor at a proper inclination, then sift powdered marble on top, and lay a coating of lime and sand*" (Morris hicky morgan, 1914). After finishing the first stage of flooring, double protection to the framework is needed for which another system of layers laid at the right angle. "*Mix the new broken stone, one third the quantity of pounded tile, and let lime be added to the mixture in the proportion 2:5. Bedding is complete, now lay the mixture of broken stone of about a foot, after beating. Then, lay the nucleus same as above, construct the floor with large cubes of 2 x 2 and provide an inclination of two digits for every 10 feet. After putting the cubes together and rubbed down properly, it will be free from all the flaws*".

Chapter IV (Morris hicky morgan, 1914)

Another type of flooring in Greek, used for dining rooms in winter which are inexpensive and serviceable. For flooring an excavation of 2 feet is made, first rammed the ground and spread broken stones or the pounded burnt brick, at an inclination that it can find vents in the drain. Next, having filled in with charcoal compactly trodden down, a mortar mixture of gravel, lime, and ashes is laid with the depth of 6 inches. The surface leveled and smoothened with whetstone which provides the look of black pavement.

There are other works described besides flooring which can be studied as a reference. Stucco work in a damp place where the polish finish lasts without defects. On the ground floor level, apply a rendering coat of mortar which is mixed with burnt brick instead of sand, to a height of about 3' above the floor, and then lay on the stucco as a protective layer from dampness. After rendering coat, apply lime whitewash and water so that base will not reject burnt brick-layer. Here, lime whitewash works as a binder between two substances and unites them, else the base would neither take nor hold the rendering coat. Moreover, apply layers of burnt brick mortar instead of sand mortar.

2.2 VENETIAN TERRAZZO FLOOR

The art of terrazzo flooring originated from Italy with Terrazzo being a municipality in the province of Verona. The Venetian terrazzo is the oldest of today known lime based floor construction techniques, therefore requires more skilled labour with experience. Venetian flooring varies according to the size of the granule, type of marble and the aesthetic composition of the decorative motifs. The essential ingredient in the construction of floor is pebble lime. According to Crovato (1999) this binder is extracted from the river pebbles at a temperature of 800°C (calcination) and then subsequently water is added to the resulting compound, said slaked lime, which is mixed with sand and marble powder in a suitable proportion. The construction of the terrazzo with slaked lime binder involves following procedures: flattening the base, laying layers, sowing of granules, rolling, beating, smoothing, curing, sanding and polishing. (Crovato, 1999)

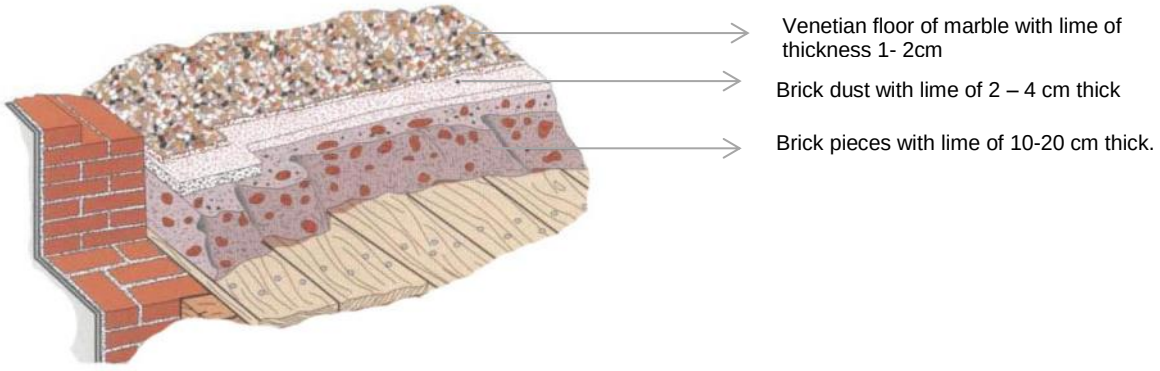


Figure 1Section of Venetian flooring

- The substrate layer is composed of crushed stones in smaller quantities, mixed with slaked lime in a 4:1 ratio.
- The intermediate layer is made up of crushed bricks that mixed with lime in a proportion of 3:1. As a result, it forms granular mortar with a pinkish colour spread on the substrate with a thickness which can vary from 2 to 4 cm. It is advisable that mortar must be mixed accurately and allowed to stand for the inert to absorb the water abundantly. Finish layer thickness varies with the size of the granule.

Figure 2 Different types of Venetian terrazzo flooring finish

- That will be sown above; generally, the thickness lies between 1 and 2 cm. it is a special mortar of fine and thick marble powder mixed with slaked lime in a proportion of 1:2. To provide particular chromatic gradations to the binder sometimes earthy colours added. (Crovato, 1999)

2.3 ROTUNDA – ONE-LAYER SYSTEM

Rotunda is one of its own types of building from the early medieval period. Precisely, it is a Romanesque church with a circular nave attached with a semi-circular apse. The oldest rotunda is still standing in the Czech Republic is St. Peter and Paul rotunda in Budeč built at the beginning of the 10th century. It is a double walled masonry structure filled with mortar with the designed brick tile floor bed shown in figure 3 (eea grants, n.d.).

(a) (b)

Figure 3 Rotunda 3D structure (Church of St. Wenceslas) at left hand side, (a) Brick tile floor (b) Cross-section of floor layers.

3. EXPERIMENTAL PART

The selection of methods for mortar analysis varies depending upon the objectives of the work. Here, the characterization of mortar is based upon the analytical methods used for determining the proportions of binder and aggregate in the historic lime-based mortar. However, other relevant characteristics can be determined and should be considered including the following:

- The composition of the mortar, including the original binder components; the mineralogy, character, and aggregates; and the presence and type of admixtures.
- The physical and mechanical properties of the mortar, including primary porosity but also colour and strength of the mortar.

The samples can be analysed with one method, but the comparison is needed between the outcomes of different methodologies for better interpretation and accuracy of the results. Accordingly, four methods were selected, out of these two methods are Chemical analysis/separation of the binder from the aggregate and petrographic analysis to determine the binder to aggregate ratio. Another two methods, Thermal analysis and Scanning electron microscopy (SEM) for analysing the binder matrix.

Table 1 The details of original floor panels recreated for building conservation purpose

Panels made 17-21.10.2016,
Panel A: Greek floor (Vitruvius) (Mixing proportions in volume units)

Sample code	Name of layers	Binder	Aggregate	Filler/Additive	Ratio B/A+F
G4	Surface layer	20 NHL DPPDR	40 Sand	5 Ash	1 : 2.25
G3	Nucleus	90 NHL DPPDR	255 Sand	15 Ash	1 : 3
G2	Rudus	100 AL K PDR	250 Sand + 50 Gavel	-	1 : 3
G1	Statumen		Dry stone construction		

Panel B: Roman floor (Vitruvius) (Mixing proportions in volume units)

Sample code	Name of layers	Binder	Aggregate	Filler/Additive	Ratio B/A+F
R6	Repair layer				
R5	Surface layer	20 AL V_{PDR}	20 Brick 0-2 + 20 Brick 0-1	-	1 : 2
R4	Nucleus (higher)	70 AL V_{PDR}	140 Brick 0–2	-	1 : 2
R3	Nucleus (lower)	70 AL V_{PDR}	210 Brick	-	1 : 3
R2	Rudus	110 NHL DP_{PDR}	275 Sand + 55 gravel	-	1 : 3
R1	Statumen		Dry stone construction		

Panel C: Venetian terrazzo (Mixing proportions in volume units)

Sample code	Name of layers	Binder	Aggregate	Filler/Additive	Ratio B/A+F
V8	Repair layer	20 NHL Z_{PDR}	40 Brick 0-4		1: 2
V7	Adhesion coat	1 AL V_{PT}	1 Brick dust	-	1: 1
V6	Surface layer	20 AL V_{PDR}	20 brick 0-1 + 20 marble dust	-	1: 2
V5	Nucleus top layer	20 AL V_{PDR}	20 Brick 0-2 + 20 Brick 0-1	-	1: 2
V4	Nucleus (higher)	70 AL V_{PDR}	140 Brick 0–2	-	1: 2
V3	Nucleus (lower)	70 AL V_{PDR}	210 Brick	-	1: 3
V2	Rudus	80 AL V_{PDR}	240 Brick	-	1: 3
V1	Statumen	AL V_{HT}	Sand	-	*1: 3^{HT}*

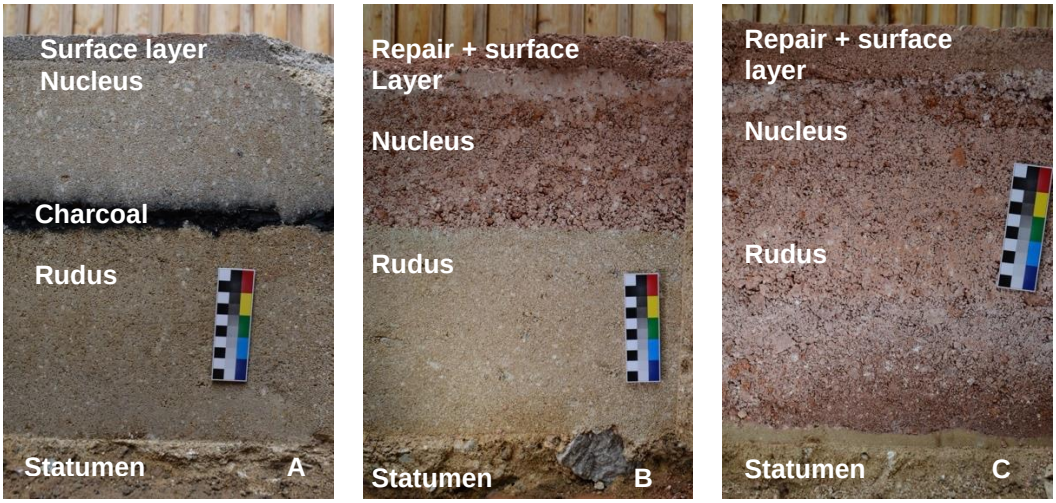


Figure 4 Cross-section of Panel A, B, and C respectively.

Panels made 3-7.4.2017

Panel D: Lime mortar cast floor (Mixing proportions in volume units)

Sample code	Name of layers	Binder	Aggregate	Filler/Additive	Ratio B/A+F
	Surface layer		Leveled and decorated with stone pieces		
L2	Nucleus /Rudus	60 NHL Z_{HT}	120 Sand		1: 2
L1	Statumen		Dry stone construction		

Panel E: Three-layer system with tiles (Mixing proportions in volume units)

Sample code	Name of layers	Binder	Aggregate	Filler/Additive	Ratio B/A+F
E4	Surface layer		Brick Tiles	-	
E3	Nucleus	NHL	RUM (recycled universal building material)	-	1: 3
E2	Rudus	NHLZ	Brick 0-4		1: 2
E1	Statumen	NHL B_{HT}	Sand - mortar layer on top of dry stone construction	-	*1: 3^{HT}*

Binders
NHL DP – Dvorce-Prokop limestone, Hvížďalka quarry (DPH/DPS 2015?)
NHL Z – Zlíchov limestone, Hvížďalka quarry (2014?)
NHL B – Dvorce-Prokop limestone, Branik quarry (2013?)
AL V – air lime Vitošov (2015?)
AL K – air lime KCS 2014
$_{PDR}$ – slaked to powder before use
$_{PT}$ – lime putty, Vitošov II
$_{HT}$ – Hot mixed

Aggregates
Sand - Černuc F0–4 mm
Brick 0-1: crushed brick F0–1 mm
Brick 0-2: crushed brick F0–2 mm
Brick: crushed brick F0-4 mm

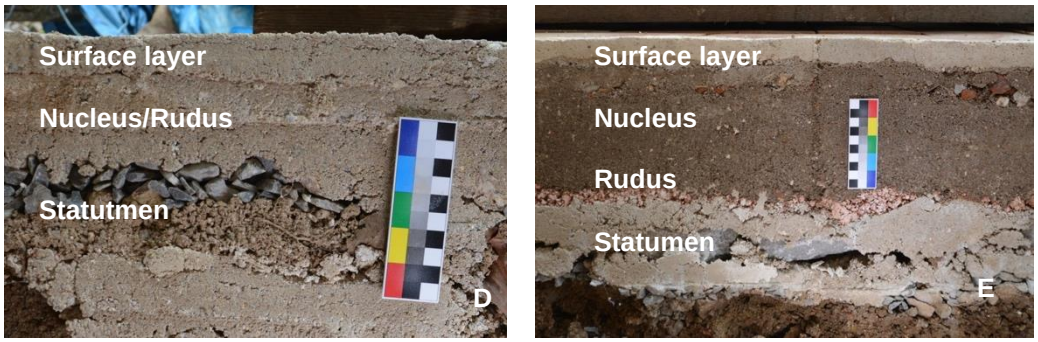


Figure 5Cross-section of the Panel D and E respectively.

From above floor panels, 11 samples were taken for above-mentioned tests (refer table 2). Selection of the samples was made up based on types of aggregates and type of lime used for the mix. To avoid repetition, out of 11 samples, 5 samples were selected for petrographic analysis and scanning electron microscopy. In thermal analysis, V1 and V8 excluded due to the loss of sample and not being able to collect the fine fraction under 63 µm respectively.

The determination of the binder to aggregate ratio was intentionally carried out without knowing the mixing proportions, type of sand and its granulometry to objectively assess the tests.

The samples were divided into four groups according to the nature of the binding system as follows:

Air lime with sand/gravel –G2, and V1

Air lime with crushed brick–R6-R5, R3, and V2

Natural hydraulic lime with sand/gravel – G4, G3, R2, L2, and E1

Natural hydraulic lime with crushed brick – V8

Table 2 A lists of the selected mortar samples with the analysis and floor typology for each sample.

Sample name	Layer	PLM	AD	TGA	SEM
Panel A: **Greek floor (Vitruvius)**					
G4	Surface layer		✓	✓	
G3	Nucleus	✓	✓	✓	✓
G2	Rudus	✓	✓	✓	✓
Panel B: Roman floor (Vitruvius)					
R6-R5	Repair layer/Surface layer		✓	✓	
R3	Nucleus (lower)		✓	✓	
R2	Rudus	✓	✓	✓	✓
Panel C: Venetian terrazzo					
V8	Repair layer	✓	✓		✓
V2	Rudus	✓	✓	✓	✓
V1	Statumen		✓		
Panel D: Lime mortar cast floor					
L2	Nucleus /Rudus	✓	✓	✓	✓
Panel E: Three-layer system with tiles					
E1	Statumen		✓	✓	

3.1 METHODS AND PROCEDURE

Samples were studied based on the three main analysis: chemical analysis, petrographic analysis, and thermal analysis. A specified procedure followed to test all the samples and asses the binder matrix and aggregates. The material medium of assessing these analyses are different such as chemical analysis: acid, petrographic analysis: thin section, and thermal analysis: sieved binder under 63 μm. However, the accuracy of the results is also important and the amount of data from an analysis.

3.1.1 CHEMICAL ANALYSIS

Acid treatment

Chemical analysis is the method used for disaggregating or separating a mortar sample by dissolving the binder using dilute acids. It also allows the determination of the chemical composition of the acid-

soluble binder and, after separation, information in the mortar's aggregate. There is one limitation of the chemical analysis if the aggregate is also soluble in acid solution. (Middendorf B. H., 2005).

Used procedure

The sample was dried in an oven at 60 ˚C until the mass consistency reached, and then weighed by a precision balance. The dried sample was dissolved in diluted acetic acid (CH_3 COOH) of ratio 1:9, then stirred it properly and left the solution for about 3 hours. The procedure was repeated until all the binder got dissolved. Concentrated acetic acid was added in the end, to make sure of separation. The dissolved solution filtered with the help of filter paper and poured some distilled water over insoluble residue. After filtering, the residue on the filter was dried and weighed to measure the exact amount of aggregates. Also, washed the insoluble aggregates for about 3-4 minutes with water to prevent precipitation of sulphates while drying in an oven (60^0 C).

The insoluble sample in acetic acid

Most binders were easily soluble in acetic acid but few binder compositions had limit saturation concentrations. Consequently, they cannot be dissolved away completely. Therefore, the procedure was repeated with diluted hydrochloric acid (1:5) and with concentrated hydrochloric acid, when needed.
Acid soluble and insoluble ratios were calculated using equations (1) and (2) respectively.

$$\text{Soluble (\%)} = [(M_m – M_a)/M_m] \times 100 \quad (1)$$

$$\text{Insoluble in Acid (\%)} = 100\% - \text{soluble (\%)} \quad (2)$$

Where: M_m = weight of mortar sample and M_a = weight of the insoluble

Sieve analysis

To determine the size distribution of aggregates, the sieve analysis is an effective method. The aggregate size distribution is defined through the mass. There are many methods for sieve analysis such as manual dry sieving method, a mechanical sieving method, and wet sieving method.
A widely used fuller's curve is used to describe the grain size distribution. It is an empirical curve for gradation of aggregates. The curve is designed by fitting either parabola or an ellipse to a tangent at the point where the aggregates fraction is one-tenth of the maximum size fraction (Anjum, 2011).

Used procedure

Here, manual dry sieving method was used. The dried insoluble matter (aggregates) were weighed and recorded. Stacked the sieve aperture in an ascending order of sieve number: 8.0 (top), 4.0, 2.0, 1.0, 0.5, 0.25, 0.125, and 0.063 (bottom) (all in mm) refer to figure 6. Poured the insoluble sample in the aperture from the top and then the stack was shacked for about 10-15 min. The weight of the fractions retained on the sieves was recorded. The result of weighing the fractions represented in a cumulative grading

curve. Based on the grading curves of aggregates, the uniform coefficient (Cu) and percentage of fines (%fines) is calculated.

Uniformity coefficient (Cu) expresses the grading homogenity of the sand and is calculated by the following equation (3) (G. De Schutter, 2004):

$$Cu = \frac{D_{60}}{D_{10}} \quad (3)$$

D_{60} and D_{10} refer to the maximum sieve opening through which passes 10 and 60% of the grains respectively. Moreover, fines are the percentage of the material that passes through 63μm sieve

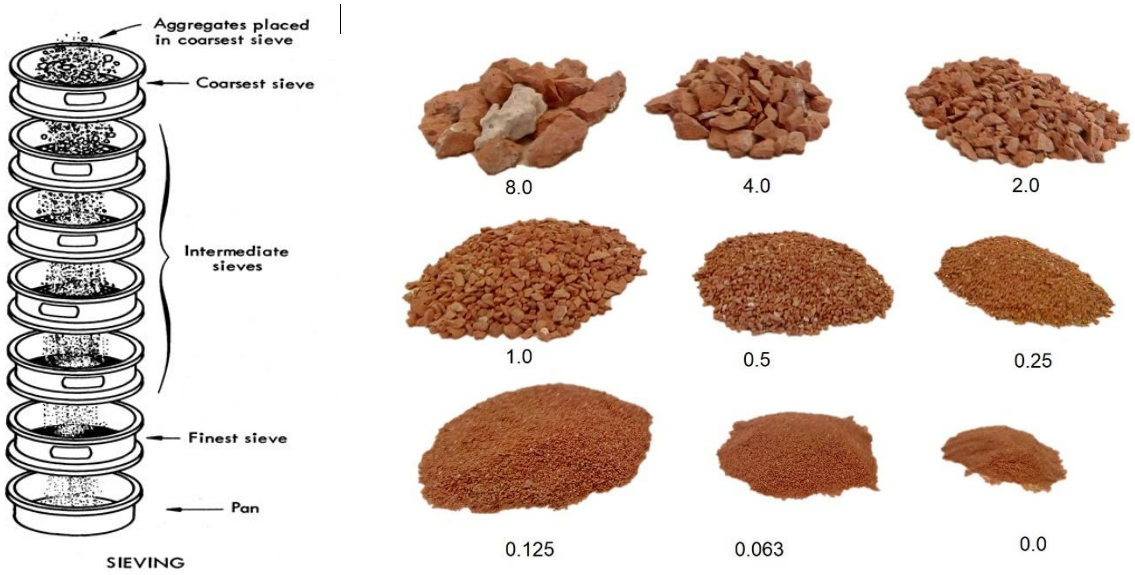


Figure 6 Sieve aperture (left side), fractions retained on the sieves (in mm) (right side).

Bulk density

The soil bulk density is the weight of dry soil (mass of soilds) divided by the total soil volume. The total soil volume is the combined volume of soilds and pores which may contain air or water, or both.
Bulk density is calculated by the following equation (Katharine Brown, 2018):

$$\text{Bulk desnsity (kg/m3)} = \frac{\text{m (dry soil weight (kg))}}{\text{v (soil voulme } m3\text{)}} \quad (4)$$

Binder and ash (additive) bulk density values were calculated at the time of making floor panel are as follows:

Table 3 Bulk density of binders used in the floor panel and ash as an additive.

Type of binder/additive	NHL DP_{PDR}	NHL Z_{PDR}	NHL Z_{HT}	NHL B_{HT}	AL K_{PDR}	AL V_{PDR}	AL V_{HT}	Ash
Bulk density (kg/m3)	800	750	750	700	650	700	800	400-600

ICP-OES

ICP-OES (induced coupled plasma – optical emission spectrometry) is an analytical technique which is widely used for the determination of major and minor trace elements. The technique is used for tracing filtrates elements. The sample is mixed with heated argon gas that has been charged with radio frequencies in the torch chamber of the ICP to produce argon plasma. The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. The resulting spectrum indicates the elements present in the sample. The test is completely controlled by computer and monitored to assure reliable processing and reporting of the wet chemical analysis results. (Ing. Alberto Viani) (Wet chemistry, 1984)

Used procedure

The calibration standard solution was prepared before the test, contained elements: Calcium (Ca), Magnesium (Mg), Silicon (Si), Sulphur (S), Aluminum (Al) and Iron (Fe). It was a transparent solution which quantify the percentage of elements present in filtrates. Then, the prepared solution was introduced to the plasma. After introducing the standard solution, stored filtrates from the dissolution test (refer table 4) were analysed to get the concentrations of the elements.

The obtained concentrations [mg/l] were multiplied by the volume of solution (filtrate) [l] to calculate the mass of the elements in it. Then, the mass of each element [g] was divided by the mass of the soluble part of the sample [g]. The elements were therefore expressed as a percentage proportion of the soluble part [wt. %].

Table 4 A list of all the filtrates obtained from the acid treatment with concertation of used acids.

Sample code	Initial Sample wt. (g)	Filtrate code	No. of turns acetic acid (1:9)used	Filtrate code	No. of turns Conc. Acetic acid (99%) used	Filtrate code	Number of turns HCL (1:5)used	Filtrate code	Number of turns HCL (1:3)used	Filtrate code	Number of turns HCL (1:2)used
Panel A: Greek floor (vitruvius)											
G4	100	G4	3	G4	1						
G3	112.8	G3A	2	G3B	1						
G2	85.8	G2	2	G2	1						
Panel B: Roman floor(vitruvius											
R6 - R5	92	R6-R5 A	2	R6-R5 B	1						
R3	64.2	R3	3	R3	1						
R2	100	R2	2	R2	1						
Panel C: Venetian terrazzo											
V8	72					V8A,V8B	2	V8C,V8D, V8E	3	V8F	1
V2	101.7					V2	3				
V1	61.6					V1	3				
Panel D: Lime mortar cast floor											
L2	100.8	L2A	2	L28	1	L2C	1				
Panel E:Tiles on motar											
E1	101.4	E1A	2	E1B	1	E1C	3				

3.1.2 MICROSCOPY

Petrographic analysis

Petrographic analysis is a microstructural examination by optical and scanning electron microscopy (SEM). The method involves examination of the sample, followed by a procedure to prepare a thin section, which is then examined under transmitted light with a polarized light microscope. The character of binder matrix and type identification (gypsum, lime, hydraulic lime, cement) is mostly possible under polarized light (Middendorf B. a., 1998) (St. John, 1998) (Callebaut, 1999). Many details can be observed under magnification which includes the following:

- Estimation of the mortar proportions of aggregate, binder and voids
- Entrained air voids can be differentiated from the entrapped air and the presence of drying shrinkage cracks.
- The composition and character of the aggregate can be observed (major and minor minerals); the character of the binder (colour, underburned or over burned lime etc.); and binder to aggregate ratios can be estimated visually.

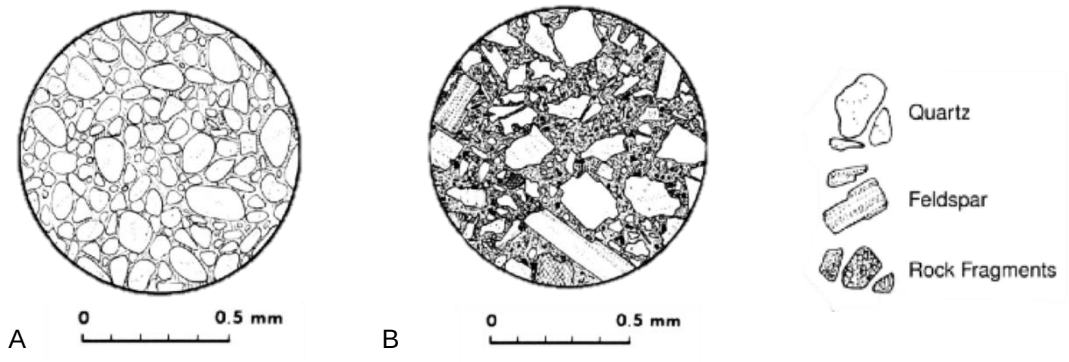


Figure 7 Sample A is sorted while sample B is poorly sorted and the identification of particle with shape.

In figure 7, a graphical representation of sorting describes the distribution of grain size of sediments. Sample A is sorted which shows that the sediment sizes are mixed from small to large; whereas sample B is poorly sorted which shows low variance. However, the identification of Quartz, Feldspar and Rock fragments can be done (refer fig 7). For further information, scanning electron microscopy (SEM) can be used which gives the opportunity for elemental analysis of the binder and aggregates.

Used procedure

Samples were studied on thin sections and polishes sections, by means of polarising microscopy (PM) under transmitted light and reflected light. The experts, prepared thin sections that is then examined mainly for the estimation of the proportion of aggregates, binder matrix, and voids by referring the figure 8, (the percentage diagram for estimating by volume). The characteristics of minerals in the aggregates were also identified, to know about the source of the aggregates.

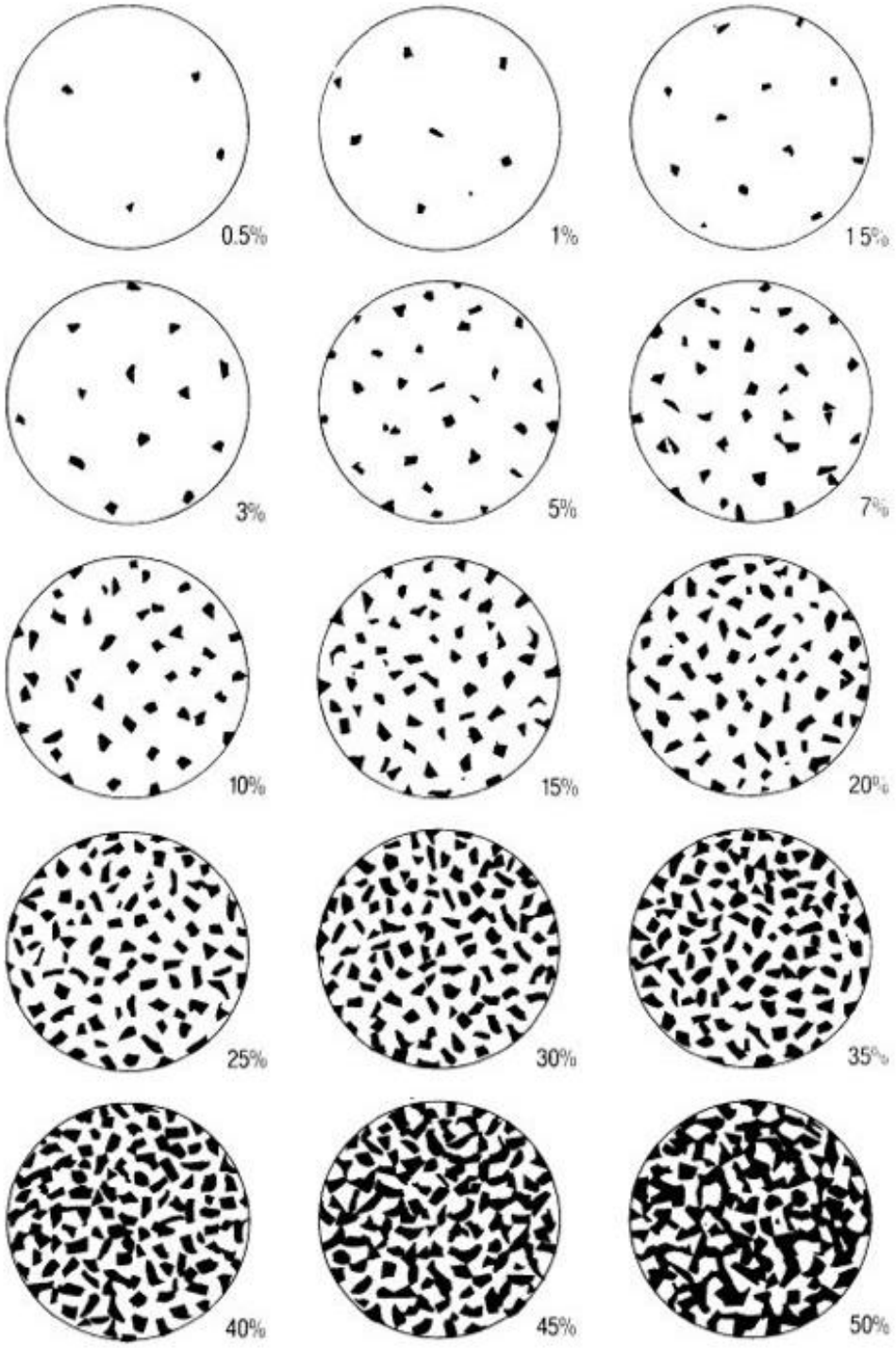


Figure 8 Percentage diagrams for estimating composition by volume (Compton, 2106)

Each circle above is a representative view of the sample through the microscope. The entire circle illustrates 100% and the black areas show the various percentage of the total circle, ranging from 0.5% to 50%. The chart is used for estimating the percentage of porosity and aggregates (G.V, 1975).

Scanning electron microscopy (SEM)

SEM is a technique where mortar structure can be analysed at a higher magnification and in three dimensions on rough, broken surfaces to directly visualize the structural components of the mortar. The sample should be small for SEM analysis and need to be covered with a conductive layer of gold carbon which will facilitate the removal of electrical charge from the sample to avoid the interferes with image formation. It also allows to trace microelements within particles and easy to recognize the type of binder. (B. Middendorf 1, 2005)

Used procedure

Before analysis, it was decided to select the area of the analysis to make it easier during the test. Marked area (on paper) was given to the expert to prepare the samples accordingly.

3.1.3 THERMAL ANALYSIS

Thermal analysis includes three techniques, Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC). Each method implies different features based on the physical transformations that compound experience during the heating process in controlled conditions. Thermogravimetry (TG) mainly measure weight loss of the sample during heating process which is specifically related to physical decompositions in the material. DTA helps to plot the graph simultaneously during heating process which represents the temperature difference between the sample and an inert standard (usually Al_2O_3). The inert standard is also heated at the same rate and at the same time. When the standard is continuously increasing in temperature while the sample temperature remains constant, an endothermic peak is recorded. This is due to the fact that sample is absorbing heat energy and using it for mineralogical transformation. This happens mostly due to the loss of chemically bound components, for instance, water from gypsum or carbon dioxide from calcite and dolomite. DSC technique works on same basic principle as DTA. Whilst the temperature difference is measured by DTA the DSC manages to maintain the sample and standard material (Al_2O_3) at the same temperature while heated and constant rate by adding energy that is recorded. (B. Middendorf 1, 2005).

In order to obtain the results for mortar samples, TGA/DTG analysis is used. TGA analysis measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in a vacuum. It can be used for quantification of the individual compounds of the lime mortar binder. Non-carbonated lime represents calcium hydroxide, which can be detected at the temperature around 450°C where it releases water during its dehydration. Carbonated lime in form of calcium carbonate decomposes between temperatures 600°C and 800°C. The released water and carbon dioxide amounts are proportional to hydroxide or carbonate content according to following equations:

$Ca(OH)2 \rightarrow CaO+H2O$
$CaCO3 \rightarrow CaO+CO2$

For example, figure 9 represents the thermogravimetric derivation of lime (one month aged). However, we can calculate the amount of calcium hydroxide and calcium carbonate with the help of the above-mentioned equations.

$Ca(OH)2 \rightarrow CaO+H2O$
74 56 + 18

$CaCO3 \rightarrow CaO+CO2$
100 56 + 44

The calculated molecular weight of CaO is 56 and H_2O is 18 (refer periodic table) which is equal to the molecular weight of $Ca(OH)_2$ i.e. 74.

The percentage weight of water = 18/74 x 100

= 24.3%

$Ca(OH)_2$ = 14.19/24.3 x 100 (refer figure 11)

Similarly, the percentage of CO_2 = 44/100 X 100

= 44%

$CaCO_3$ = 16.2/44 x 100

= 58.4%

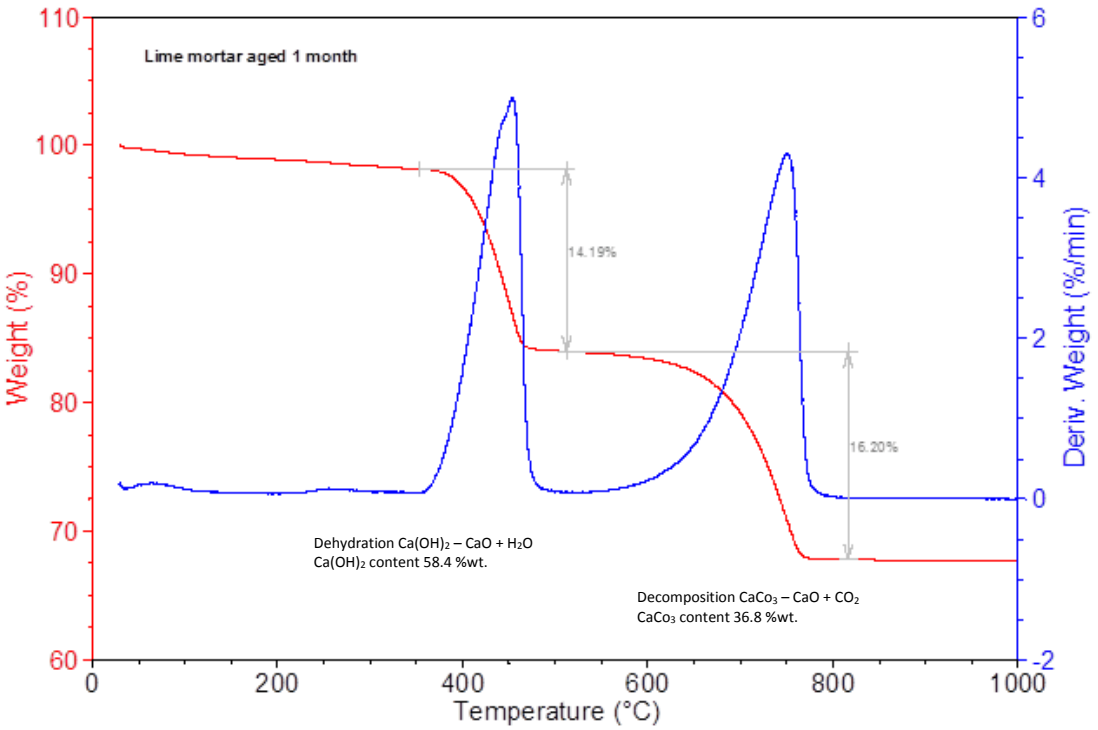


Figure 9 Shows the thermogravimetric line in red and blue line represents derivation of thermogravimetric.

Used procedure

Small pieces of the mortars (app. 20-30 g) were gently crushed in a porcelain pot and the fractions with grains under 0.063 mm were used for thermal analysis. Thermal analysis was performed with instrument TA Instruments SDT Q600. Samples were heated in an air atmosphere in alumina cups up to a temperature of 1000°C at a rate of 20°C/min to obtain the TGA/DTG (thermogravimetric/derivative thermogravimetric analysis) traces.

4. RESULTS

4.1 WET CHEMICAL SEPARATION (ACID DISSOLUTION)

From the chemical analysis, as shown in table 5, binder to aggregate ratio of selected samples is compared with the mortar mixing ratio of the original floor panels. As a result, ratios between indentified by the analysis and the original mixing ratios are different in most of the cases, except for G4, R6-R5, R3, V8, V2, and for L2 it is more or less similar. Rest, G3 is higher in aggregate proportion may be due to the presence of ash content as an additive and hydraulic lime as binder. On the contrary G2, R2, V1, and E1 samples contain low proportion of aggregate than the original. However, two things are common between these four samples which are gravel content either hot mix binder lime (refer table 1). Initially, before starting the acid dissolution test gravel was removed because of the intention to analyse the sand only. Another fact is the use of hot mix lime because the slaking takes place at the time of mixing the mortar. Its gauging is in general quite imprecise when done by volume.

Table 5 Result of analysed samples with binder and aggregate (B/A) ratio (volume units)

Sample code	Layers	Initial Sample Wt. (g)	Insoluble (g)	Soluble wt. %	Insoluble wt. %	B/A ratio (samples)	B/A ratio (FP)
Panel A: Greek floor (Vitruvius)							
G4	Surface layer	100	75.25	24.80	75.21	1: 2.5*	1: 2.25*
G3	Nucleus	112.8	93	17.53	82.47	**1: 3.7***	**1: 3***
G2	Rudus	85.8	66.40	22.61	77.40	**1: 1.5**	**1: 3**
Panel B: Roman floor(Vitruvius)							
R6 - R5	Repair layer surface layer	92	62.76	31.81	68.20	1: 1.9	1: 2
R3	Nucleus (lower)	64.2	50.94	20.54	79.46	1: 3.4	1: 3
R2	Rudus	100	76.82	23.18	76.82	**1: 2.2**	1: 3
Panel C: Venetian terrazzo							
V8	Repair layer	72	50.5	29.86	70.14	1: 2.1	1: 2
V2	Rudus	101.7	75.96	25.31	74.70	1: 2.6	1: 3
V1	Statumen	61.6	47.76	22.52	77.50	**1: 2.3**	1: 3
Panel D: Lime mortar cast floor							
L2	Rudus	100.8	70.68	29.45	70.56	1: 1.6	1: 2
Panel E: Tiles on mortar							
E1	Statumen	101.4	74.12	26.89	73.12	**1: 1.8**	1: 3

FP – Floor panel
B/A – Binder/aggregate
*ash

The soluble content was calculated in weight units and the floor panel is in volume units. For the conversion, binder bulk density is used as per given table 3. Aggregate bulk density was determined for the dry soil collected after acid dissolution test, table 6. There are two types of aggregates which are used in the samples, sand and crushed brick. The presence of gravel was neglected as it was removed before the testing.

Table 6 Average bulk density calculated based on selected samples.

Aggregate	Sample code	Weight of soil (g)	Volume (ml)	Bulk density (kg/m3)
Sand	V1	47.28	30	1576
	G4	75.04	54	1390
	G3	91.17	59	1545
	R2	74.65	52	1436
Average bulk desity				≈1490
Crushed brick	V8	70.62	63	1121
	R3	50.66	48	1055
	R5R6	62.34	52	1199
Average bulk desity				≈1130

4.2 DETERMINATION OF THE AGGREGATE GRADING CURVE

The gradation curves of the undissolved residue are shown in figure 10 and 11. They were divided based on the nature of the aggregate, sand and crushed bricks. The obtained results are compared to the granulometry of the sand used to make the floor panels. The sand selected for all the floor panels were ordered twice which resulted in slight differences but its gradation was almost same. Comparing the gradation curve of all the samples where sand was used as aggregate with the original sand, one can see that all the floor panel curves follow almost similar inclination points except for three positions. The lower amounts of a finer fraction of 0.125 and 0.250 mm for G4, G3, G2, R2, and V1 and another is a coarser fraction of 4- 2 mm where G4 is richer than original sand. Lastly, all the samples percentage of finer fractions under 63 µm are richer than original sand, in contrast, G3 is on the lower side.

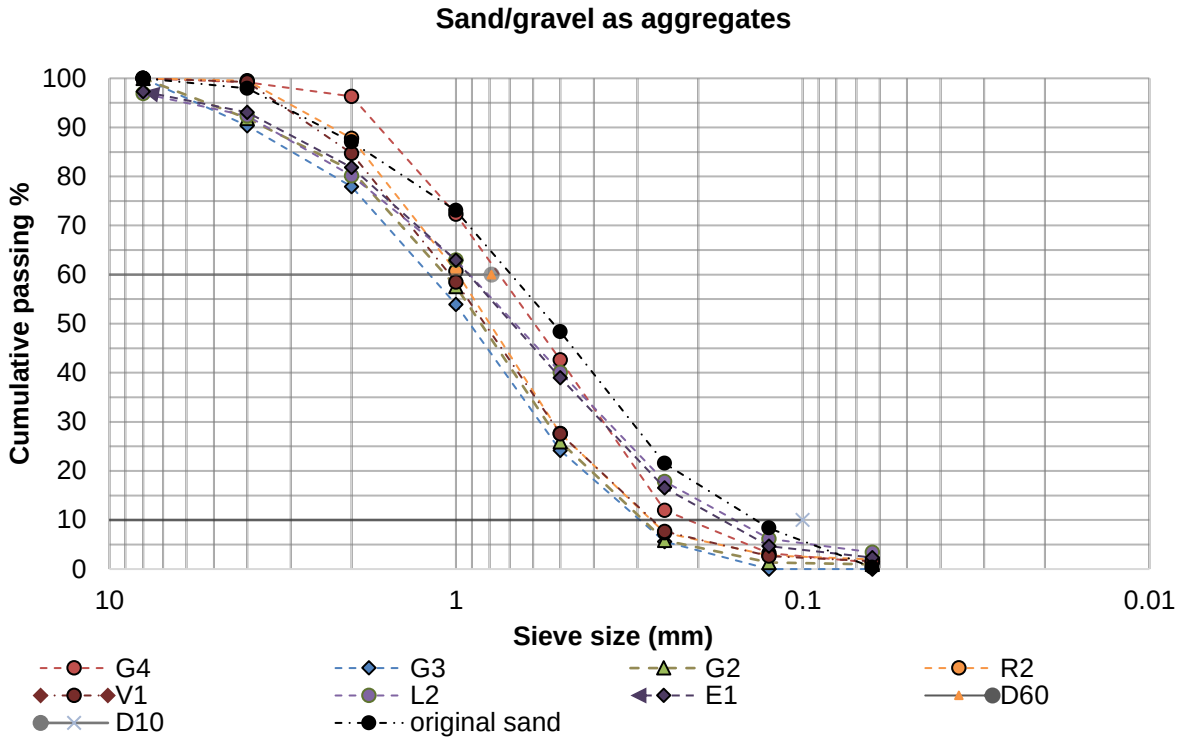


Figure 10 Cumulative aggregate grading curves depicting the main difference on grain-size distribution between the floor panels.

Figure 11 presents the grain size distribution with the Fuller's curve. R6-R5 and V8 contains finer fractions which was sieved under 4mm. These two samples are richer in finer fractions then other two samples. However, R3 follows the same curve as the Fuller's curve which represents that it is well compacted.

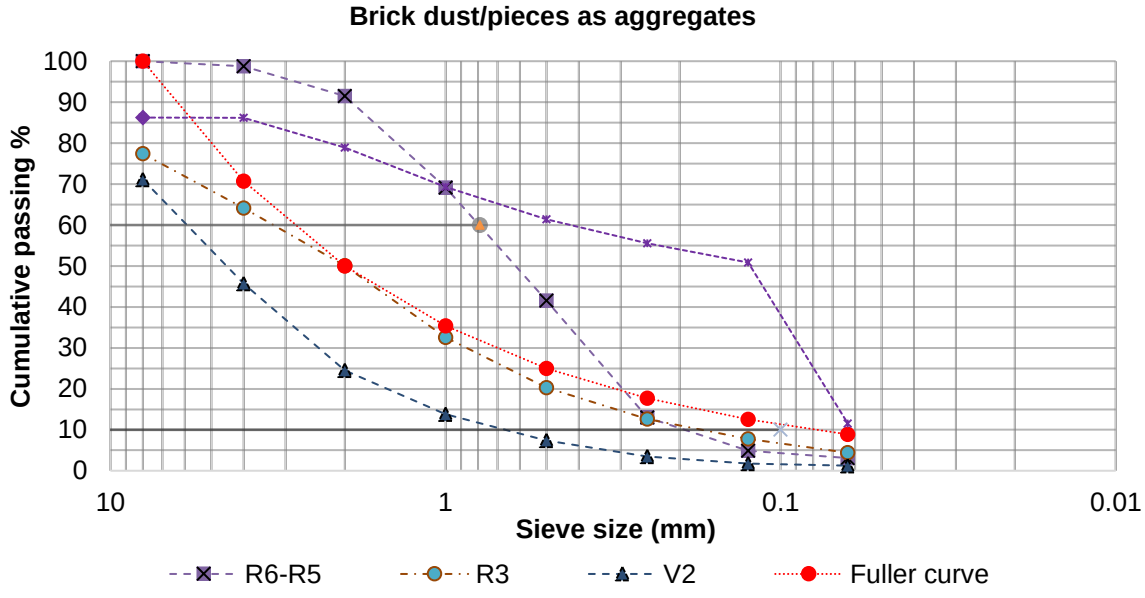


Figure 11 Cumulative aggregate grading curves depicting the main difference on grain-size distribution.

An alternative graphic depiction of the grain size distribution is shown in Figure 12. The aggregate V8 is richest in finer fraction (63 µm) near to 40%. This corresponds to the fact that the sample V8 (top repair layer of Venetian flooring) where brick dust was used as aggregates proved to be the finest particles. Similarly, V2 has a higher fraction in gravel 4, almost 38%. On the contrary, other samples shows higher fraction percentage in sand from range 1 to 0.25 mm.

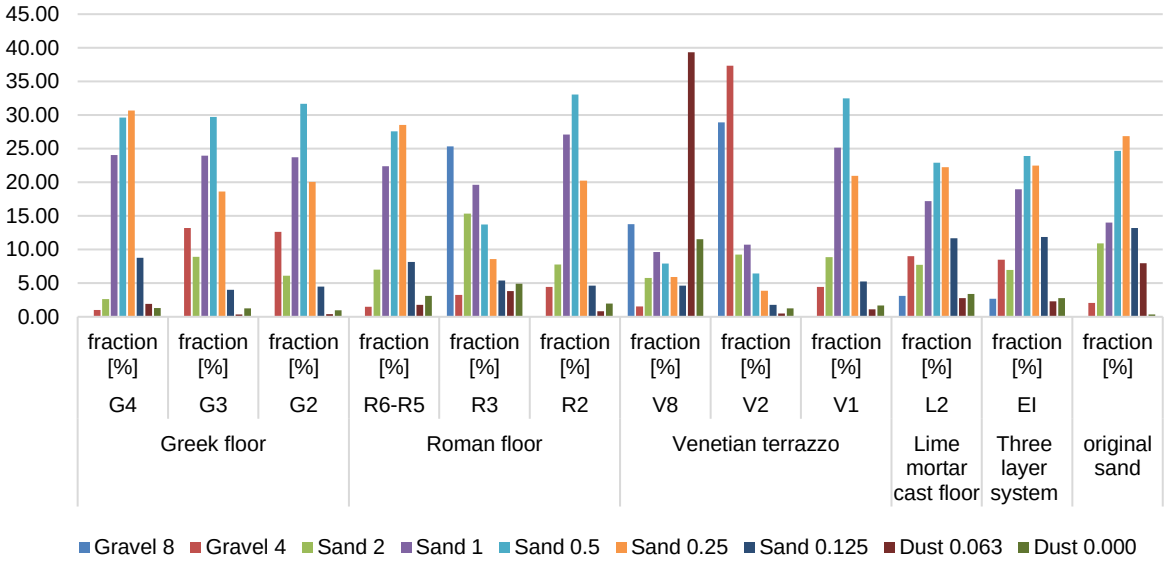


Figure 12 Histogram of grain size distribution by weight% retained.

Based on the grading curves, uniformity coefficient (Cu) and percentage of fines (% fines) were calculated (refer table 7). When Cu is greater than 4 to 6, it is understood as a well-graded soil and when Cu is less than 4, they are poorly graded or uniformly graded. Uniformly graded here means the soil has an identical size of the particle.

Table 7 Gradation characteristics and physical properties of the sand selected

	G4	G3	G2	R6-R5	R3	R2	V2	V1	L2	E1	V8
Cu	3.57	4.05	3.65	4.79	18.70	4.25	8.86	3.78	4.98	4.67	8.06
Fines%	1.318	1.250	0.961	0.961	4.386	1.973	1.242	1.597	3.403	2.768	11.518

4.3 ELEMENTAL CONTENT IN SOLUTION

The major and minor elements traced in the soluble part of the mortar samples are shown in table 8. To find the percentage of these elements ICP analysis has been carried out where calcium is the highest as expected and other minor elements such as Mg, Si, S, Al, and Fe are found as shown in the table 8.

Table 8 Proportions of major and minor elements found in the filtered solutions of the acid treated samples.

Sample code name	c [mg/l]					
	Ca	Mg	Si	S	Al	Fe
G2	12731.2	109.6	78.2	100.1	121.6	72.7
G3A	11077.9	208.9	101.5	100.6	241.0	159.4
G3B	2909.8	50.7	7.9	16.1	235.7	124.5
G4	11059.4	178.4	147.0	91.2	221.2	136.7
R2	12594.2	189.7	112.0	108.7	229.4	145.0
E1A	10780.1	125.4	324.2	79.5	93.7	115.0
E1B	9583.1	212.5	80.6	66.4	528.6	361.0
E1C	1425.0	19.9	2.6	4.9	35.5	71.6
V8A	10679.5	198.3	1076.8	84.4	629.0	146.5
V8B	9491.1	233.3	219.7	76.8	960.9	249.8
V8C	2639.3	51.8	36.0	16.3	191.9	79.8
V8D	2938.6	70.8	24.6	20.2	264.5	143.0
V8E	839.0	24.8	26.9	6.5	100.5	68.8
V8F	403.2	11.5	17.7	3.2	50.6	44.1
L2A	8175.6	183.7	209.2	57.6	477.4	290.3
L2B	6935.0	71.0	55.1	48.2	18.8	31.7
L2C	1551.5	26.6	24.6	10.2	42.2	34.7
V2	12776.4	128.5	102.8	138.9	92.1	85.0
V1	8084.8	56.5	46.5	56.9	56.8	39.1
R3	8963.7	63.2	71.4	65.3	99.5	19.4
R6-R5A	11386.0	77.8	61.8	88.9	49.6	6.5
R6 R5 B	5836.5	24.2	5.2	31.4	69.7	8.5

Most elements were dissolved in the first round of the acid attack and in the following cycles, the content of elements decreased, as visible for Ca from the figure 13.

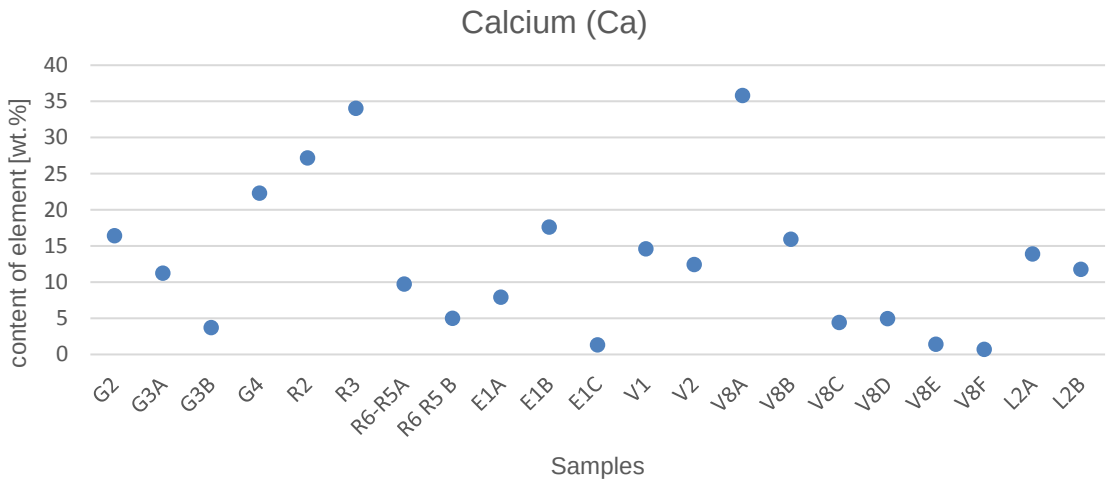


Figure 13 Content of calcium found in the stored filtrates according to the number of cycle marked.

The elemental composition of the raw material used as the binder of the flooring panels was taken from the previous experiment and it was used for comparison with the obtained data. However, not all soluble parts of samples could be directly compared with the raw material as not all filtrates from all cycles were collected. The exception was the sample V8. Based on Figure 14, where the total amount of five main elements of the sample V8 was relatively comparable and the fact that the solution of the first cycle was always collected completely, it was estimated that the total amounts were still comparable with some caution.

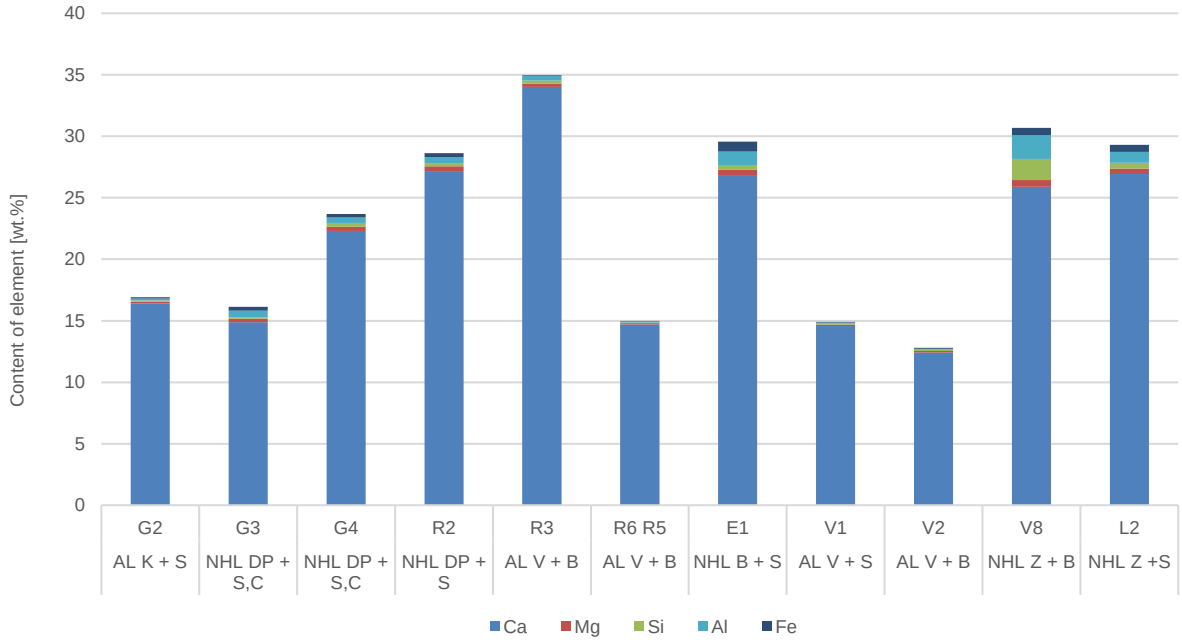


Figure 14 Content of calcium, magnesium, silica, aluminium, and iron in soluble part of samples.

The presence of sand, brick, and charcoal does not seem significantly influence the dissolution in terms of the amount of soluble elements. This can be observed in the samples with the same binder but different aggregate, like V8, L2, or V1 and V2. However, the aggregate contributes to some elements like Al and Fe as discussed below.

The dissolution of the various binders is compared in Figures 15, 16, 17, 18, and 19. Lower Calcium content in the solutions probably corresponds to the loss of filtrates during the experiment. Si content in the solutions is lower than in the raw materials, apart from the sample R3 (Air lime Vitosov + Brick). Some small amount of silica can possibly originate from the brick. The raw material for the NHL binders contains a higher amount of silica than found in the solutions. The content of silica in the raw material includes all its forms, the solution includes only the soluble proportion. Aluminium dissolves readily, in the samples G2, R3, L2, E1 and V8 where the amount of aluminium is bigger than in the raw material. Also iron dissolves readily and in more than half of the samples there is more iron in the solution than in the original sample. In both cases, the additional elements originate from the aggregate, i.e. sand or brick.

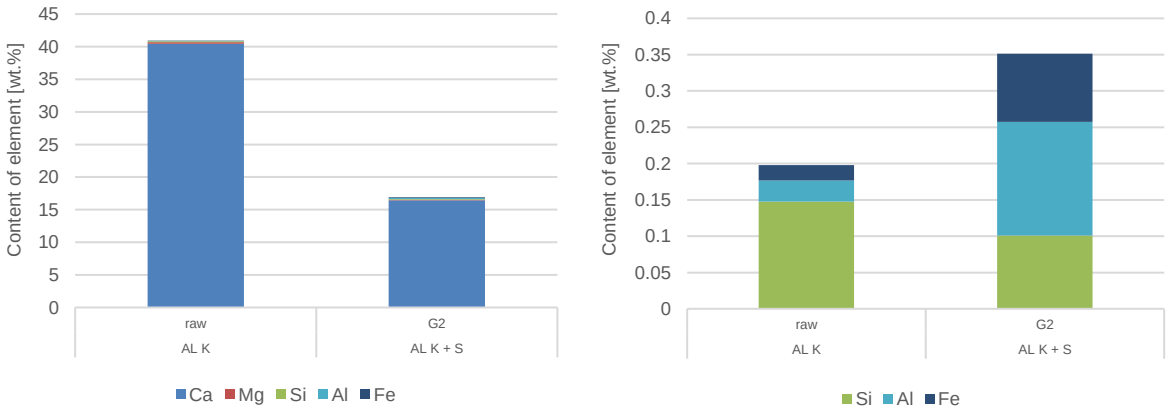


Figure 15 Mortar binder - Air lime Koněprusy

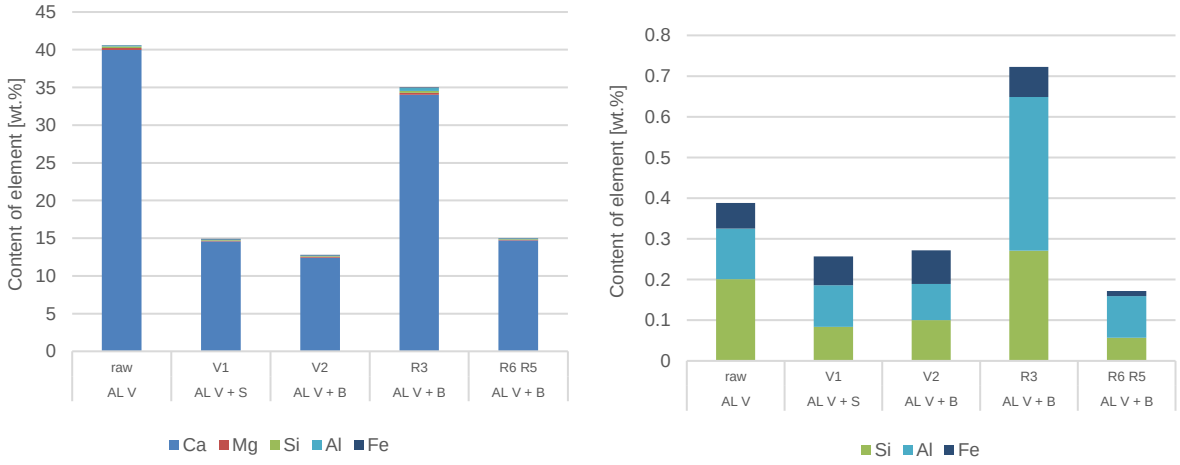


Figure 16 Mortar binder - Air lime Vitošov

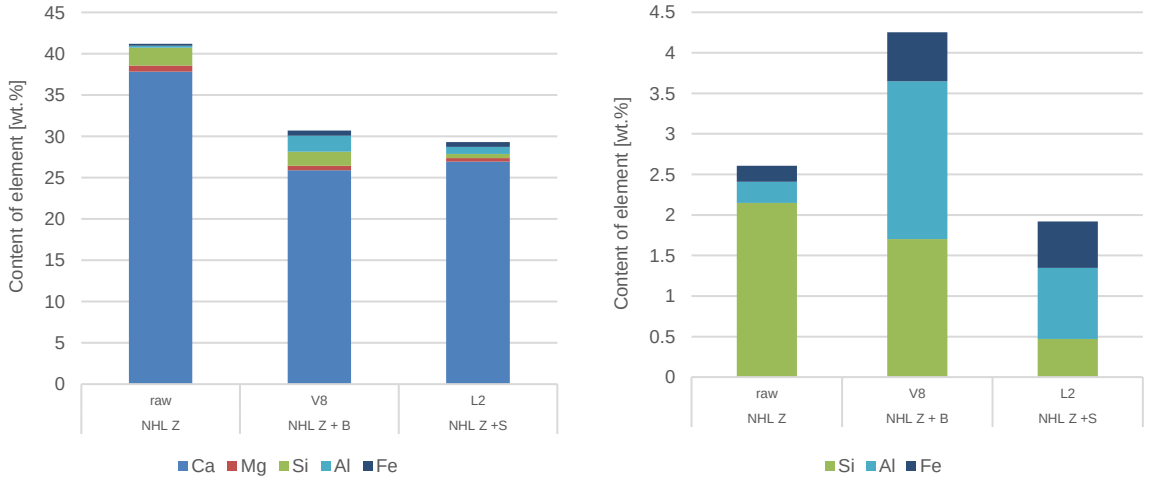


Figure 17 Mortar binder - Natural hydraulic lime Zlíchov

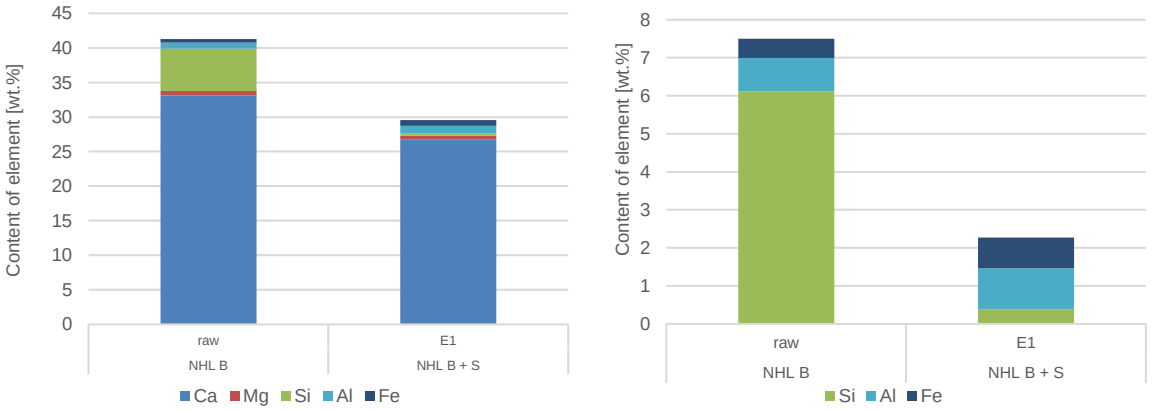


Figure 18 Mortar binder - Natural hydraulic lime Braník

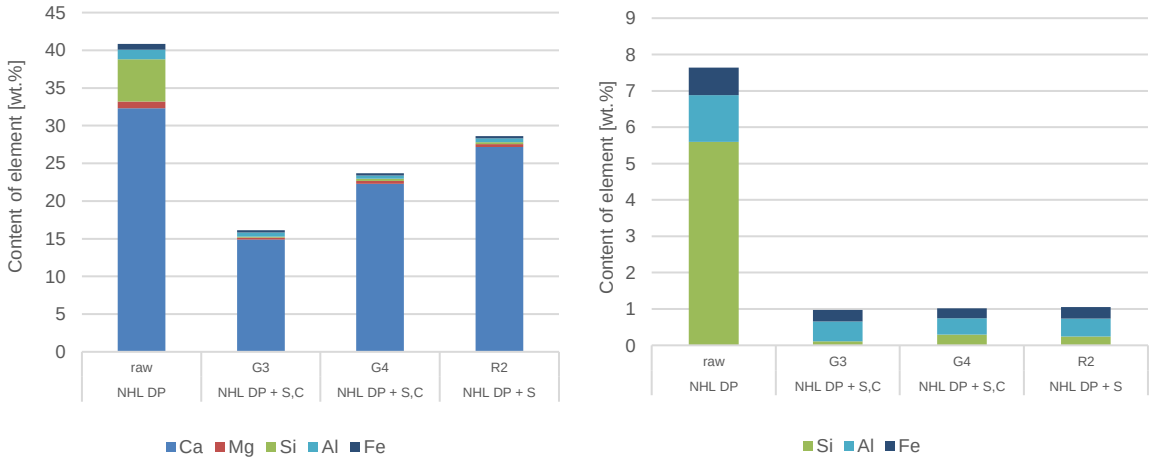
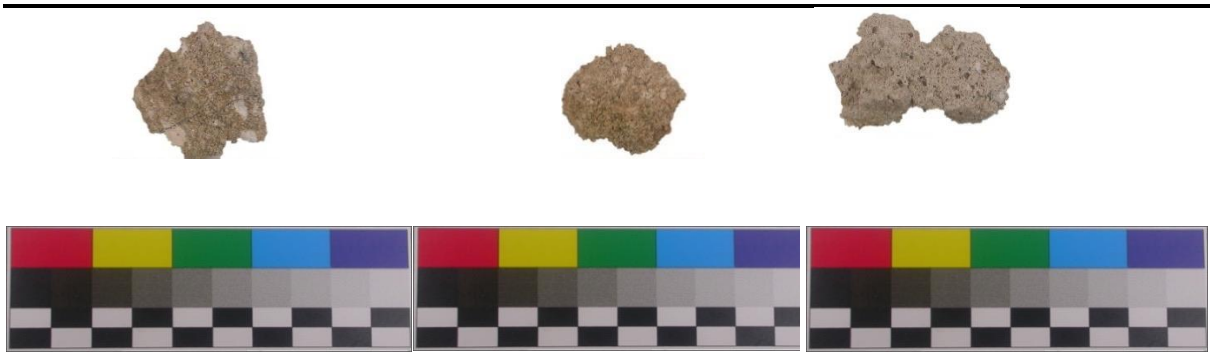


Figure 19 Mortar binder - Natural hydraulic lime Hvížďalka

4.4 PETROGRAPHIC AND MICROSTRUCTURAL FEATURES

Mortar samples selected for petrographic analyses of the Greek floor group (G3 and G2), Roman floor (R2), Venetian terrazzo (V2 and V8) and lime mortar cast floor (L2) are shown in table 9. The mortar samples have the specific composition, textural characteristics, aggregate compositions and matrix properties are as follows:

Table 9 Selected samples with the mix of natural hydraulic lime and sand/gravel.



G3 R2 L2

i. G3 is a second layer (nucleus) from the top with the light base colour (beige) and characterized by moderate cohesion. The sample consists of minerals which are majorly milky to colourless quartz grain with various shapes. The quartz grain has a maximum and minimum length of 0.29 cm and 0.0.25 cm respectively. Minor particles are brick and burnt ash which are clearly observable with colour and shape (refer figure 20). There are small green colour particles which can be the product of iron or silicate. The binder matrix has medium colour (beige to brown) . The estimated percentage of porosity and binder to aggregate ratio is 10% - 15% and 1: 3 respectively. Annexure A represents the complete optical plane polarised image for G3.

ii. R2 is the fourth layer from the top with light base colour (cream to beige) and characterized by high cohesion. The main filler of the sample is quartz grain of cream colour with various round and sharp-edged organic shapes. The length of the quartz grain varies from 0.008 to 0.019 cm. Minor particles are microcrystalline quartz grain, mica, and brick. The sample also consists of unidentified green colour particle same as G3 (refer figure 20). The binder matrix has earthy brown colour and the portion of lime lump shows in annexure A. The estimated percentage of porosity and binder to aggregate ratio is 5% -7% and 1: 3 respectively.

iii. L2 is the intermediate layer with light base colour (milky to grey) and characterized by high cohesion. The sample filler comprises mainly cream to colourless quartz grain with different sizes of rectangular round edged shapes. The fraction size ranging from 0.0152 cm to 0.575 cm. The sample is further consisting of long elongated shaped mica and black colour

impurities. The binder matrix has a dark brown colour and evenly mixed aggregates with the prominent portion of lime lump. It is noteworthy that the porosity of the sample is 1%, comparing to all other samples its very low and estimated binder to aggregate ratio 1: 2.5.

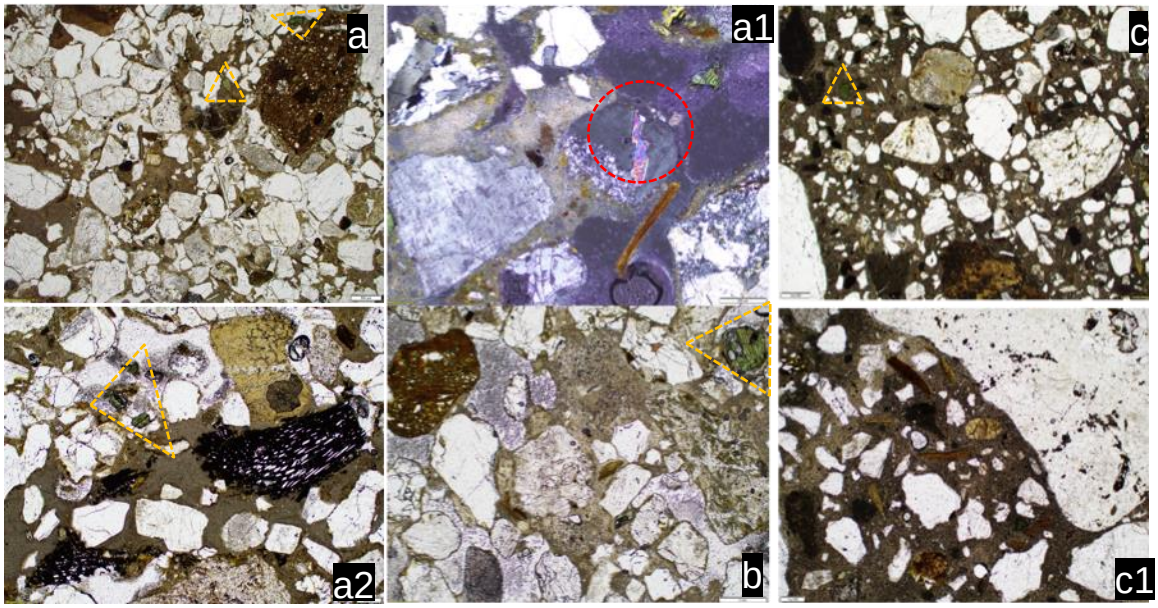


Figure 20 (a) Sample G3, (plane polarised light) the reddish brown colour piece with black spots at the left corner is brick. All milky to colourless grains are quartz grain surrounded by (beige to brown colour) binder matrix at scale 500µm. (a1) Cross polarised light image reveals the presence of some multicolour minerals which seems to be a group of several minerals marked in red circle, the presence of mica under this mineral at scale 200µm. (a2) Burnt ash mark clearly visible in the plane polarized light image at scale 200µm. (b) Sample R2, optical plane polarised light image shows quartz grain surrounded by binder matrix and a brick piece at the left side top corner at scale 500µm. (c) Sample L2, optical plane polarised image shows various size of quartz grain with green colour grain which is common in all the samples, at the bottom dark brown grain is present which is the product of burnt brick at scale 500µm. (c1) A higher magnification of long elongated shape mica in different colours with black colour impurities at scale 200µm (optical plane polarised image). * Green colour grain which is common in all three samples mentioned above marked in yellow colour triangle shape.

G2 is a third layer (rudus) from the top with the light base colour (cream to brown) and characterized by moderate cohesion. The sample composed of minerals mainly milky quartz grain with various organic rounded shapes. The average length of quartz grain is 0.21 cm and the maximum length is 0.454 cm. Minor particles are brick, opaque, polycrystalline quartz and long elongated shaped mica (refer figure 21). Similar to G3, L2, and R2 green color particles are present in small quantity. The binder matrix has a dark color (golden to brown) which includes the prominent portion of lime lumps with cracks inwardly (refer annexure A). The estimated porosity is 5% and binder to aggregate ratio is 1: 3.

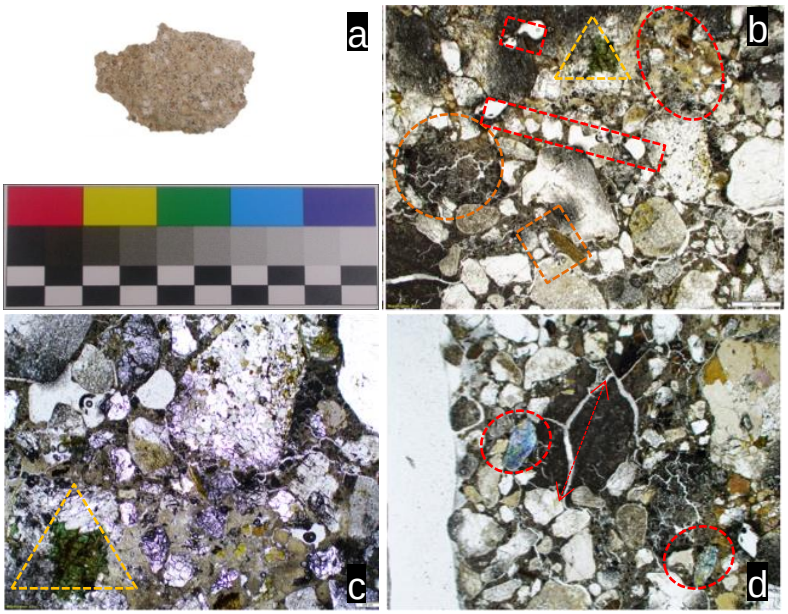


Figure 21 (a) Selected samples G2 (Air lime and sand + gravel) observed under the optical plane polarised light,(b) the milky colour quartz grain with small portion of brown colour binder matrix marked in red colour circle. The long elongated mica marked in rectangular orange colour. Porosity marked in red colour rectangle at scale 2 mm. (c) A magnification of distinctive cracks within quartz grain at the top and binder matrix at the bottom (scale 200µm). (d) Higher magnification of distinctive cracks within lime lumps of length 0.24 cm and width 0.0095 cm. There are two multicolour particles which seems to be a group of several minerals marked in red circle at scale 2 mm. * Green colour particle is the unidentified particle marked in yellow triangle.

V8 is the topmost layer from the surface with brick red colour as a base and characterized by strong cohesion. The material is robust in nature and sample mainly consists of crushed brick with the undefined shapes. There are other fillers such as polycrystalline quartz grain and clay minerals with some black color impurities in a small amount. It's hard to define the length of aggregates and also difficult to identify the binder matrix due to homogenous red colour shows in annexure A. The estimated porosity lies between 1.5% and 3% and binder to aggregate ratio is 1: 2. (refer figure 22).

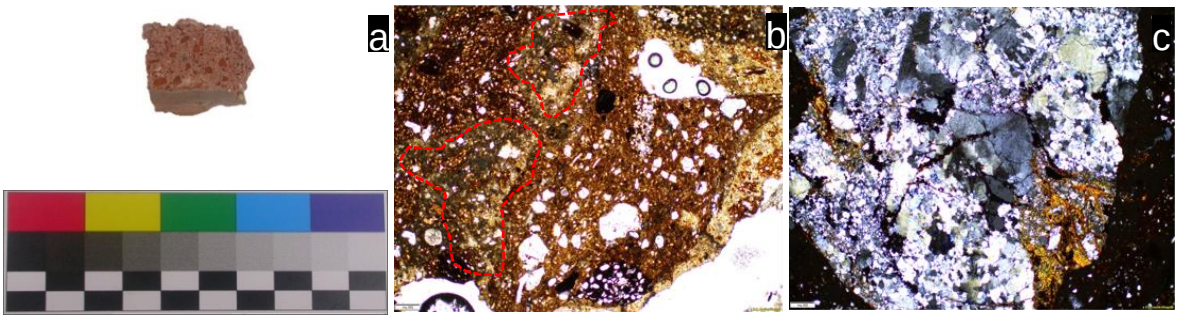


Figure 22 (a) Selected samples V8 (NHL + brick) observed under optical plane polarised light, (b) the binder matrix is highlighted by red dotted line, though it is hard to differentiate binder from aggregates for this sample. Another portion is brick, which includes porosity within the form at scale 200µm. (c) a higher magnification of polycrystalline quartz grain with clay mineral (yellow color) on the edge of the grain at scale 200µm.

V2 is the seventh layer from the top with brick red colour as a base and characterized by low cohesion. The core material of the sample is brick with various sharp-edged organic shapes and minor minerals are colourless quartz grain (refer figure 23). The binder matrix has cream colour but in low proportion comparatively with other samples. The sample shows high porosity (10%-15%) but it can be possible that the original material will not have same amount of porosity. The high proportion of porosity may be developed during the procedure of making the thin section or the selection of sample piece is not appropriate . As a result, the estimated binder to aggregate ratio is 1: 5.

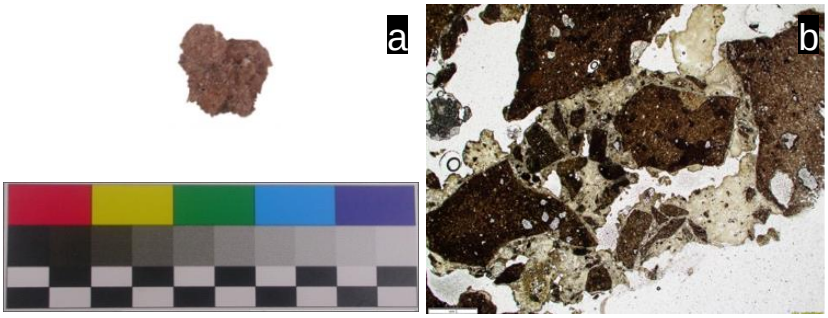


Figure 23 (a) Selected samples V2 (Air lime and sand + brick) observed under optical plane polarised light , (b) a magnification of brick pieces and less portion of binder matrix, where porosity is the dominant part of the sample at scale 2mm.

Table 10 Result of analysed samples with estimated binder and aggregate (B/A) ratio and pororsity % (by volume)

Sample code	Layers	Aggregate %	Porosity %	B/A ratio (selected samples)	B/A ratio (original mortar mixing ratio)
Panel A: Greek floor (Vitruvius)					
G3	Nucleus	30	10 - 15%	1: 3*	1: 3*
G2	Rudus	35	5%	1: 3	1: 3
Panel B: Roman floor (Vitruvius)					
R2	Rudus	35	5 - 7%	1: 3	1: 3
Panel C: Venetian terrazzo					
V8	Repair layer	50	1.5 - 3%	1: 2	1: 2
V2	Rudus	20	10 - 15%	1: 5	1: 3
Panel D: Lime mortar cast floor					
L2	Rudus	40	1%	1: 2.5	1: 2

*Ash, FP- Floor panel

4.5 SEM-EDS ANALYSIS OF BINDER MATRIX

Analysis of the mortars by SEM reveals the details of the unidentified aggregates under optical microscopy, distinctive binder matrix and the weight percentage of elements. The green colour particle

is the silicate mineral with high amount of iron oxide (refer annexure C). Presence of iron oxide more than 10% is not usually found. High amount of iron oxide is responsible for green colour. Multicolour grain is feldspar which contains 40% of Al_2O_3.The determination of binder matrix is estimated on the basis of cementation index (CI).

The cementation index (CI) is calculated as per equation:

$$Cementation\ Index = \frac{1.1\ Al_2O_3 + \ 0.7\ Fe_2O_3 + 2.8\ SiO_2}{CaO + 1.4MgO} \quad (5)$$

The classification of lime based on Cementation Index (CI) ranges (Jan Valek, 2012) is:

0.0 < CI < 0.30 – air lime

0.30 < CI < 0.50 – feebly hydraulic

0.50 < CI < 0.70 – moderately hydraulic

0.70 < CI < 1.10 – eminently hydraulic

Greater than 1.10 – natural cement

Table 11 Chemical composition of binder matrix at different position

Sample code name	**Area**	**Cao**	**SiO_2**	**Al_2O_3**	**MgO**	**Na_2O**	**K_2O**	**SO_3**	**FeO**
G3	2	90.46	6.49	1.65	1.4				
	3	83.96	12.65	1.89	0.47	0.35	0.68		
	4	88.67	8.04	1.92	1.36				
		Cementation Index (CI) – 0.33				**Lime** – Weakly Hydraulic			
G2	4	90.89	3.23	0.63	3.67			2.82	
	5	85.47	7.31	1.57	2.93			2.82	
	6	97.83	1.62	0.15	0.39				
		Cementation Index (CI) – 0.13				**Lime** – Air lime			
R2	7	74.96	16.16	4.36	2.31		1.04		1.17
	8	80.75	15.38	2.39	1.48				
		Cementation Index (CI) – 0.60				**Lime** – Moderately hydraulic			
V2	1	96	1.56		2.44				
	2	98.01	0.61		0.59			0.78	
	5	97.51	1.08	0.61	0.8				
		Cementation Index (CI) – 0.16				**Lime** – Air lime			
V8	2	55.39	29.51	12.04	2.49	0.56			
	3	56.91	28.62	11.46	2.34	0.67			
	4	60.4	13.77	22.83	1.6				1.39
		Cementation Index (CI) – 1.57				**Lime** – Natural cement			

L2	1	72.19	20.99	1.98	3.34		1.49
	7	93.22	3.76	0.17	1.54		1.3
		Cementation Index (CI) – 0.42				**Lime** – Weakly Hydraulic	

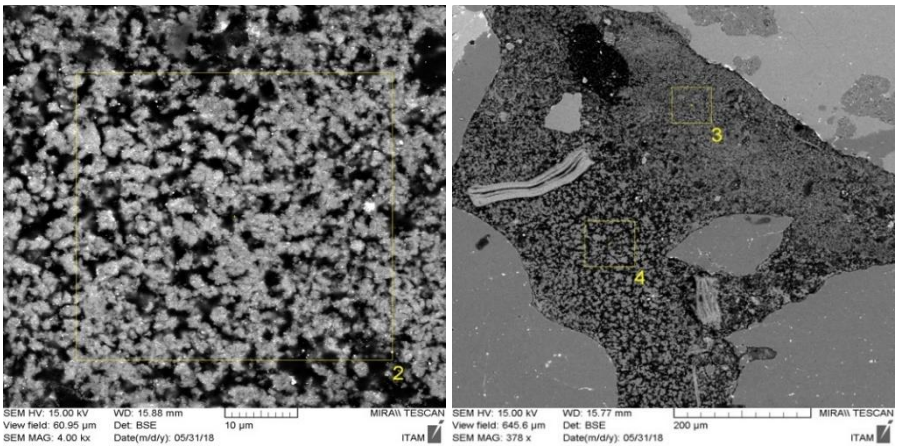


Figure 24 SEM analysis of sample G3 (binder matrix)

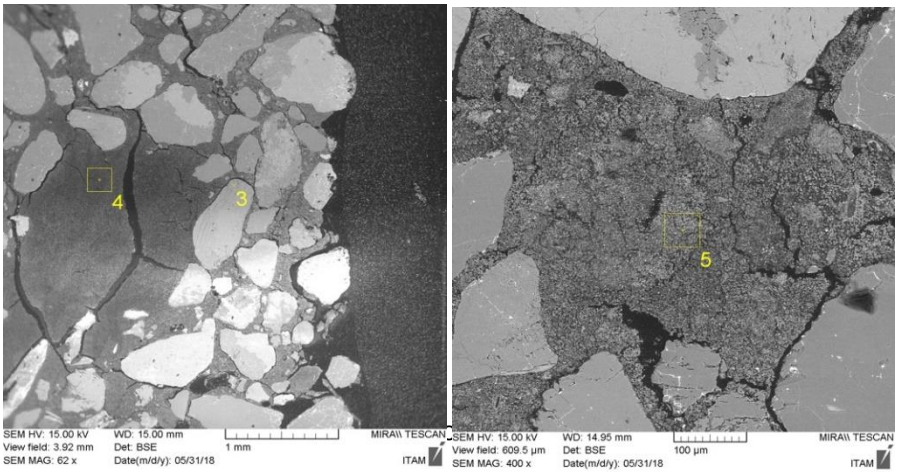


Figure 25 SEM analysis of sample G2

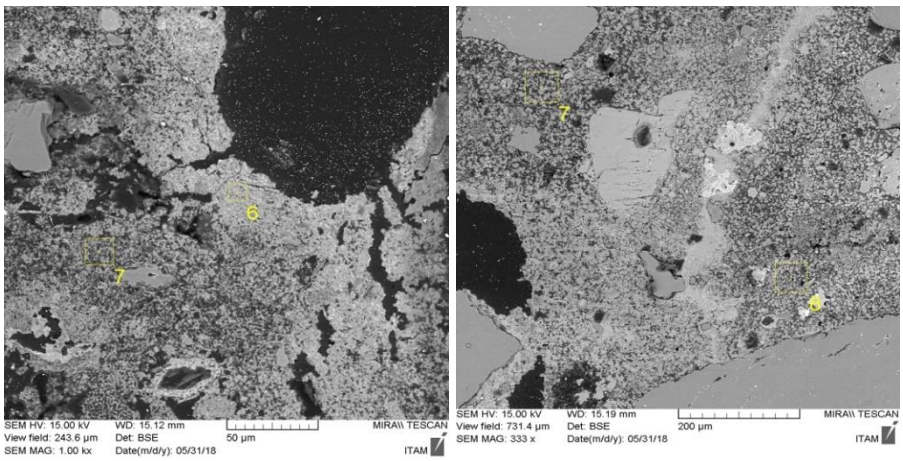


Figure 26 SEM analysis of sample G2 (left side) R2 (right side) (binder matrix)

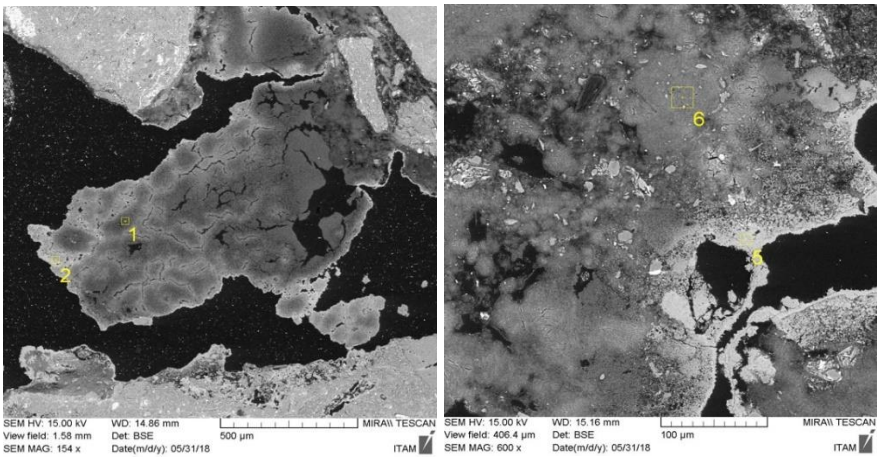


Figure 27 SEM analysis of sample V2 (binder matrix)

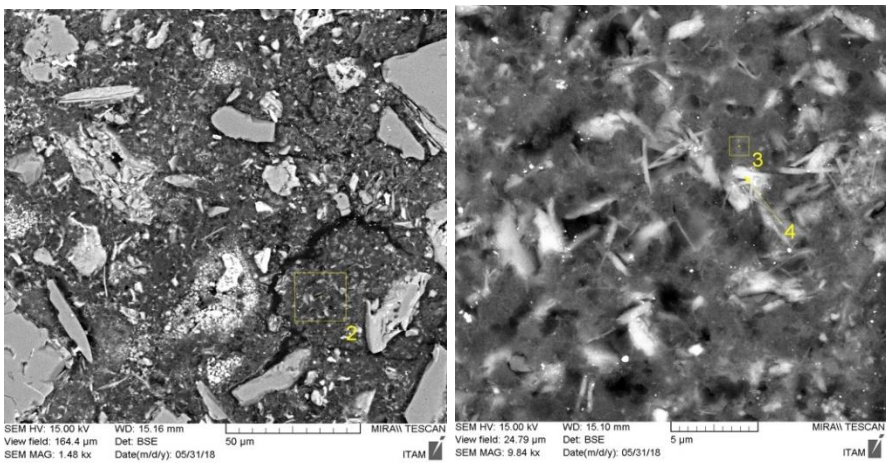


Figure 28 SEM analysis of sample V8 (binder matrix)

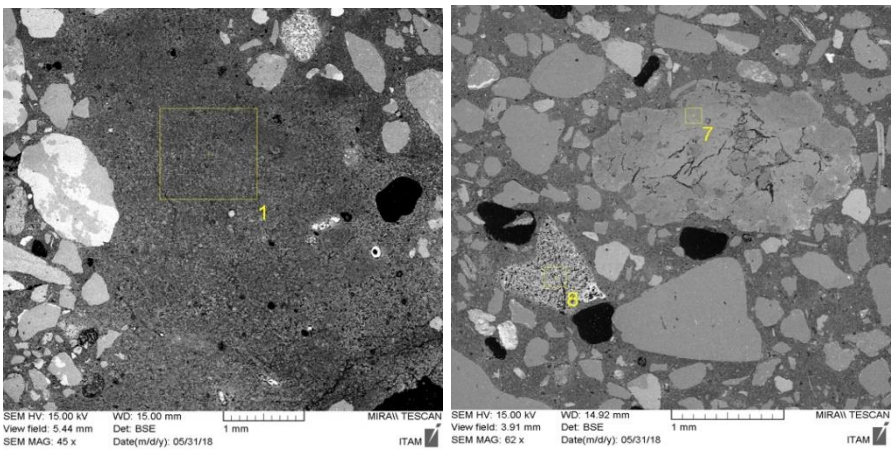


Figure 29 SEM analysis of sample L2 (binder matrix)

4.6 THERMAL ANALYSIS OF BINDER MATRIX

In TGA analysis of samples R6-R5, R3, R2 (Roman floor) and G3 (Greek floor) is carbonated lime. Whereas, samples are G4, G2, V2, L2 and E1 are still under carbonation process (refer table 12).

Table 12 Results of Thermal Analysis.

Sample code name	Weight loss per temperature range (%)			Content (%wt.)		Ratio
	100-380ºC	380-520ºC	520-850ºC	$Ca(OH)_2$	$CaCO_3$	CO_2/H_2O
G4	3.9	1	26.9	4.1	61.1	6.9
G3	4	2	19.3	0.0	43.9	4.8
G2	3.6	9.5	11.5	39.1	26.1	3.2
R6-R5	1.4	1	16.4	0.0	37.3	11.7
R3	1.6	0.9	15.4	0.0	35.0	9.6
R2	2.9	1.6	23.9	0.0	54.3	8.2
V2	4	1.2	20.8	4.9	47.3	5.2
L2	5	6.2	8.8	25.5	20.0	1.8
E1	3.7	4.2	16.7	17.3	17.3	4.5

In table 13 chemical characteristics of the most typical mortars are mentioned, which allows determining the binder matrix (A. Moropoulou *, 2005). It is not necessary to follow the exact mentioned figures in the table because the data was derived based on research work on 400 samples from Greek, Hellenistic, Roman, Byzantine, post-Byzantine and many other ancient mortars. Due to this structurally bound water% and CO_2% amount may differ, mainly CO_2% to structurally bound water ratio is important to determine the binder matrix.

Table 13 Chemical characteristics of historic mortars as deriving from the thermogravimetric analysis

Mortar type	Physically bound Water (%)	Structurally bound Water (%)	CO2%	CO2/structurally bound water
Lime mortars	<1	<3	>32	10[a], 7.5 – 10[b]
Lime mortars with unaltered portlandite	>1	4 – 12	18 – 34	1.5 – 9
Hydraulic lime Mortars	>1	3.5 – 6.5	24 – 34	4.5 – 9.5
Natural pozzolanic mortars	4.5-5	5 – 14	12 – 20	<3
Artificial pozzolanic mortars	1-4	3.5 – 8.5	22 – 29, 10-19[C]	3 – 6

[a] Aggregates of calcareous nature.

[b] Aggregates of silicoaluminate nature.

c Byzantine ‘‘concrete’’.

G4 and G3 consist of a high percentage of structurally bound water 3.9% and 4% respectively but R2 has a low content of 2.9%. The CO_2 content of G4 lies between 24% and 34% but other two samples have less than 24%. The ratio of CO_2 and structurally bound water of these three samples lies between 4.5 and 9.5 which indicates the category of hydraulic lime mortar. Comparing typical curve of NHL with the resultant curve of these three samples, it is clear that binder matrix contains hydraulic lime mortar. (A. Moropoulou *, 2005). Annexure B shows the result of G3 and R2.

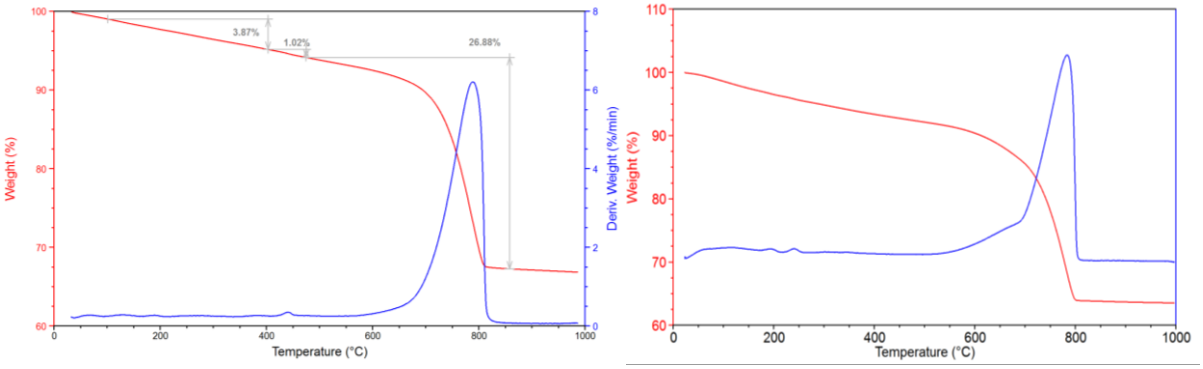


Figure 30 TGA (red) and DTG (blue) curves of G4 sample (left side), typical TGA/DTG curves of natural hydraulic lime mortars (right side).

For samples G2, L2 and E1, it is difficult to determine the type of lime because all three samples are still under the process of carbonation. In the figure 31, shows the clear peak of portlandite for G2 sample, it may occur due to the pozzolanic reaction. Based on the CO_2 to structurally bound water ratio which is 3.2 (G2), 1.8(L2) and 4.5(E1) and the typical curve of the lime binders, the samples possibly considered in the category of lime mortar with unaltered portlandite. The setting of this kind of mortars is extremely slow when not exposed directly to the air (A. Moropoulou *, 2005). The position of these three samples marked at the bottom which clearly shows the air contact is very less. Annexure B shows the result of L2 and E1.

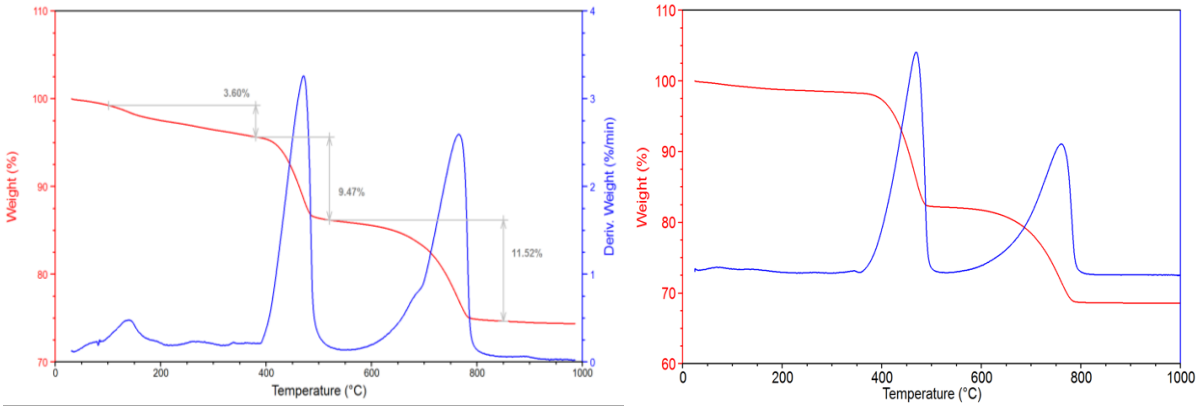


Figure 31 TGA (red) and DTG (blue) curves of G2 sample (left side), typical TGA/DTG curves of lime mortars with unaltered portlandite (right side).

V2 falls in the category of artificial pozzolanic mortars. The structurally bound water is 3.6%, the content of CO_2 is 20.8 which is near to byzantine concrete CO_2% (10-19). The CO_2 to structurally bound water ratio is 5.2. Mortars of this category are effective as waterproofing and contain brick fragments in the matrix of the aggregates (A. Moropoulou *, 2005).

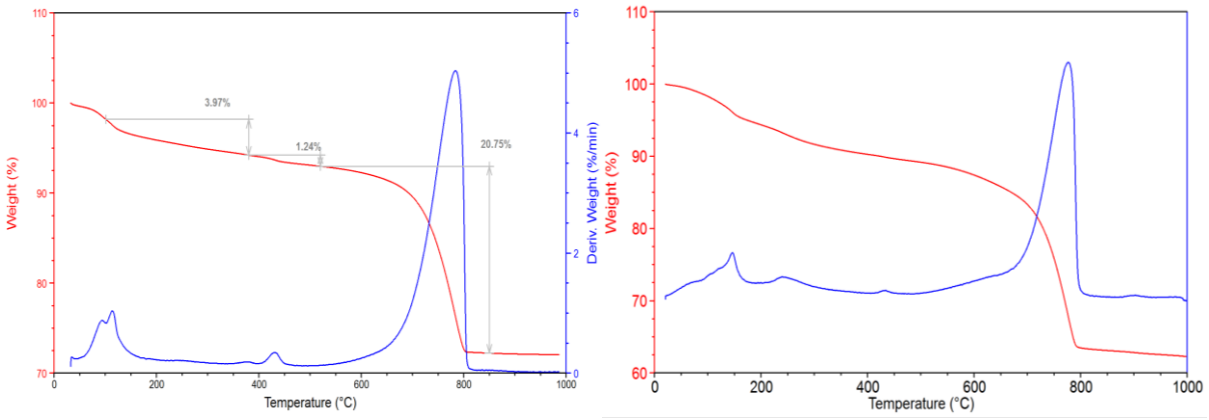


Figure 32 TGA (red) and DTG (blue) curves of V2 sample (left side), typical TGA/DTG curves of air lime mortar with brick (pozzolanic material) (right side).

R6-R5 and R3 ratio of CO_2 to structurally bound water are high i.e. 11.7% and 9.6% respectively. This directly indicates towards the lime mortar category but strangely calcium carbonate content is very less 37.3% (R6-R5) and 35% (R3). It supposed to be 80-90% of $CaCO_3$. Maybe in this case calcium hydroxide ($Ca(OH)_2$) reacted with brick and consumed by the pozzolanic reaction, else the proportion of aggregate is high. It is difficult to say that both samples are carbonated or hydrated. Comparing with the typical curve of air lime mortar with the samples, it is established that both the samples are air lime (refer figure 33). Annexure B shows the result of R3.

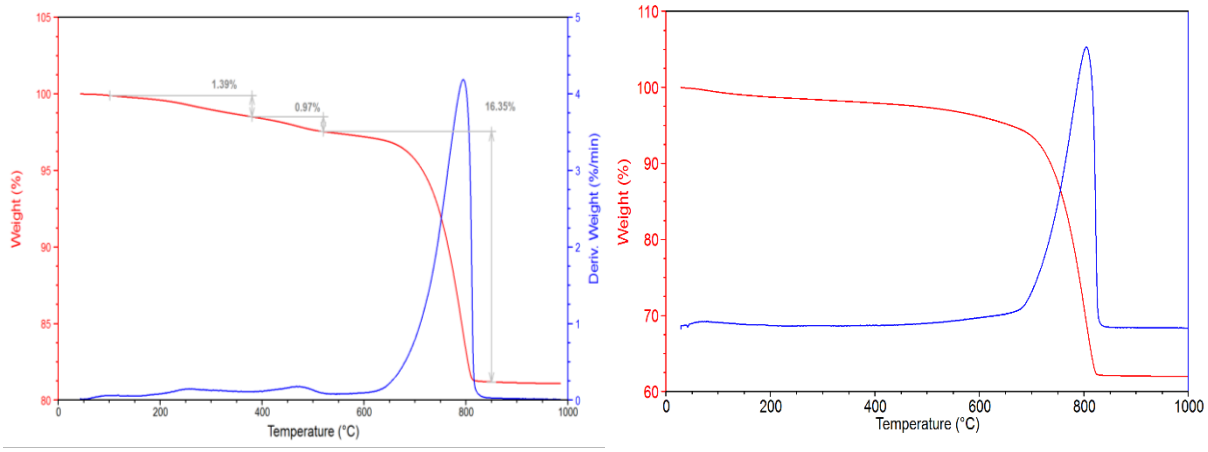


Figure 33 TGA (red) and DTG (blue) curves of R6-R5 sample (left side), typical TGA/DTG curves of air lime mortar (right side).

Figure 34 illustrate the two exponential correlation. One is derived from a number of historic samples representative of various structural periods and production techniques and another derived from the selected samples for the assessment. Main aim is to examine that if there is any correlation between chemical characteristics of historic mortars derived from thermal analysis (CO_2, structurally bound water).

The exponential correlation of CO_2 to structurally bound water/ CO_2 content illustrates the Air lime, semi-hydraulic and the hydraulic character of the composites during setting, hardening and ageing of mortars (A. Moropoulou *, 2005).

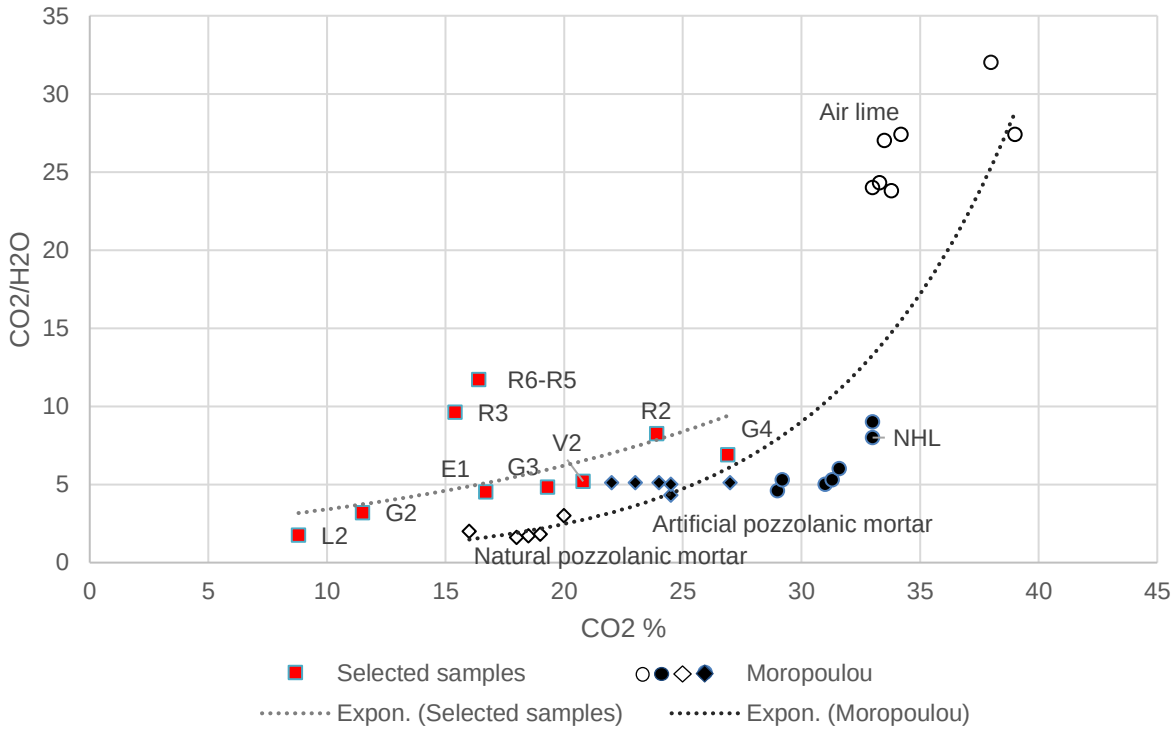


Figure 34 CO_2 to structurally bound water ratio in relation to % CO_2

5. DISCUSSION

The obtained results relating to the ratio, binder to aggregate, were mainly from acid dissolution test and optical microscopy test. These two tests also analysed the type of binder and aggregate. In acid dissolution test, most of the analysed samples showed different results, when compared to the original mixing ratios. G4, R6-R5, R3, V8, V2, and L2 samples were the exceptions; they represented nearly the same proportion as in the original panels. Whereas, G3 showed a high proportion of aggregate 1:3.7, while the original ratio was 1:3. On the contrary, G2, R2, V1, and E1 samples show the low proportion of aggregates, especially G2 (1: 1.5) and E1 (1: 1.8) are almost half of the original floor panel ratio (1:3). The discrepancy between binder to aggregate ratio could possibly happen due to some error while performing the test, for instance, decision of removing the gravels before starting the test as the main intention was to analyse the sand. Due to the absence of gravels G2 and R2 shows less proportion of aggregate. Another possible reason could be the type of raw material used for the mortars. In case of G3, ash is used as additive and natural hydraulic lime as a binder which may be responsible in increment of aggregate ratio. After sieve analysis, there are some white colour grains found in the sand that are the remains of the binder. Natural hydraulic lime is the impure form of lime, this impurity can behave as aggregate and the undissolved white colour grains are the proof of this fact (refer figure 35).

Figure 35 White grains with sand after sieve analysis of the sample E1 (left side), white grains with crushed after sieve analysis of the sample V8 (right side).

In case of V1 and E1, hot mix of lime is used to prepare binder; as a result, the binder can contain some not fully burned particles and other calcium-silicate minerals that are newly formed during the burning process. Presence of such particles make the analysis less reliable and it has to combine with a detailed characterisation by optical microscopy in order to be able to interpret it correctly.

In optical microscopy, five samples were selected to be observed, i.e. G3, G2, R2, V2, V8, and L2. They represented the different binders and aggregates used to produce the floor panels. The estimation of the ratio based on optical microscopy is nearly same as original mortar mixing ratio except for V2, which represents high aggregate proportion 1: 5. After observing a thin section of V2, it is difficult to estimate the binder to aggregate ratio due to the high amount of porosity and less amount of binder matrix. In this situation, it is not possible to obtain the correct outcome. Whereas, it is also clear that the selection of the sample piece is matching the expectation of optical microscopy result. Another sample L2 is also

slightly on higher side of aggregate proportion (1:2.5) in comparison with the original mixing ratio (1:2). There can be a possibility of minor error due to the manual estimation of binder to aggregate ratio. Moreover, it is established that for better interpretation and accuracy of the result more than one method is necessary. For example in case of G3, G2, and R2 estimated ratio in optical microscopy is same as original mixing ratio (1:3), whilst the result of the dissolution test is completely different for the same.

Table 14 Comparison between the ratio of the dissolution test, optical microscopy test and original mortar mixing ratio (volume units).

Sample code	**Layers**	**B/A ratio (selected samples)**		**B/A ratio (original mortar mixing ratio)**
		Dissolution test	Optical microscopy test	
Panel A: Greek floor (Vitruvius)				
G4	Surface layer	1: 2.5*	-	1: 2.25*
G3	Nucleus	**1: 3.7***	1: 3*	1: 3*
G2	Rudus	**1: 1.5**	1: 3	1: 3
Panel B: Roman floor (Vitruvius)				
R6 - R5	Repair layer surface layer	1: 1.9	-	1: 2
R3	Nucleus (lower)	1: 3.4	-	1: 3
R2	Rudus	**1: 2.2**	1: 3	1: 3
Panel C: Venetian terrazzo				
V8	Repair layer	1: 2.1	1: 2	1: 2
V2	Rudus	1: 2.6	**1: 5**	1: 3
V1	Statumen	**1: 2.3**	**1: 2.3**	1: 3
Panel D: Lime mortar cast floor				
L2	Rudus	1: 1.6	**1: 2.5**	1: 2
Panel E: Tiles on mortar				
E1	Statumen	**1: 1.8**	-	1: 3

*Ash

Apart from binder to aggregate ratio, it is also important to understand the binder matrix and its chemical properties in order to correctly interpret the obtained proportions. Thermal analysis was the source of data regarding the nature of the binder and quantification of the calcium carbonate and hydroxide proportion. Scanning electron microscopy equipped with a probe (EDS) allowed to carry out a point or area analyses at a certain grain or position on matrix of the thin-sections. It reveals that four samples (R6-R5, R3, R2, G3) are completely carbonated while other five (G4, G2, V2, L2, E1) are still under the process of carbonation. Remaining samples V1 and V8 excluded for thermal analysis due to the loss of sample and difficulties to collect the fine fraction under 63 µm respectively. The TA results are assessed mainly by two means, one is the comparison of obtained data with the typical curve of a particular binder type. The research institute – ITAM, provided the typical TA curves of binders. The other way of

assessment was based on the reference table derived from the research work of Moropoulou et al. on historic mortars (refer table 13). G4, G3, and R2 demonstrate the properties of hydraulic lime mortar according to the table and follow the identical inclination of the typical curve. Similarly, R6-R5 and R3 fits in the category of air lime mortar. Whereas G2, L2, and E1 are unidentified lime-based binders because of the portlandite peak. It is difficult to categorise the binder in this case. Portlandite also takes part in pozzolanic reaction. In the case of pozzolanically active aggregate like the crushed brick potentially was the portlandite (calcium hydroxide)of possibly partially reacted to form calcium-silicate hydrates and did not carbonate. This was probably the case of the last group discussed here. V2 contains brick fragments in the matrix of the aggregates as well as R6-R5 and R3, and the curve and CO_2 to structurally bound water ratio indicates towards the category of artificial pozzolanic mortar, specifically byzantine concrete.

Scanning electron microscopy unfold the detail of G2 sample as air lime through the value of cementation index 0.13 (refer table 15). Similarly, L2 is evaluated under the category of weakly hydraulic lime and V8 is natural cement but it was complicated to recognise the binder due to the homogenous dark red colour of the thin section. Contemplating the results of thermal analysis with scanning electron microscopy, both provides the details of a binder including carbonation process and characterization of lime. However, there were also some discrepancies in the results between TA and SEM. In the case of lime-pozzolanic binding system, like the V2 and V8, the SEM-EDS point analysis was difficult to interpret. The binding matrix was not divided into specific recognisable areas and therefore the analysed positions did not correctly represent the binding system.

Table 15 Comparison between the binder matrix of thermal analysis, scanning electron microscopy and original mortar binder.

Sample code	Layers	Binder matrix (selected samples)		Binder matrix (original mortar binder)
		Thermal analysis	SEM	
Panel A: Greek floor (Vitruvius)				
G4	Surface layer	Hydraulic mortar	-	Hydraulic mortar
G3	Nucleus	Hydraulic mortar	Weakly hydraulic	Hydraulic mortar
G2	Rudus	**Unaltered portlandite mortar**	Air lime	Air lime
Panel B: Roman floor (Vitruvius)				
R6 - R5	Repair layer surface layer	Air lime	-	Air lime – crushed brick
R3	Nucleus (lower)	Air lime	-	Air lime – crushed brick
R2	Rudus	Hydraulic mortar	Moderately hydraulic	Hydraulic mortar
Panel C: Venetian terrazzo				
V8	Repair layer	-	**Natural cement**	Hydraulic mortar – crushed brick
V2	Rudus	**artificial pozzolanic mortar**	Air lime	Air lime – crushed brick
V1	Statumen	-	-	Air lime
Panel D: Lime mortar cast floor				
L2	Rudus	**Unaltered portlandite mortar**	Weakly hydraulic	Hydraulic mortar
Panel E: Tiles on mortar				
E1	Statumen	**Unaltered portlandite mortar**	-	Hydraulic mortar

Deducing all the methods each one has its own pros and cons. For acid dissolution test, around 100g material needs to be collected from the site for each sample. The position of the material was also important for example considering the size of the aggregates and the amount of gravel. However, using invasive methods is definitely a disadvantage to the cultural heritage but at the same time, it is necessary to perform such tests to imitate the mortar. Time is also the limitation of the acid dissolution test; it took around 20 days to analyse 11 samples considering three samples at one time with seven working hours per day. Perhaps, another method like optical microscopy and thermal analysis are the counter balance of the assessment. Optical microscopy demand only the small piece of the mortar to make the thin section of about 30 x 50 x 20 mm (Elsen, 2006). Sometimes it is easier to collect the pieces as it is expected that the plaster or mortar will be falling off due to the surface damage. Time is also not an issue, on an average it takes two samples per day to observe. Sample preparation takes some time – should be mentioned. The essential part is the piece that must be representative of the material otherwise; the interpretation will be unreliable. Similarly, less invasive method is the thermal analysis where the small piece of mortar (app. 20-30 g) crushed gently to collect the fractions under 0.063 mm

is needed. Fractions must be the part of the binder only, participation of a small portion of the sand will affect the result.

The chemical analysis provides however also a possibility to study the soluble and insoluble portions. The gradation of sand is of course a crucial part if the aim is to imitate the mortar for the conservation of cultural heritage purposes. Depending upon the site the best way can be opted for the material collection according to the aims of analysis.

Table 16 Basic properties determined by the below mentioned methods and their limitations.

Performed experiments	Advantages	limitations
Acid dissolution test	Determination of the binder and aggregate ratio by the acid digestion of the sample.	Presence of pozzolans may disrupt the determination of the original composition of the mortar by altering the amount of soluble silica.
	Determination of the chemical characterisation of the acid soluble fraction of the mortar by ICP.	Carbonate aggregate will also get dissolve by acid attack.
	Measurement of dissolved silica into acid solution for the estimation of hydraulicity of mortar.	Time consuming.
Optical microscopy	Determination of the mineralogy of mortar composition and characterisation of the components.	Identification of the binder is difficult, if the brick powder and fragments are used as the aggregate.
	Identification of aggregate, binder, additives including pozzolans, porosity, cracks and secondary mineral formation.	If the selected piece is not representative of the original material then the interpretation is non-reliable.
	Less time consuming and less invasive method.	
Thermal analysis	Identification of characteristics patterns of temperature change or weight loss during heating.	Sieved sample must contain pure form of binder in order to interpret it as the complete binder composition. Else, the results can be used as proportional. Ie. proportion of CO2 to chemically bound water.
	Distinguish between carbonated and non-carbonated sample.	Presence of pozzolans may disrupt the inclination of the curve.
	Characterisation of binder matrix.	
	Fastest out of the four studied. If a representative binder is obtained the amounts needed for analysis are very low.	
SEM	Characterisation of the binder matrix and other particles by their elemental composition.	Potential danger of misinterpreting the measured elements due to limited representativeness. Only very small areas are studied.
		It is expensive. Time consuming when carried out in details.
	Very detailed. Time depends upon the user and the objective of the analysis. Uses thin-sections or especially polished sections.	

6. CONCLUSION

- The experimental results of the present study have clearly demonstrated the adequacy and applicability of the methods for the conservation practice with some limitations. Acid dissolution test shows variance in the result due to the raw material. Natural hydraulic lime and hot mix lime as binder happen to increase and decrease the aggregate proportion respectively. Some not expected materials like ash as additives and presence of gravels in the matrix of aggregate proportion will affect the results in the same way as binders do. Considering the discrepancy of the binder to aggregate ratio, it is also important to understand the results with another complimentary analysis to characterise the binder.

- Optical microscopy is more efficient in terms of time consumption and the estimation of the binder to aggregate ratio. Brick based sample is the exception here. It is hard to distinguish between the binder and aggregate due to homogenous red colour and various fineness of the particles that to a certain degree take part in the pozzolanic reaction. Scanning electron microscopy is the complimentary analysis to categorise the binder by tracing the elements.

- Thermal analysis is the appropriate method for analysing the binder matrix but the precaution is needed while preparing the sample. If the sieved binder is contaminated with the non-binder particles, then the curve and TG quantitative results will be affected and thus it may hinder the right interpretation of the binder type or its quantitative assessment, e.g. presence of carbonates.

- Conclusively, above-mentioned analytical methods are effective and suitable for conservation practice. For practical approach, the objective of the analyses must be clear before any sampling can take place. Selection of the analytical methods must be balanced in between invasive and non-invasive methods. Determining the amount of sample will minimise the effort, cost and damage to the cultural heritage.

REFERENCES

A. Moropoulou *, A. B. (2005). Composite materials in ancient structures. In *Cement & concrete composites* (pp. 295-300).

Anjum, M. I. (2011). *Simple Approach for Determination of Optimum Gradation Considering the Combined Index and Angularity Number of Stone Aggregates.* London.

Ashurst, J. (1983). *Mortars, Plasters and Renders in Conservation.* Ecclesiastical Architects and Surveyors Association.

B. Middendorf 1, J. J. (2005, october). Investigative methods for the characterisation of historic mortars-Part 1: Mineralogical characterisation. *Material and Structure*, 761-769. Retrieved from https://link.springer.com/content/pdf/10.1007%2FBF02479289.pdf

C.J Brandan, R. H. (2014). *Building for eternity.* United kingdom: Oxbow books.

Callebaut, K. V. (1999). Petrographical, mineralogical and chemical investigation of 17thand 19thcentury lime mortars in the St.- Michael's church. Leuven: Internationale Zeitschrift J'~r Bauinstandsetzungen und Denkmalpflege.

centre, T. S. (2003). Technical advice note. In *Preparation and use of lime mortars* (pp. 1-10). Historic Scotland.

Compton, R. R. (2106). In *Geology in the field* (p. appendix). Earthspun Books 2016 1b Achilles Way, Pinelands 7405 Cape Town, South Africa.

Cowper. (n.d.). A D. Lime and Lime Mortars. *Facsimile of 1927 publication*. Donhead Publishing 1998.

Crovato, A. (1999). *I Pavimenti Valla Veneziana.* Italy : Edizioni Grafi.

eea grants. (n.d.). Retrieved from http://www.nase-rotunda.cz/en/

Elsen, J. (2006). Microcopy of historic mortars - a review. In *Cement and concrete research 36* (pp. 1416-1424). Leuven .

G. De Schutter, A. P. (2004). Quantification of the water demand of sand in mortar, Constr. Build.

G.V, C. K. (1975). *Compaction of coarse - grained sediments, I.* NEW YORK: Elsevier scientific publishiing company .

Graymount. (n.d.). Retrieved from http://www.graymont.com/en/markets/construction/building/mortar-applications/history-lime-mortar.

Graymount. (2016). Retrieved from http://www.graymont.com/en/markets/construction/building/mortar-applications/history-lime-mortar

Ing. Alberto Viani, P. (n.d.). *Czech Academy of Sciences.* Retrieved june 2018, from http://www.itam.cas.cz/CET/o-nas/laboratore/laborator-materialovych-analyz-a-mikroskopie/index.html

J.P.Oleson. (2014). The Bindisi pila reproduction. In R. H. C.J. Brandon, *Building for eternity* (pp. 109-110).

Jan Valek, J. J. (2012). Hydraulicity. In *Historc mortars: Characterization, Assessment and Repair* (pp. 126-127).

John J Hughes, J. V. (2003). Mortars in historic buildings. Scotland: ISBN 1903570 R2 4.

Katharine Brown, A. W. (2018). *face sheets bulk density - measurement*. Retrieved from soil quality.org.au: http://soilquality.org.au/factsheets/bulk-density-measurement

Lanas, J. L. (2004). Mechanical properties of natural hydraulic lime-based mortars. In *Cement and Concrete* (pp. 2191-2201).

Middendorf, B. a. (1998). *Conservation of Historic Brick Structures: Case Studies and Reports of Research.* England: Donhead Publishing Ltd.

Middendorf, B. H. (2005). Investigative methods for the characterisation of historic mortars - Part 2: Chemical characterisation. *Material and structure* , 771-780.

Modena, L. &. (2005). Ancient binding materials, mortars and concrete technology:. *Structural Analysis of Historical Constructions*. Taylor & Francis Group, London, ISBN 04 1536 379 9.

Morris hicky morgan, P. L. (1914). Floors and stucco work . In *The ten books on architecture* (pp. 201-204, 208-210). London : Harvard university press.

R. Ravia, M. R. (2018). Mechanical and physical properties of natural additive dispersed lime. *Journal of Building Engineering*, 70-77.

St. John, D. P. (1998). Concrete petrography. In *A handbook of investigative techniques* (pp. 127-133). London: Arnold .

Wet chemistry. (1984). (Laboratory Testing INC.) Retrieved 2018, from https://www.labtesting.com/services/materials-testing/chemical-analysis/wet-chemistry/

ANNEXURE A OPTICAL PLANE POLARISED IMAGES OF SELECTED

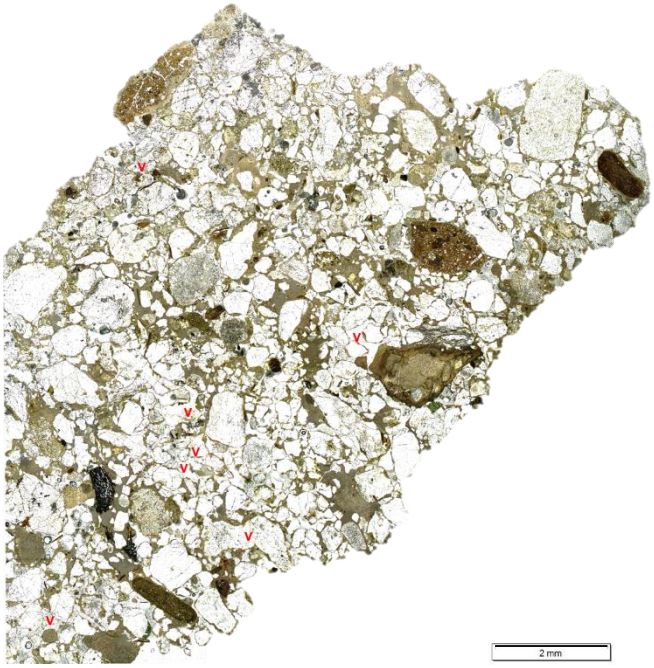


Figure 36 Optical plane polarised image of sample G3, where voids are marked as ‘v’.

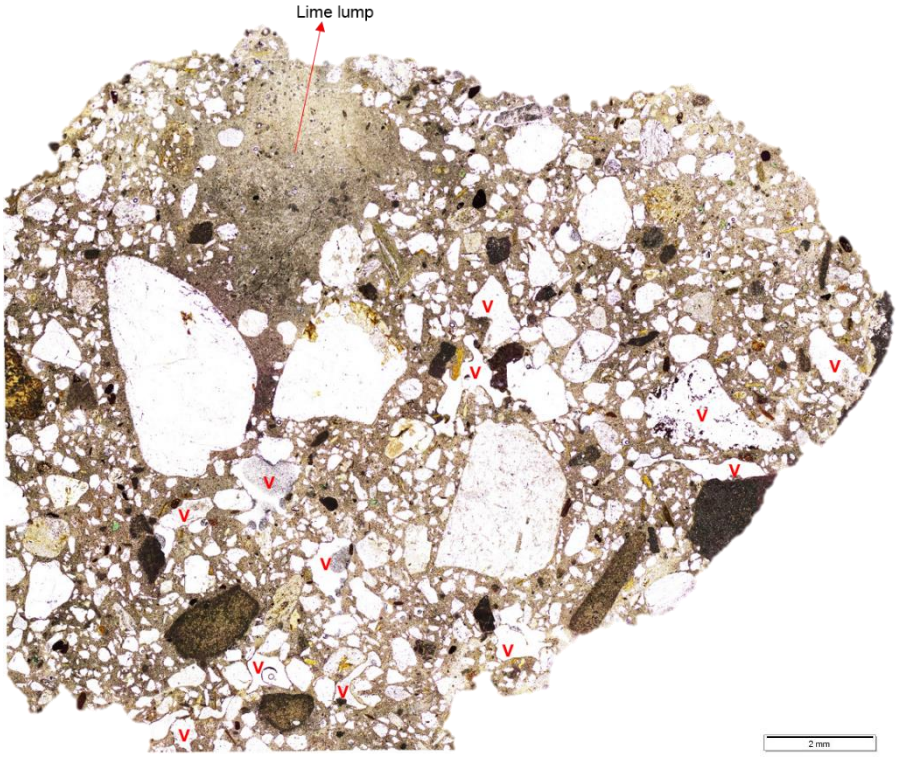


Figure 37 Optical plane polarised image of sample L2, where voids are marked as ‘v’ ** and the presence of lime lump.

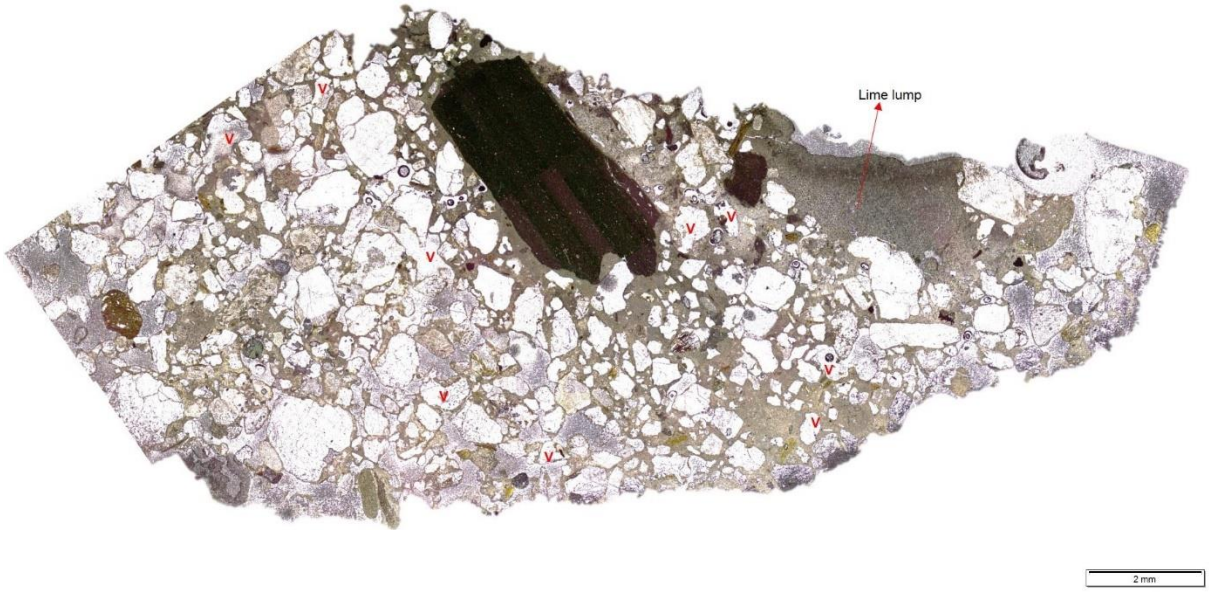


Figure 38 Optical plane polarised image of sample R2, where voids are marked as ‘v’ **and prominent portion of lime lump.

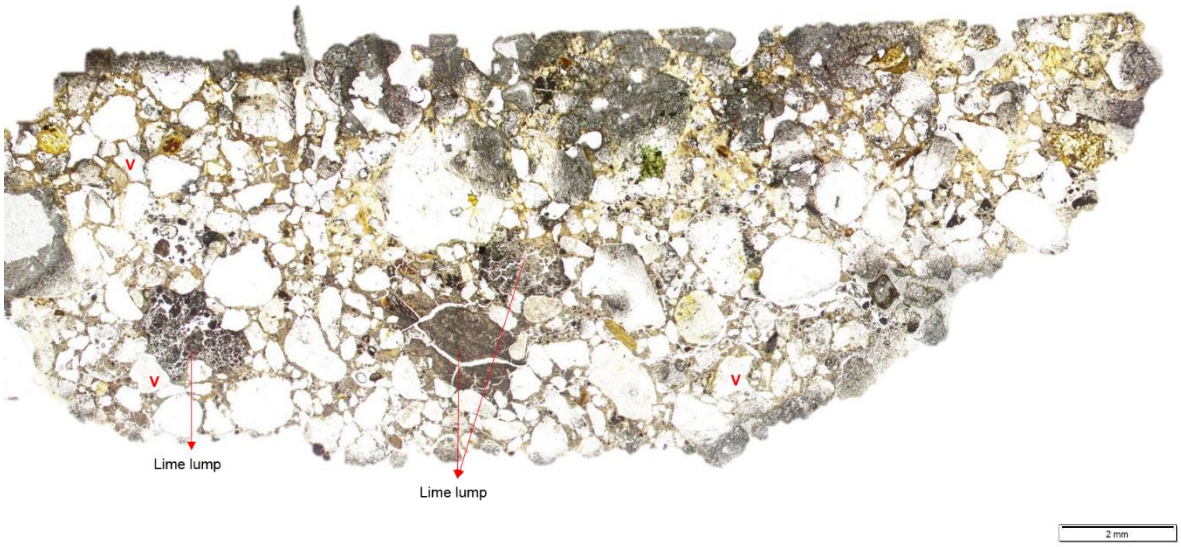


Figure 39 Optical plane polarised image image of sample G2, where voids are marked as ‘v’ ** and two significant lime lump.

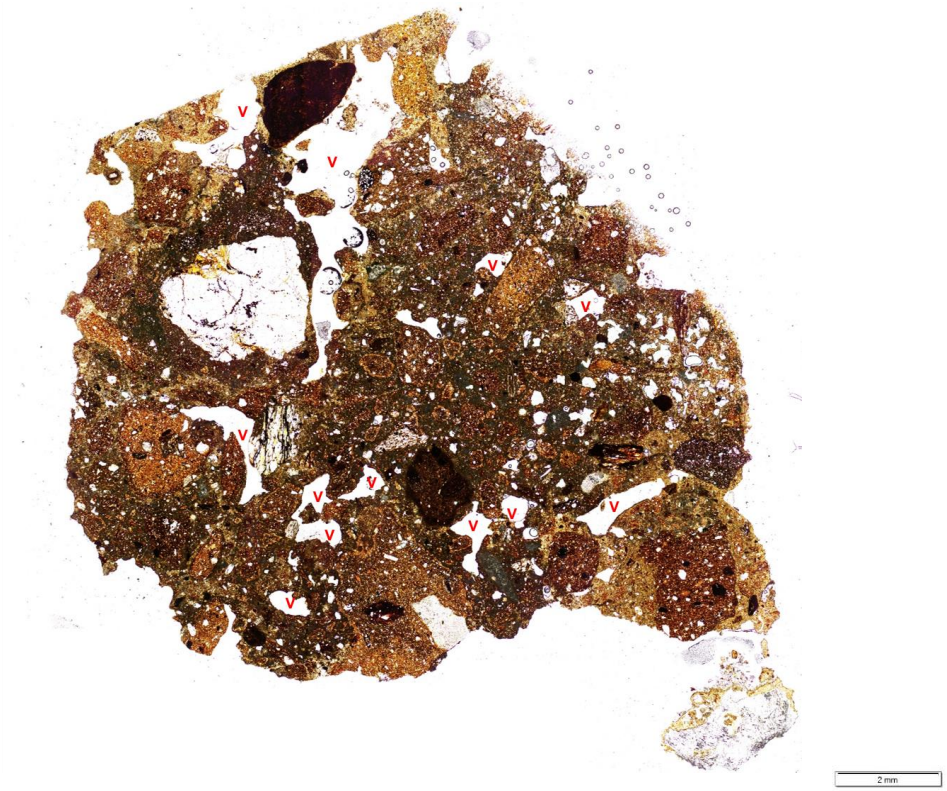


Figure 40 Optical plane polarised image of sample V8, where voids are marked as ‘v’**

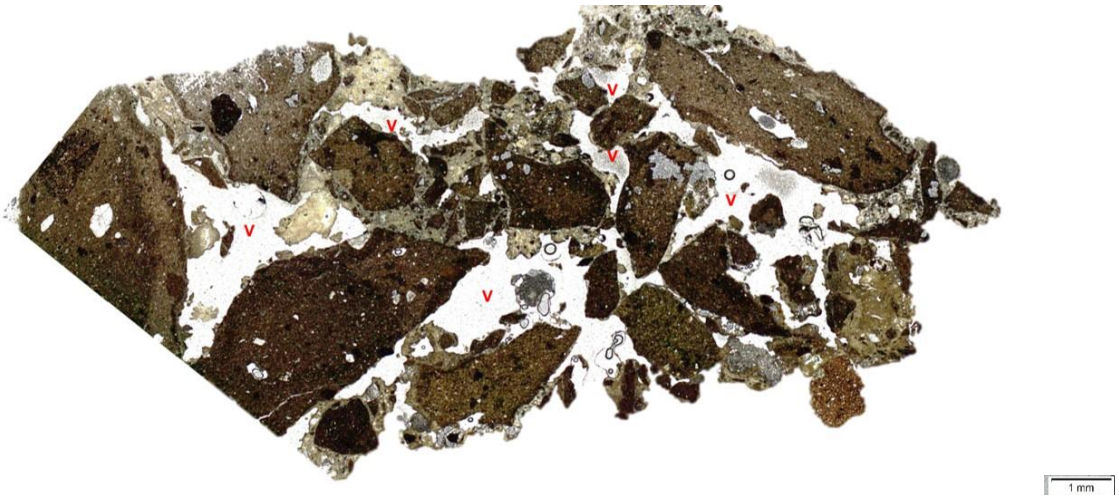


Figure 41 Optical plane polarised image of sample V2, where voids are marked as ‘v’**

**consider not marked small voids

ANNEXURE B: THERMAL ANALYSIS OF THE SELECTED SAMPLES.

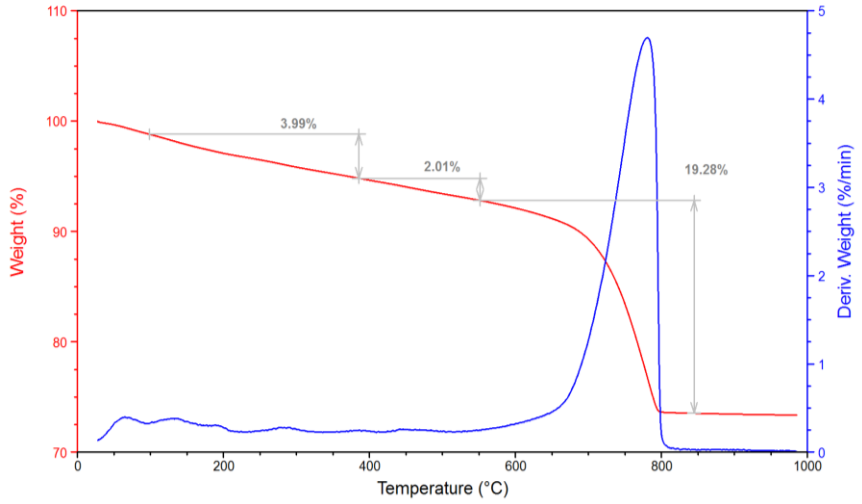


Figure 42 TGA (red) and DTG (blue) curves of G3 sample.

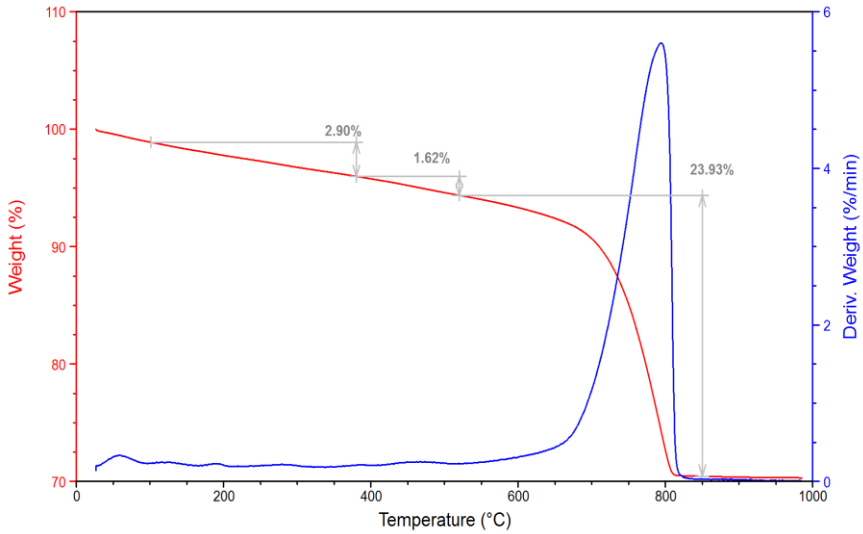


Figure 43 TGA (red) and DTG (blue) curves of R2 sample.

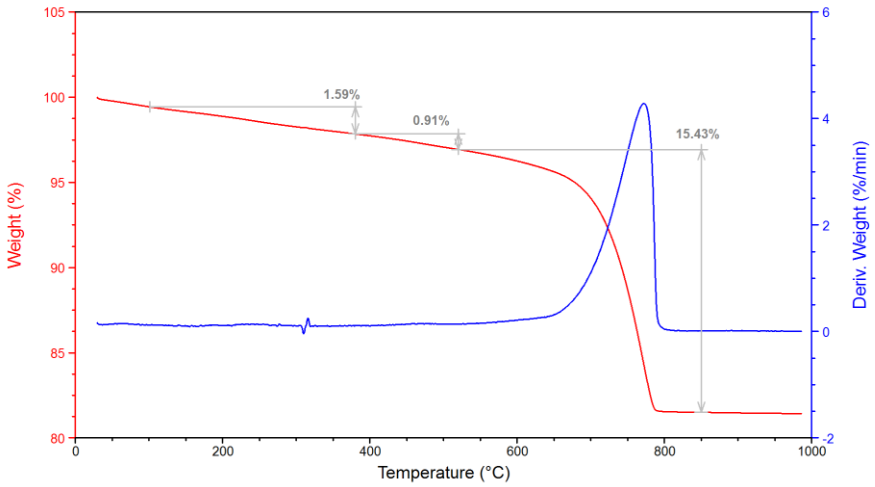


Figure 44 TGA (red) and DTG (blue) curves of R3 sample.

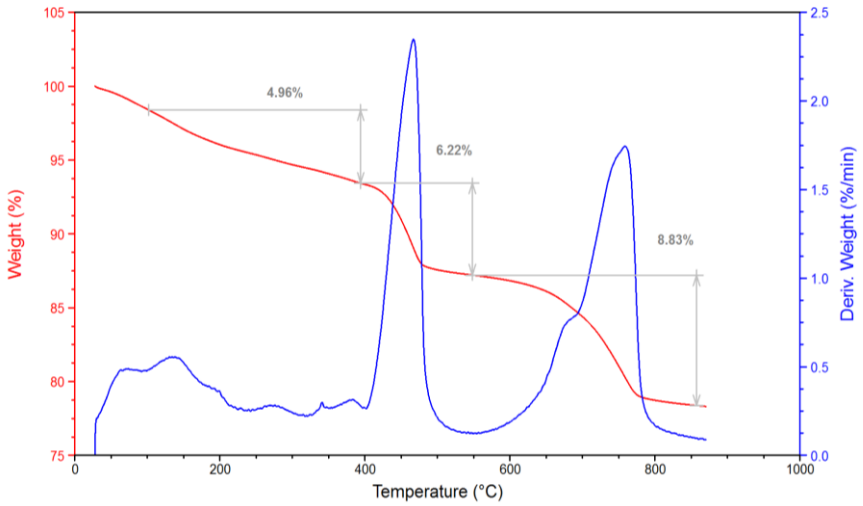


Figure 45 TGA (red) and DTG (blue) curves of L2 sample.

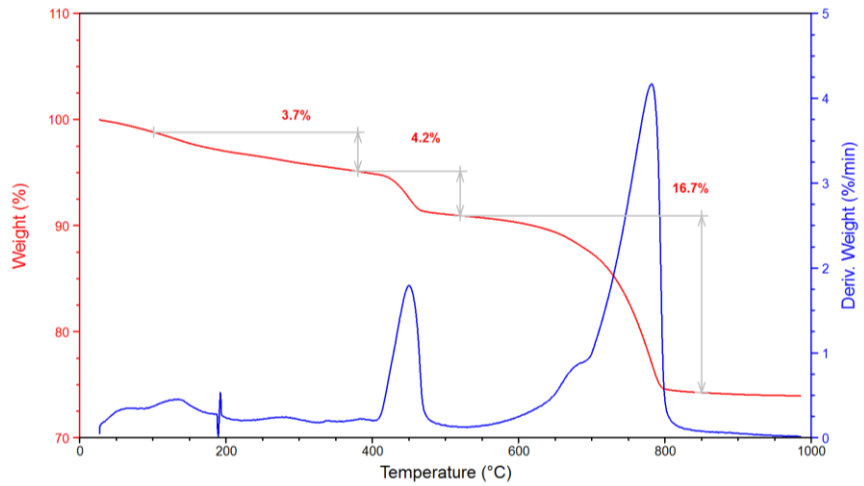


Figure 46 TGA (red) and DTG (blue) curves of E1 sample.

ANNEXURE C: SEM-EDS ANALYSIS OF GREEN COLOUR PARTICLE AND FELDSPAR

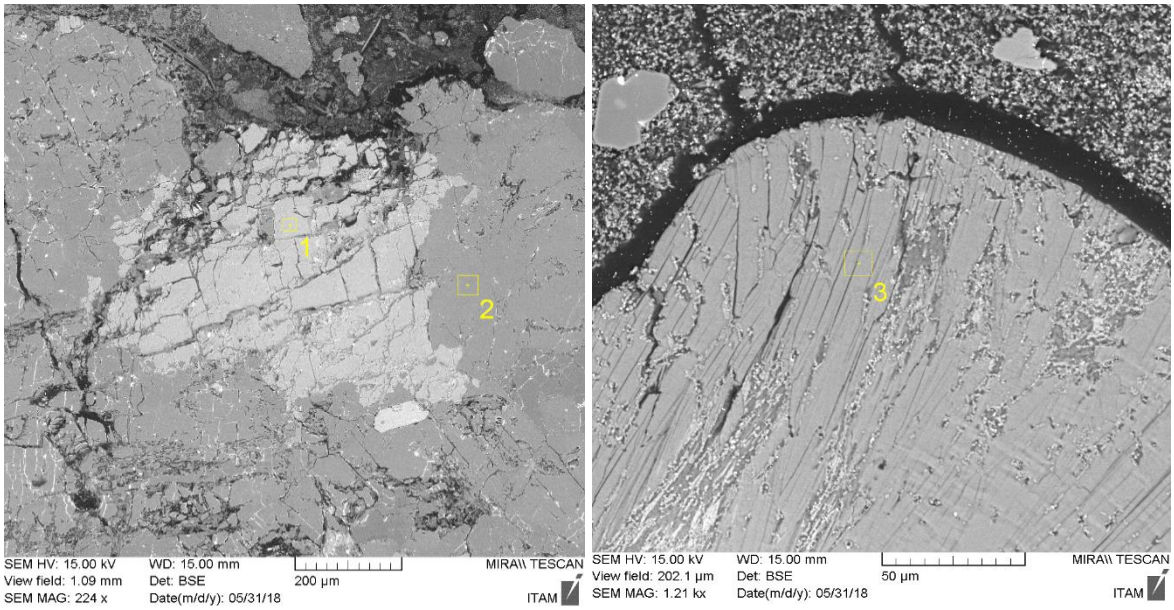


Figure 47 SEM-EDS analysis of green particle marked area 1 and feldspar area 3.

Table 17 Chemical composition green colour particle.

Sample code name	Area	Cao	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	SO_3	FeO
G2	1	12.14	46.49	8.79	10.64	1.13	0.41		18.88
G2	3		47	40	0.61	0.68	10.46		0.52