"OVIDIUS" UNIVERSITY OF CONSTANTA

DOCTORAL SCHOL OF APPLIED SCIENCES

FIELD OF DOCTORATE : CIVIL ENGINEERING

DOCTORAL THESIS ABSTRACT

Doctoral Advisor
Prof.univ.dr.eng. Carmen Elena MAFTEI

Doctoral student
Eng.Mociu Nicolae Costin

CONSTANȚA, 2023

OVIDIUS" UNIVERSITY OF CONSTANTA

DOCTORAL SCHOL OF APPLIED SCIENCES

FIELD OF DOCTORATE : CIVIL ENGINEERING

Investigating the secrets of Roman mortars and proposing new mortar compositions in the context of sustainable urban regeneration

-Abstract-

Doctoral Advisor
Prof.univ.dr.eng. Carmen Elena MAFTEI

Doctoral student
Eng.Mociu Nicolae Costin

CONSTANȚA, 2023

Table of contents

Acknowledgements

First of all, I would like to thank in particular Prof. Dr. habil.eng. Maftei Carmen Elena, my scientific coordinator, for her constant guidance, attention to detail, support and, last but not least, the patience she showed throughout the elaboration and writing of my thesis. I would also like to express my gratitude for the openness of the professor towards any topic of study in the field.

I would also like to thank the members of the mentoring committee, who were actively and constantly involved in the preparation of the thesis with helpful suggestions and advice. To Prof. Dr. Eng. Ionela Cărăzeanu Popovici for her help in carrying out the chemical analyses and interpreting the results, and to prof.univ.dr.ing. Ana-Maria Grămescu, for the opportunity to carry out the internship at the International College of Continuing Professional Education for Experts and Specialists. I would like to thank Prof. Monica Vlad and Prof. Carmen-Adina Ciugureanu, who were my tutors for one year in the project "Program for increasing performance and innovation in doctoral and postdoctoral research of excellence - PROINVENT Contract no. 62487/03.06.2022 POCU/993/6/13 - SMIS Code: 153299".

At the same time, my appreciation also goes to the staff of the Faculty of Construction of the Ovidius University of Constanta, Mr. dean, s.l.univ.dr.eng. Cosmin Filip, Mr. Conf. Dr. Eng. Constantin Buta, Ms.Ș.l.univ.dr.ing. Mădălina Stănescu and Ms. Ș.l.univ.dr.ing. Geanina Mihai, for their help and understanding during the elaboration of the thesis. I would also like to thank Prof. Dr. Eng. Georgeta Voicu for her support in the chemical analysis of the researched materials. At the same time, I would like to thank the Mayor of Ovidiu, George Scupra, for the access to the necessary documents and to the archaeological site and also to Constantin Băjenaru.

Last but not least, I would like to express my gratitude to my family, who has been with me from the beginning, encouraged me and helped me whenever I needed it in all the activities involved in the elaboration of the thesis.

1. Urban regeneration - context, definitions, principles

The term urban regeneration has been approached in different ways in the history of city development and has, over time, different connotations starting with the urban development programmes for Paris proposed and carried out by Baron Haussmann [30].

Recently there has been a global and European focus on urban development based on the principles of sustainability and integrity, coupled with ensuring environmental sustainability and climate change mitigation. With regard to terminology, in the image below we present an evolution of terms according to Roberts and Sykes [19] characterised by strategy and level of development, approach and social context.

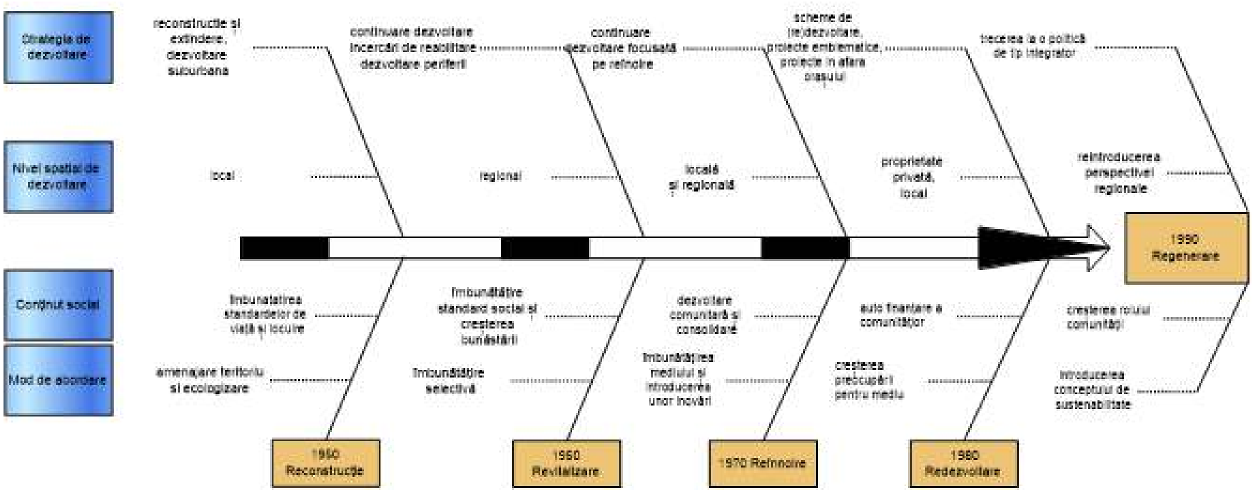


Figure 1 Outline of the evolution of the concept of urban regeneration

In Robets and Sykes' understanding the term urban regeneration can be defined as: "*Comprehensive and integrated vision and action leading to the solution of urban problems and aiming to bring about a lasting improvement in the economic, physical, social and environmental condition of an area that has undergone change.*" [19].

With reference to the issue of built heritage regeneration, we believe that the term is not clearly understood and defined in European documents on urban development/regeneration. Examples of urban regeneration aimed at preserving heritage have shown that it is a driving force for economic growth, employment and social cohesion, helping to revitalise towns or rural areas and promote tourism. [31]. This is why we believe that the regeneration of the built heritage helps to develop a competitive and productive city/town.

In this context we note that in the conservation work of historical/archaeological monuments that are part of the historical and cultural heritage, an important role is played by the materials used. Until the 1970s and 1980s, the characterisation of historic mortars was generally carried out only on the basis of traditional chemical analyses ("wet chemical analysis") [6], using an acid, usually HCl (hydrochloric acid). An impressive series of such analyses was carried out in Poland by H. Jedrzejewska. This process allowed her to classify mortars from three determinations: carbon dioxide, sand and soluble matter content. The main limitation of this technique is that if carbonate is present in a mortar then it will be dissolved. Lately optical microscopy and X-ray diffraction (XRD) techniques are proposed as a first step in the determination of mortar components. Alongside these, infrared spectrometry, thermal analysis (thermogravimetry - TG, Differential Thermal Analysis - DTA), electron microscopy, physical and mechanical tests can also be used, depending on the purpose of the investigations to be carried out and the amount of material available.

The main aim of this study is to determine a suitable mortar composition to be used in the rehabilitation works of historical monuments located in archaeological sites in Romania.

The research objective will be achieved by studying, on the one hand, the mortars used at the archaeological site of the Roman fortification of Ovidiu to determine their physical and chemical properties and, on the other hand, by producing new lime-based mortar compositions that will be subjected to the same analysis in order to make a comprehensive comparison with the results obtained on Roman mortars and to choose the optimal composition for subsequent use.

At the same time, in the current context of sustainable development, some of the newly developed recipes will contain waste obtained from the processing of mortars obtained from restoration work on historical monuments, which could lead to a lower consumption of new materials, a lower quantity of waste and, at the same time, a reduction in pollution.

The novelty brought by the present PhD thesis consists in the use of a set of analyses aimed at highlighting the chemical and mineralogical properties of the mortars obtained from the Roman castrum and of the mortars made in the laboratory (XRD, XRF, SEM, TGA-ATD), analyses that complement the classical ones (porosity, apparent density, compressive strength) and contribute to the elaboration of a more objective comparison between the two materials.

The way in which the proposed objectives are achieved, together with the results of the research, are presented in this paper structured in 7 chapters as follows:

Chapter 1, which provides an overview of urban regeneration and the importance of preserving cultural heritage, as well as the study of building materials used in the rehabilitation of historic monuments. This chapter also argues the motivation of the research and lists the main objectives of the study.

Chapter 2 deals with the "Current status of mortars in the field of construction", starting with a brief history of mortars, then describing the types of mortars, their classification and their component materials.

In **Chapter 3** the characteristics of the study area are highlighted, such as climate, geology, hydrology, as well as information on the Roman aqueduct that in antiquity supplied the Citadel of Tomis and originated on the shore of Lake Siutghiol. Also described in this chapter is the Roman fortification on the shore of Lake Siutghiol in Ovidiu, from where mortar samples were extracted and subsequently analysed for their physical and chemical properties.

Chapter 4 is devoted to "Research methods and methodologies", starting with the classical methods for determining the physical and mechanical properties of the studied mortars, then continuing with the analyses for determining the chemical and mineralogical properties of the mortars, such as X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Thermal Analysis (TGA-ATD) and Electron Microscopy (SEM).

The experimental programme is outlined in **Chapter 5** by presenting how the mortar samples were taken from the archaeological site and the results obtained from the analyses carried out. Also described here are the mortar recipes made in the laboratory, how they were prepared and the results of the analyses to determine the properties of the materials.

In **Chapter 6** the interpretation of the results takes place by centralising all the data obtained, analysing them graphically by means of charts and graphs, followed by processing and interpreting the results. Last but not least, papers are presented in which the urban development areas of Ovidiu were highlighted.

Chapter 7 presents general conclusions, personal contributions, the valorisation of the results obtained and future research directions.

2. Research methods and methodologies

The methodology used in this paper is a mixed methodology based on the use of both qualitative and quantitative methods (Figure 2).

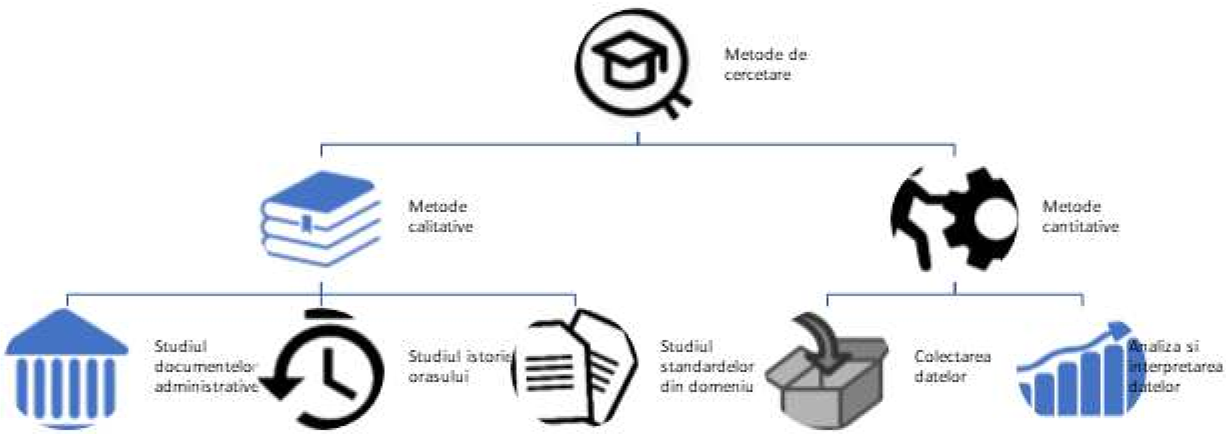


Figure 2 Research methods

Qualitative methods refer to: (i) exploratory methods based on documentary analysis of literature with reference to the development of the Ovidian coastline, cultural heritage conservation, data analysis methods and a synthesis of recent urban development; (ii) exploratory analysis of data on the Ovidian quadriburgium from various documents/sources and representing a review of various published information over time; (iii) a detailed study of the existing data in the literature on lime mortars both from a historical perspective with reference to Roman mortars and from a current perspective by analysing the regulations in force containing information on mortar compositions and their preparation.

Quantitative methods refer to: (i) collection of data on the development of Ovidiu over the last 20 years, their analysis and interpretation, and the creation of a map highlighting the areas of development in the context of urban regeneration;(ii) sampling of mortar used in the construction of masonry in the archaeological site of Ovidiu, determination of their physical and chemical characteristics and interpretation of the results. The data refers in particular to the physical characteristics such as compressive strength, porosity, water absorption, as well as chemical and mineralogical composition of the mortars used; (iii) preparation of different mortar compositions using lime as binder and testing them to determine their physical and chemical characteristics in order to make a comparison in order to highlight which one is the most suitable to be used for future rehabilitation works.

The information on the current state of knowledge in the field of urban regeneration both globally and in our country required a detailed study of the literature in the field, as well as a significant number of scientific articles on urban regeneration and sustainable development. After consulting the above-mentioned materials, we were able to make a synthesis of the current situation and the evolution of the term urban regeneration, as well as of the concept itself at national and international level.

In order to make a retrospective on the way Ovidiu's coastline has evolved in recent years, as well as a brief history of the town, it was necessary to carry out a thorough research of a series of documents on the development of the town such as: administrative documents, articles, specialized books, archaeological research reports, etc. [29, 34]. Also, a series of satellite images captured over several years was used to identify the main development areas of Ovidiu, and with the help of GIS software it was possible to produce a map showing these areas.

To remove the mortar problems we used a hammer and a chisel and tried to remove as large pieces as possible to be able to process them later. The mortar samples taken are unevenly shaped and vary in size from 7 to 17 cm. The citadel has been substantially rebuilt, therefore access to the old mortar samples was limited, but it was possible to collect them from several locations, namely: tower C, tower D and the two sides between towers C and D and towers D and A, where the restoration work has not yet been completed.

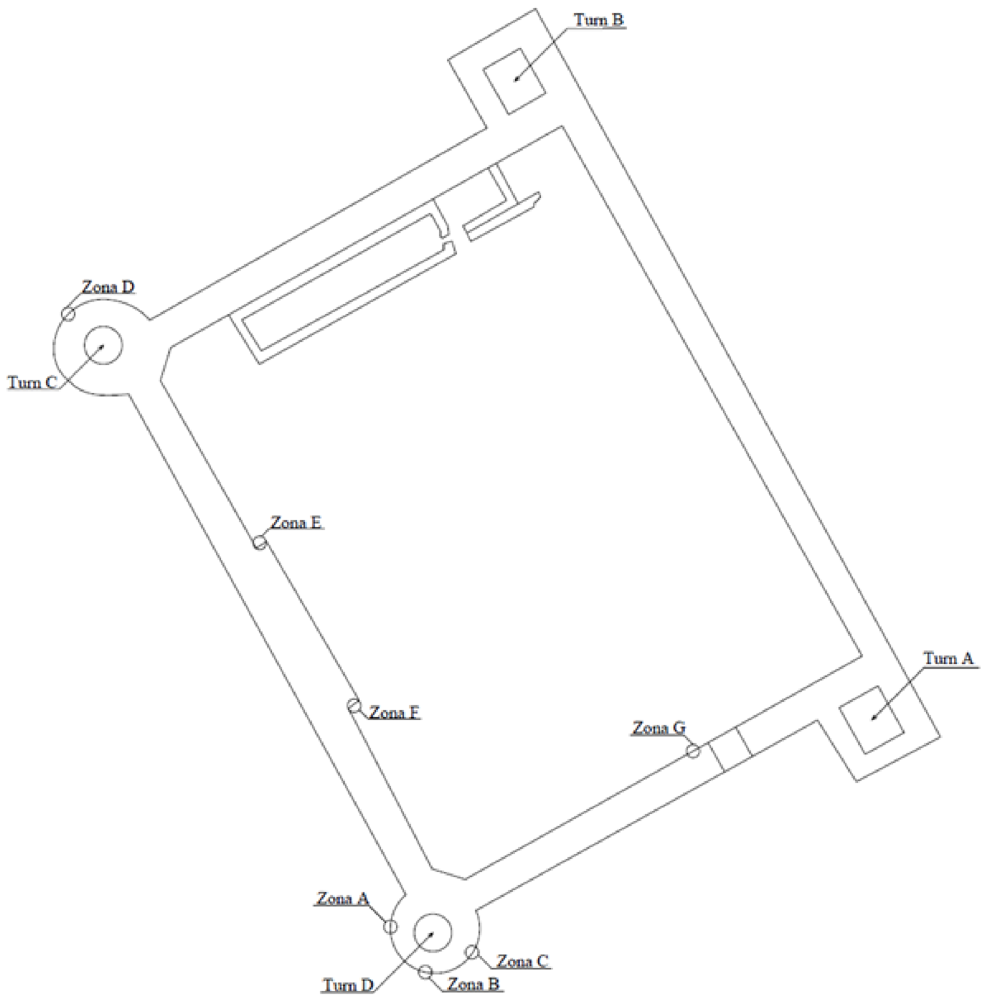


Figure 3 Sketch of the fortification showing mortar sampling locations

In order to achieve the aim of this thesis, i.e. to find a lime mortar composition with properties as close as possible to those of the mortars used by the Romans in the construction of the castle, we made 9 mortar compositions (one contemporary cement-based composition and 8 different lime-based compositions). In order to be able to compare them with Roman mortar, the compositions were made and poured in standardized shapes in order to obtain prismatic specimens with dimensions of 40x40x160mm. The compositions are as follows:

- Cement-based mortar composition - R1
- Mortar composition based on slaked lime paste - R2
- Mortar composition based on lump lime - R3

- Mortar composition based on hydrated slaked lime in which 5% of the aggregate mass has been replaced by waste obtained by grinding mortars taken from the Roman castrum - R4
- Hydrated slaked lime-based mortar composition in which 10% of the aggregate mass has been replaced by waste obtained by grinding mortars from the Roman chasm - R5
- Mortar composition based on hydrated slaked lime in which 15% of the aggregate mass has been replaced by waste obtained by grinding mortars from the Roman mortar pit - R6
- Mortar composition based on slaked lime lumps in which 5% of the aggregate mass has been replaced by waste obtained by grinding mortars from the Roman castle - R4'.
- Mortar composition based on lump lime in which 10% of the aggregate mass has been replaced by waste obtained by grinding mortars from the Roman castle - R5'
- Mortar composition based on lump lime in which 15% of the aggregate mass has been replaced with waste obtained by grinding mortars taken from the Roman castles - R6'

3. State of art on mortars in construction

Mortars are composite geomaterials (i.e. geological materials or materials derived from technical transformations of geological materials) consisting of aggregates, additives that react with the hydraulic or airborne binder and the binder itself, which undergo changes during the curing process [5, 13].

In general, mortars are composed of a combination of aggregates and binders that are unique to the location of the structure and the historical setting in which they were created. The study of mortars provides information about the raw materials, their origin and manufacturing procedures [10, 12, 22]. With the help of mortar characteristics, it is possible to determine historical building sequences [14, 18, 23] and ages of structures themselves [2, 15, 20, 21, 24].

The main ancient source we have on Roman mortars is found in the work of Vitruvius Marcus Polo, a Roman architect and engineer, written in about 30 BC and entitled De Arhitectura. In Book II he describes the main materials used in construction: sand, limestone, pozzolana, stone, as well as building technologies. "The "Imperial Mortar" as described by Vitruvius in „De Arhitectura” [17] is a mixture of sand, lime and water. During the First Roman Republic, Cato the Elder in de Agri Cultura [28] describes mortar as "calx harenatus" i.e. a mixture of lime and sand.

Today, mortars are very varied and can be classified according to a number of factors, as each of them fulfils a certain function and has well-defined roles. According to current standards:”SR EN 998-1:2011 – Specificaţie a mortarelor pentru zidărie: Mortare pentru tencuire şi gletuire”, [32] respective “SR EN 998-2:2011 – Specificaţie a mortarelor pentru zidărie: Partea 1 Mortare pentru zidărie”, [33] depending on the field of use, we can distinguish between masonry mortars, plastering mortars - exterior or interior and special mortars.

The main characteristic that mortars must have is compressive strength, which is their basic property.

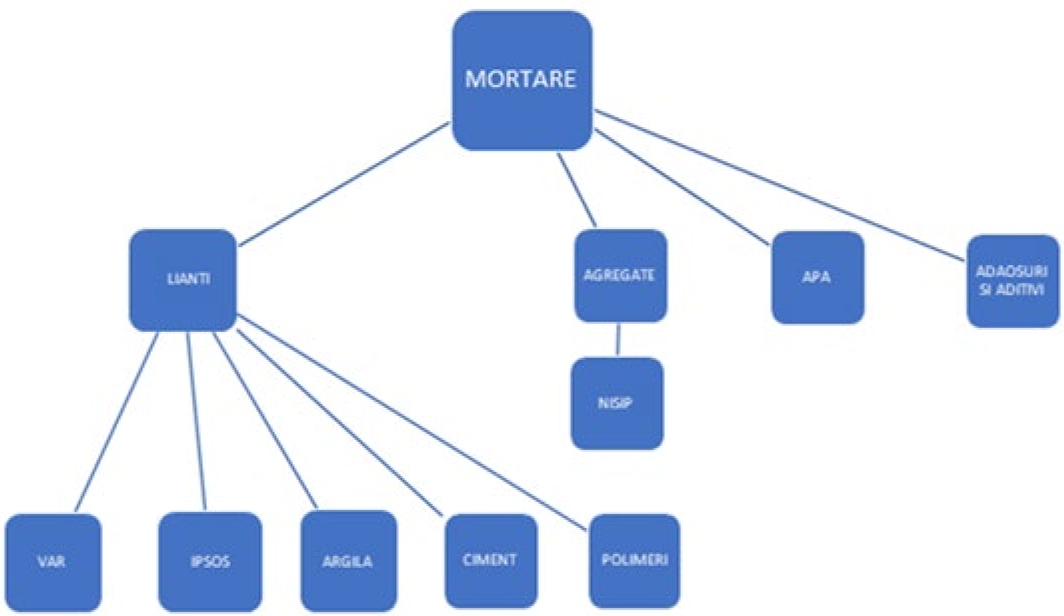


Figure 4 Mortars' component materials [16]

Table 1 - Classification of contemporary mortars according to compressive strength

Type mortar		Compressive strength [N/mm^2]
Mortar of masonry	M 1	1
	M 2.5	2.5
	M 5	5
	M 10	10
	M 15	15
	M 20	20
	M d	d - is a compressive strength declared by the manufacturer and greater than 25 N/mm^2
Mortar of plaster	CS I	0.4-2.5
	CS II	1.5-5.0
	CS III	3.5-7.5
	CS IV	≥6.0

For the preparation of mortars, the main materials used are binder, sand, water and in some cases additives.

The binders used to make mortars are lime, clay, gypsum, Portland cement and some polymers used in special mortars. The type of binder used is determined by the field of use, the role or purpose of the mortar and the physical, chemical or mechanical properties it must have [16].

Sand makes up 75-80% of the mortar volume and has a significant influence on the properties of the mortar in both the fresh and hardened state. The maximum grain diameter can be 8 mm, so the following sand sorts are used in mortars: 0/1; 0/4; 0/8mm [16].

The grain size of the sand is an essential characteristic that has a notable effect on the characteristics of the mortar. Grain size can be represented by the grain size curve of the sand which must fall within the limit curves given by the standards.

The water used to prepare the mortar can be potable or non-potable water. If seawater is used, the mortar should not be applied in contact with metal surfaces to prevent corrosion [16].

Admixtures and additives are added in small and very small quantities to the mortar mass (admixtures 1-5% of the binder mass, additives 0.01-0.03% of the binder mass) and are intended to improve certain properties of the mortar.

4. Description of the study area

The town of Ovidiu is located in Dobrogea, 11 km north of Constanta, on the shore of Lake Siutghiol (Figure 5).

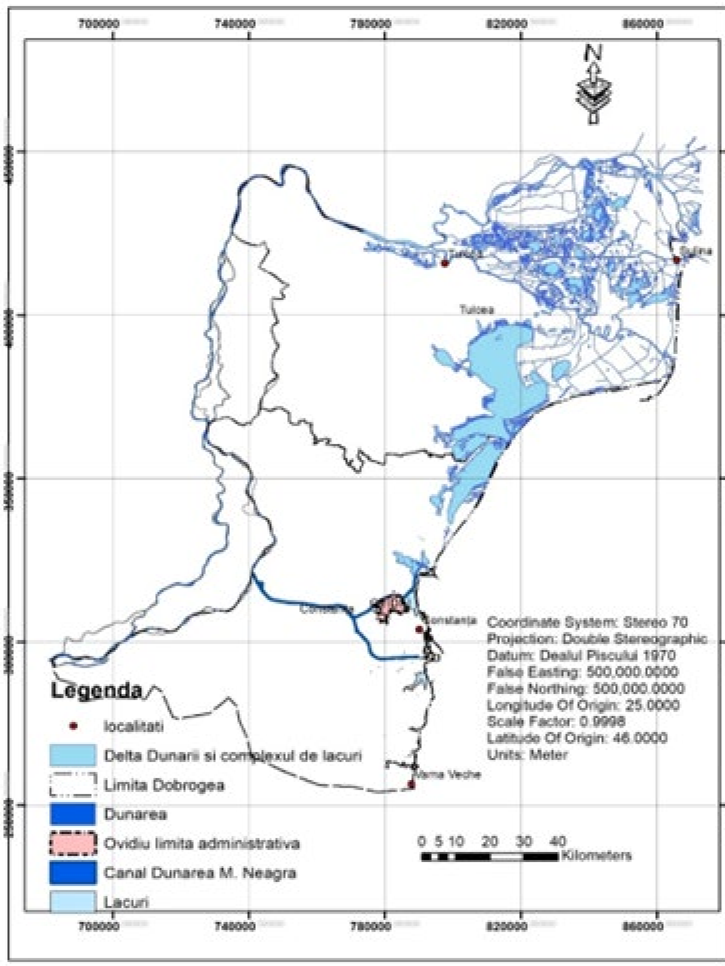


Figure 5 Location of Ovidiu Town

Although it has an ancient history, it is little valued and not readily available. This is why we try in the following to bring together the main writings about the present town of Ovidiu, which took its name as early as 1930 after the poet Publius Ovidius Naso, and became a town only in 1989.

Today, from an administrative point of view, Ovidiu has two municipalities: the town of Ovidiu and the village of Poiana. According to the Ovidiu town hall website, the town of Ovidiu is said to have been founded in 1650, under the name Siliște, but the town hall does not provide a document to support this claim.

From a morphological point of view, the Dobrogea area is made up of two large morphological units: the Dobrogea Plateau and the Lunca, Delta, plain and Razim-Sinoe lagoon complex. In the studied area of the Administrative Territorial Unit (UAT) Ovidiu the relief varies between 0 and 140m (Figure 6).

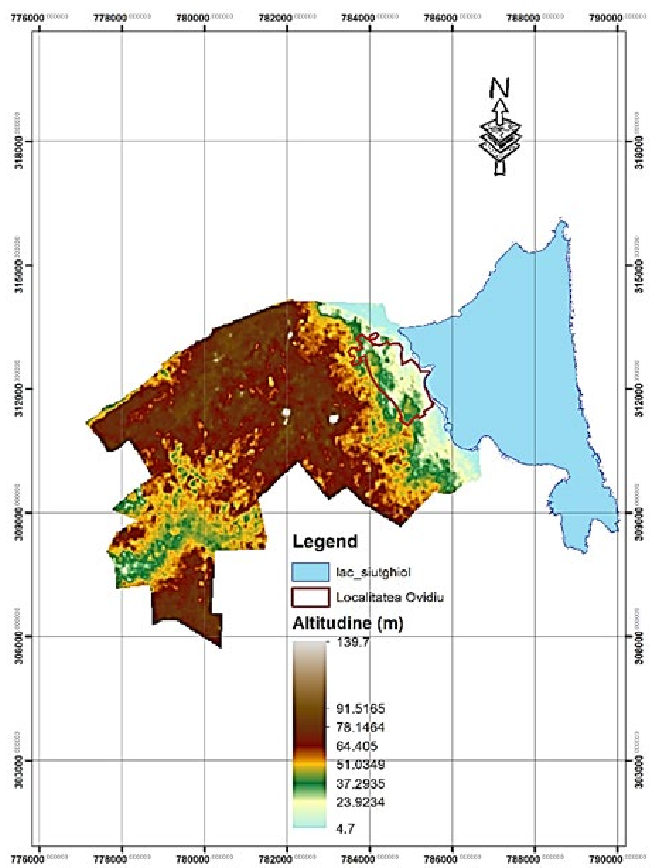


Figure 6 Digital terrain model for Ovidiu TAU

From a geological point of view, Ovidiu is located between the Peceneaga Fault to the north and the Palazu Fault to the south. In general, the geology of the area is mostly composed of loessosoid deposits. In the area of the lake there are currently limestone and chalk deposits with flint. In the north of the area there are dolomitic limestone formations.

The most important hydrographic element of the area is undoubtedly Lake Siutghiol. The lake's reception area is 73,7k sq.m. The main morphometric characteristics of the lake are: surface 1900ha, length of the shoreline 30km. Median length 8km, maximum width 4km, minimum width 2,5m, maximum depth 17,05, average depth 4,65 and depth to the black sea -14,90m. According to Nicolae Tatiana's calculations, the groundwater inflow into Lake Siutghiol is over 1200 l/s.

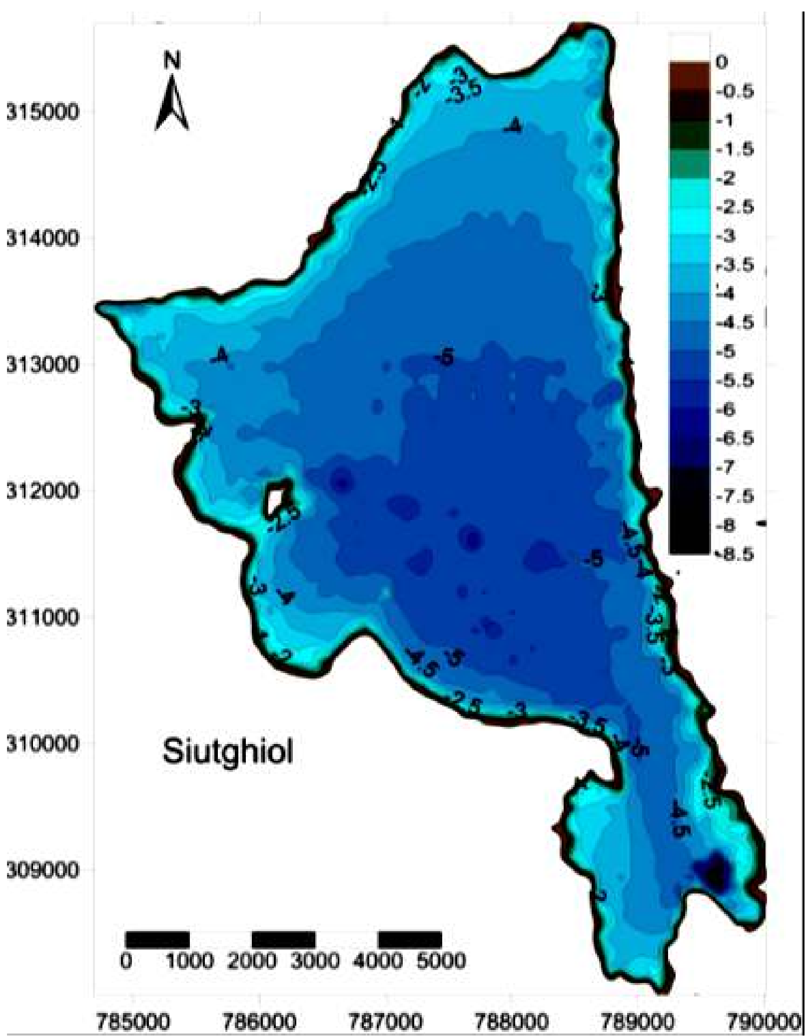


Figure 7 Lake Siutghiol - bathymetric map

In the town of Ovidiu there is also our area of interest, namely, the location of the archaeological site "Castrul Roman", an area from which we took the materials necessary for the analysis, as well as part of the Roman aqueduct that fed the old fortress Tomis, the current city of Constanta.

Roman aqueducts are hydrotechnical constructions built to supply water to large cities [7–9]. The construction of the aqueducts was carried out by army and hydraulic experts [4].

From research and studies conducted [26], it appears that the Tomis citadel was supplied with drinking water by two methods, namely by the aqueducts outside the citadel that brought water from underground springs and by the reservoir galleries inside the citadel, made with a draining bottom to capture and filter water from the groundwater. The aqueduct that brought water from the Ovidiu spring, on the shore of Lake Siutghiol, mentioned in the studies carried out by C. Allard and J. Michel in the middle of the 19th century, has been analysed repeatedly by Gh.Papuc [27] and M.Bucovală [25], the proof being their publications on the archaeological discoveries stretching from the shore of Lake Siutghiol to Constanta in the Pescărie and Modern beach area.

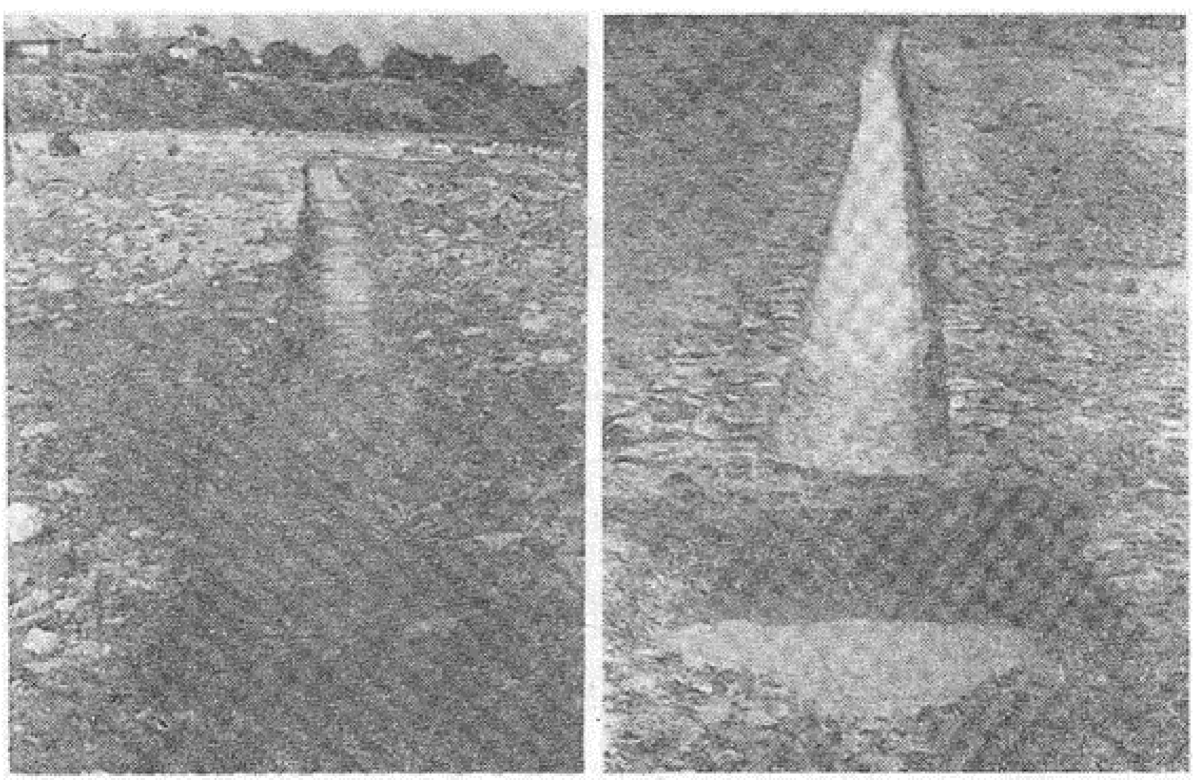


Figure 8 Image of the aqueduct basin near the bay of Lake Siutghiol [27]

The archaeological site is located on the southern outskirts of Ovidiu, about 10 km north of Constanta. It is located in a newly created residential area on the western shore of Lake Siutghiol (Figure 9), which was originally the Black Sea Bay. The site's proximity to the island of Ovidiu makes it an important area for further research and exploration. Due to the proximity of the site to a residential area, it is easily accessible for research and educational purposes, allowing a better public knowledge and understanding of the cultural heritage and history of the region. The archaeological site of Ovid offers a rare opportunity to explore the rich history of the area and preserve it for future generations. The site has the potential to become a significant attraction and a useful resource for the surrounding community if given adequate resources and support[1, 3].

Figura 9 Locația sitului arheologic

5. Experimental programme

In the present experimental program, we started by determining the physical and chemical characteristics of the 7 mortar samples taken from the Roman castrum in the town of Ovidiu, in order to make a comparison between their properties and those of the mortars made in the laboratory.

Further, 9 new mortar compositions were made, of which 1 cement-based mortar composition and 8 lime-based mortar compositions. For each composition, 3 moulds with 3 prismatic specimens were poured to be subjected to the compressive strength determination test at 30, 60 and 90 days for lime mortars and 7, 14 and 28 days for cement mortars, respectively.

The lime mortars tested at 90 days were further subjected to various analyses to determine their chemical and mineralogical properties.

Finally, the results obtained on the new mortars were compared with those of the mortars used at the archaeological site in order to determine the most suitable composition to be used in the rehabilitation works of historical monuments.

The mortar samples taken from the Roman fortification had irregular shapes, ranging in size from 7 to 17 cm. In order to be tested, they had to be processed to bring them as close as possible to the standard dimensions of mortar specimens. Following processing, 3 mortar prisms, numbered A, B and C, were obtained from the processing of the samples taken.

Figure 10 Unprocessed mortar samples

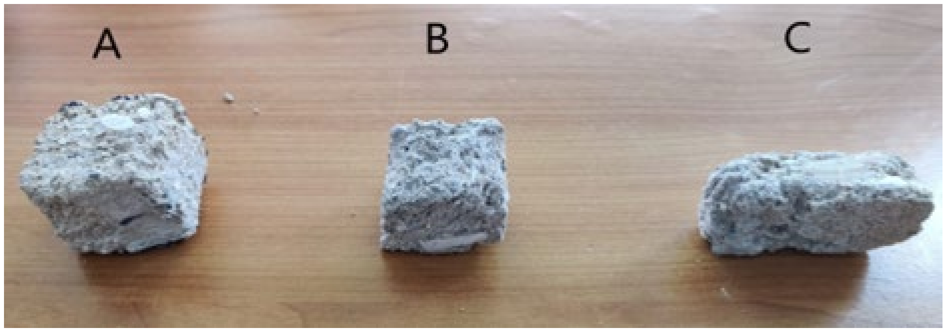


Figure 11 Processed mortar prisms

Table 2. Measured volume of the 3 specimens

Sample	Initial volume [cm3]	Final volume [cm3]	Sample volume [cm3]	Sample mass [kg]
A	500	581	81	0.1174
B	500	554	54	0.0889
C	500	556	56	0.0831

Using the information in the previous table, we determined the following bulk densities for specimens A, B and C:

- Sample A - 1467,5 kg/m3
- Sample B - 1646,3 kg/m3
- Sample C - 1483,9 kg/m3

Following the test to determine the compressive strength of the specimens, only for specimens A and B we obtained values, while specimen C, not having a conforming surface, the press could not display the compressive strength. For specimens A and B we obtained an average strength of 0.6 MPa.

To perform X-ray diffraction (XRD) mineralogical analysis, the mortar samples were carefully crushed in a mill, allowing segregation of the aggregates from the construction matrix, but trying to avoid crushing the aggregates (e.g. sand grains) , and the powder was separated from the aggregates by sieving. The samples were hetero-genetic and the aggregates showed different shapes, sizes and colours.

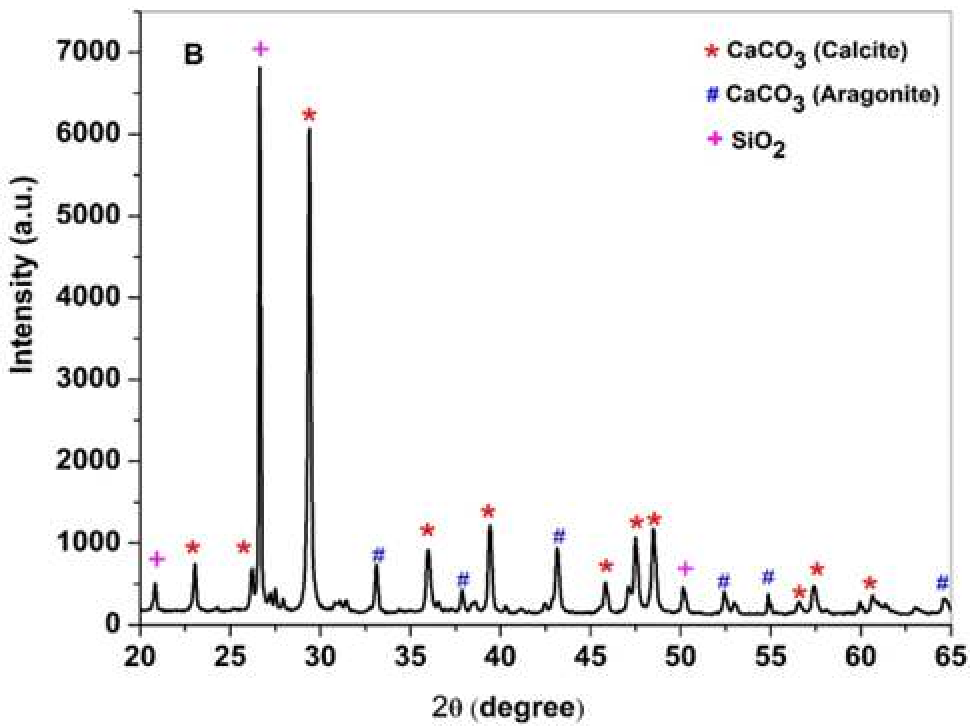


Figure 12 Diffraction image for sample B

The samples are similar, with quartz being the predominant mineralogical phase, followed by calcite. This may indicate a conventional mortar composition, with calcite as binder and quartz as skeleton; the study reveals that calcite mixed with quartz (silica) was a common mortar mix before the widespread use of mortars.

XRD (X-ray diffraction) results showed that several crystalline phases are present (Table 3). The diffraction maxima correspond to a mixture of carbonate (calcite) and siliceous aggregates. The main diffraction maxima were assigned to calcium carbonate (calcite - ICDD 00-081-2027, aragonite - ICDD 00-003-1067), silicon oxide (quartz - ICDD 00-077-1060) and ankerite (ICDD 00-041-0586).

Table 3. Semi-quantitative XRD analysis of mortar samples A-G

Sample	Crystalline phase	Abundance
A	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	++
	SiO_2 (Quartz)	+
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-
B	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	+
	SiO_2 (Quartz)	+++
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-
C	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	++
	SiO_2 (Quartz)	+++
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	+
D	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	+
	SiO_2 (Quartz)	+
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-
E	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	-
	SiO_2 (Quartz)	++
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-
F	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	-
	SiO_2 (Quartz)	+
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-
G	$CaCO_3$ (Calcite)	+++
	$CaCO_3$ (Aragonite)	-
	SiO_2 (Quartz)	++
	$Ca(Fe,Mg)(CO_3)_2$ (Ankerite)	-

+++ Abundent, ++ present, + in small quantity, - untraceable

X-ray fluorescence (XRF) allowed the determination of major elements in oxide form, (CaO, MgO, Al_2O_3, SiO_2, Fe_2O_3, P_2O_5, K_2O, MnO and SO_3) and trace elements expressed in ppm (parts per million): Ti, V, Cr, Ni, Cu, Zn, Pb, Ga, Ge, As, Ba, Rb, Sr, Y, Zr, Nb, Ce and Sn (Table 4).

Table 4. XRF analysis of mortar samples taken from the walls of the Roman fortification archaeological site

Oxide (%)	Sample						
	A	B	C	D	E	F	G
CaO	62.83	52.57	55.99	59,03	53,42	57,80	57,20
MgO	6.85	6.25	7.13	6,34	7,11	6,06	7,29
Al_2O_3	0.87	1.20	2.33	1,15	1,59	1,14	1,50
SiO_2	9.42	14.26	12.54	9,69	8,94	9,25	7,95
Fe_2O_3	1.11	0.49	0.89	1,772	0,934	0,685	0,804
P_2O_5	0.06	0.10	0.16	0,07	0,13	0,11	0,12
K_2O	0.23	0.28	0.64	0,32	0,49	0,36	0,46
MnO	0.03	0.02	0.04	0,035	0,031	0,026	0,03
SO_3	0.06	0.07	0.10	0,05	0,087	0,067	0,107
Oligoelements (ppm)							
Ni	n.d.	3.20	12.09	6,55	9,16	6,51	7,07
Cu	34.27	30.45	33.11	8,96	9,15	6,71	5,59
Zn	36.76	52.2	122	27,60	38,34	63,8	30,37
Ga	2.25	2.51	4.13	2,68	4,52	2,37	2,76
Ge	0.400	n.d.	0.470	0,341	n.d.	n.d.	n.d.
As	1.62	1.71	3.41	3,71	4,10	2,43	2,97
Ba	91.7	141	151	137	166	183	165
Br	5.03	7.12	11.02	5,88	8,46	7,90	8,74
Rb	10.92	10.10	21.46	16,90	22,78	18,47	20,30

Sr	812	742	654	524	315	342	437
Y	7.62	7.97	10.55	14,17	12,87	10,05	14,60
Zr	36.56	24.01	102	34,34	85,1	59,1	70,1
Nb	n.d.	2.41	3.43	2,21	4,02	3,08	2,76
Pb	3.18	3.60	8.13	4,64	7,49	4,71	6,07
Ce	n.d.	27.64	n.d.	n.d.	n.d.	42,53	n.d.
Sn	n.d.	1.10	n.d.	n.d.	1,50	1,49	3,15
Loss on ignition (LOI)	18.53	24.75	20.19	21,54	27,27	24,50	24,54
Hydraulicity index (HI)	**0.16**	**0.29**	**0.27**	**0,18**	**0,20**	**0,18**	**0,17**
Cementation index (CI)	**0.39**	**0.68**	**0.58**	**0,44**	**0,43**	**0,42**	**0,36**

The microstructural characteristics of the mortars were determined by SEM-EDX analysis. Scanning electron microscopy (SEM) was used to visualize the morphology and textural relationships of the different mineral phases identified by XRD.

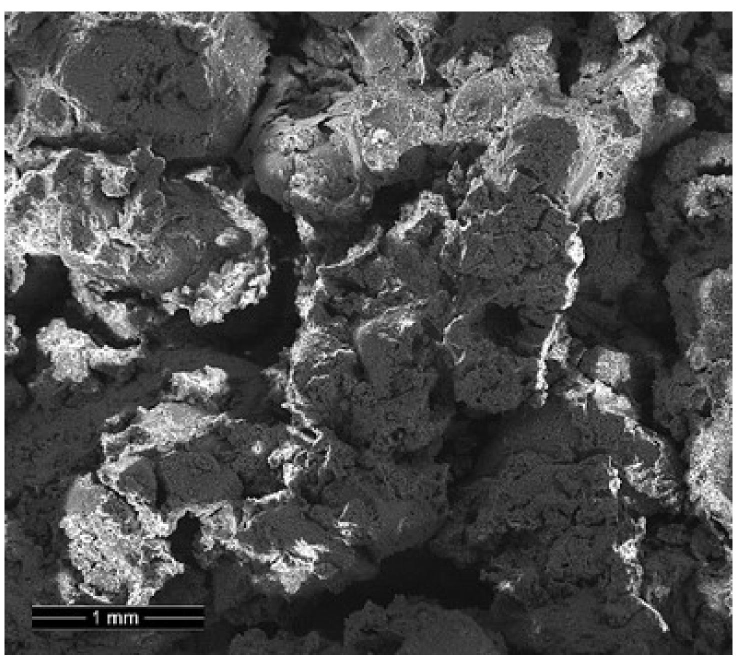


Figure 13 Scanning electron microscopy images for sample B

In the mortar samples there is a mixture of large and small grains with different morphologies. The SEM investigation shows a matrix of the lime-based mortar that is consistent with information from the literature [11].

Thermal analysis (TGA-DTA) showed a total mass loss in the investigated mortars between 32% and 37% as well as some endothermic effects. The endothermic effect of temperatures between 30 and 300 degrees Celsius is usually attributed to physically related water loss and hydraulically related water loss processes. Table 5 shows the weight losses (%) of mortar samples A-G.

Table 5. Mass losses (%) of mortar samples A-G.

Sample	Temperature (ºC)			Total mass loss (%)
	35 – 660	660 – 860	860 – 1000	
A	4,115	32,578	0,285	36,978
B	3,687	32,406	0,183	36,275
C	4,329	27,450	0,248	32,028
D	4,997	32,373	0,402	37,773
E	7,038	26,881	0,463	34,382
F	4,891	31,215	0,516	36,622
G	5,448	28,637	0,599	34,685

6. Interpretation of the results

After centralising the results obtained from testing the specimens for compressive strength, we produced a series of graphs designed to facilitate the interpretation of these data.

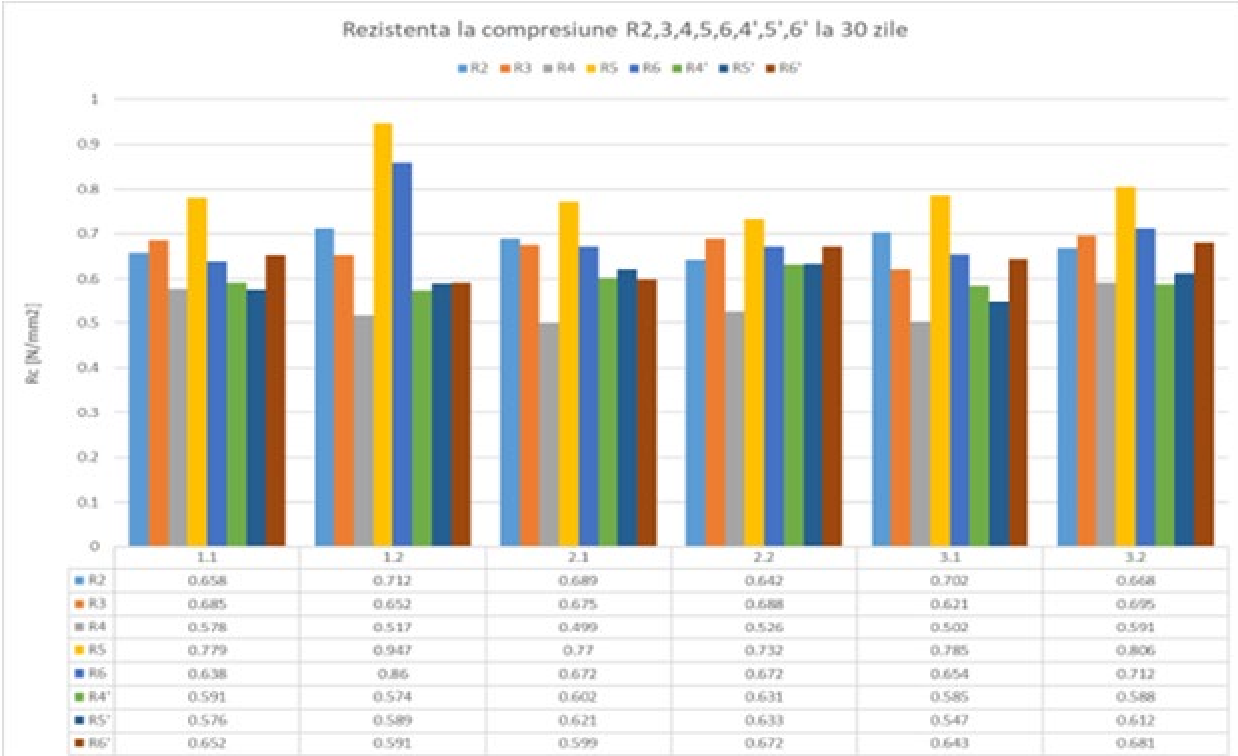


Figure 14 Compressive strength for R2-R6' at 30 days

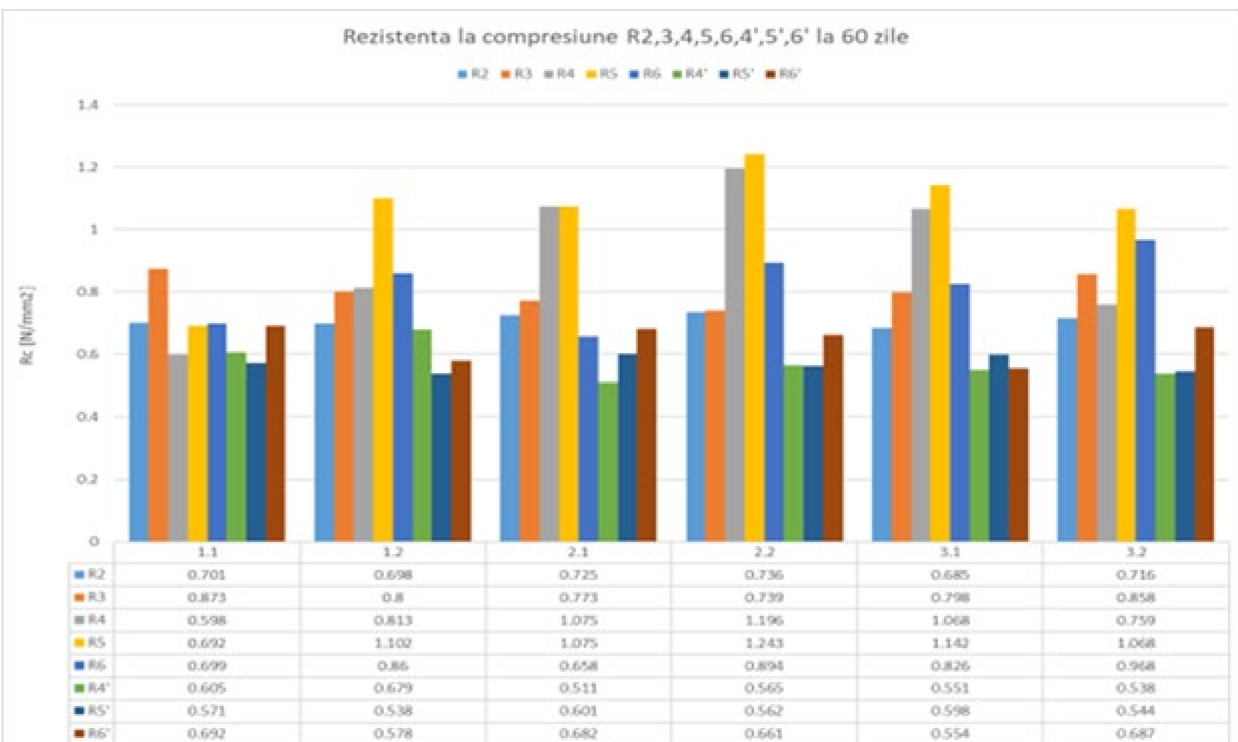
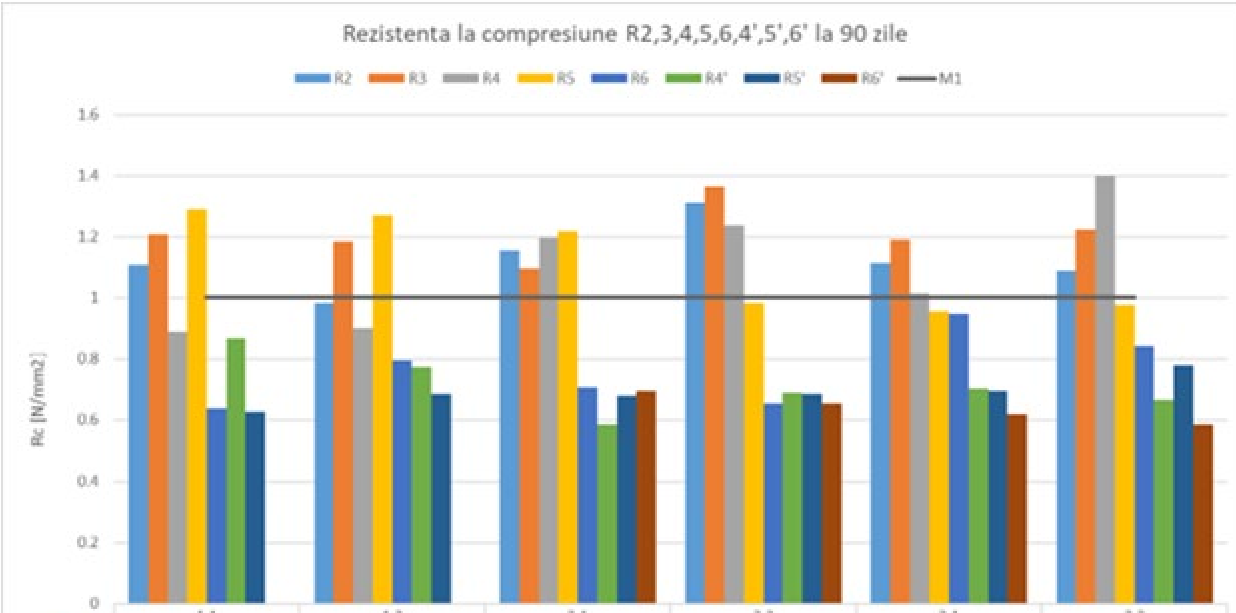


Figure 15 Compressive strength for R2-R6' at 60 days

By comparing all the values of compressive strengths for R2-R6' compositions tested at the 30-day term, we can see that they have quite close values, while at the 60-day term, we can see that the values of R2-R6' compositions have higher values than those of R4'-R6' compositions based on unbound lime.



	1.1	1.2	2.1	2.2	3.1	3.2
R2	1.109	0.981	1.156	1.31	1.114	1.087
R3	1.209	1.183	1.095	1.364	1.189	1.223
R4	0.887	0.9	1.196	1.236	1.015	1.398
R5	1.29	1.27	1.216	0.981	0.954	0.977
R6	0.638	0.793	0.705	0.652	0.947	0.84
R4'	0.867	0.773	0.585	0.687	0.702	0.665
R5'	0.625	0.685	0.679	0.685	0.692	0.779
R6'	0	0	0.692	0.652	0.618	0.585
M1	1	1	1	1	1	1

Figure 16 Compressive strength for R2-R6' at 90 days

At 90 days, we see that only mortars of compositions R2-R5 still showed significant increases compared to the previous values and only the averages of these mortars exceed the threshold of 1 N/mm2 and can be classified as mortar class M1.

After studying the images obtained by electron microscopy (SEM), we came to the conclusion that a mixture of large and small grains with different morphologies is present in the mortar samples. The SEM investigation shows a calcium carbonate matrix in the investigated mortar structure which is in agreement with the information in the literature[11].

Following the thermal analysis and the observation of the resulting graphs, we centralized in a table the percentage mass losses for each of the 8 samples studied, by the temperature ranges used.

The results were centralized and highlighted in the table with two colours according to the type of lime used to make the mortar composition, unslaked lime for the first part of the table and slaked lime for the second half of the table.

Table 6 Centralisation of thermal analysis results

Sample	**Temperature (ºC)**					**Total mass loss (%)**
	30 – 420	**420 – 500**	**500 – 650**	**650 – 850**	**850 – 1000**	
R3	1,067	1,144	0,818	14,407	0,308	17,744
R4’	1,178	2,349	0,747	12,090	0,346	16,711
R5’	0,671	2,089	0,662	10,710	0,298	14,429
R6’	0,766	2,278	0,719	12,162	0,308	16,233
R2	0,505	0,787	0,668	6,761	0,230	8,950
R4	0,519	0,843	0,853	11,213	0,333	13,761
R5	0,599	0,892	0,699	10,095	0,278	12,564
R6	0,320	1,341	0,918	12,317	0,404	15,300

Another step in the interpretation of the results was the ratio between the percentage of carbon dioxide and structurally bound water, CO_2/H_2O, which provides information on the hydraulicity of the mortars.

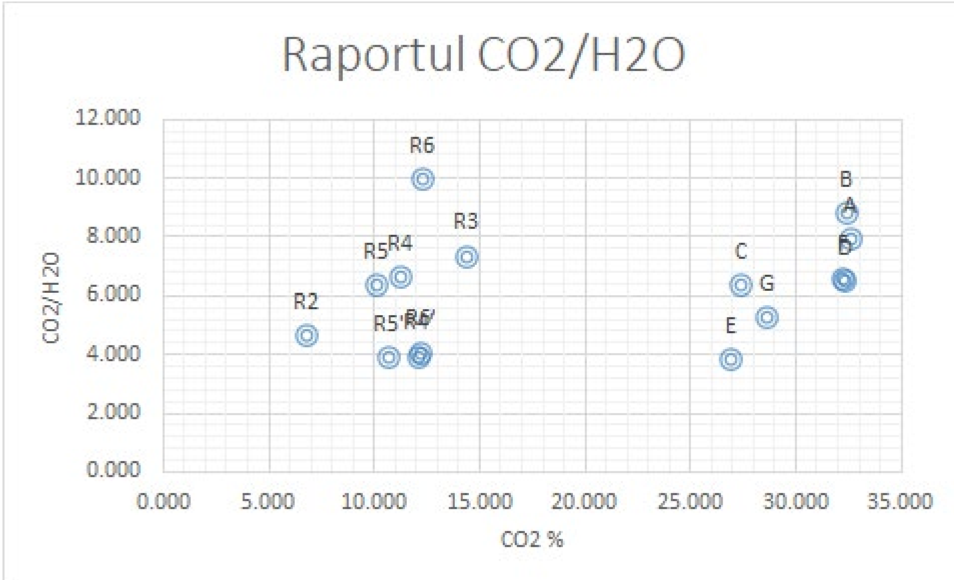


Figura 17 CO_2/H_2O ratio

From the figure above we can see a clear differentiation between the mortars taken from Castrul Roman and those prepared in the laboratory in terms of the percentage of carbon dioxide, while in terms of CO_2/H_2O ratio, we can see that all samples are in the range 3-10.

7. Conclusions

This paper mainly studies mortar as a building material, starting with its history and evolution up to the contemporary period and going into detail by investigating the mechanical and chemical properties of mortars.

The research topic aims to identify lime-based mortar compositions in various forms as potential candidates for rehabilitation works on historic buildings within historical areas, and the possibility of reusing recovered materials in the restoration process by introducing a percentage of the recovered waste into the new mortar compositions.

Last but not least, of particular importance is the trend towards sustainable development, in which context, in this research we have been collecting data on the development of the entire study area over several years, with the aim of highlighting the value of cultural heritage and the phenomenon of urban regeneration in the evolution of a city.

The present study focuses on the accounting and interpretation of the results obtained from the tests carried out both on the mortar samples taken from the archaeological site of the Roman Castrum in Ovidiu and on the new mortar compositions made in the laboratory.

The masonry mortars are of particular importance because they ensure the connection between the masonry blocks, and in our case, in addition to the structural role, being used in the restoration works of the monuments, there is also the condition of the visual appearance and the preservation in the highest proportion of the characteristics of the materials used previously.

In order to obtain the most relevant results, the types of tests to which the studied mortars were subjected were carefully selected.

In contrast to the classical cement-based mortar recipe, the properties of lime-based mortars are much more difficult to follow, as lime has a significant influence on the final characteristics of the material through its strong exothermic reaction in contact with water, especially in the case of unbound lime.

In order to reduce the consumption of materials, as well as the level of pollution caused by the storage of materials resulting from the restoration process, we have designed a set of mortar compositions based on slaked lime and un slaked lime, in which we have replaced part of the aggregate with ground waste obtained from the old materials extracted.

The difficulty was that, in the case of unburnt lime used in mortar compositions, the literature and standards in the field do not provide recipes, considering that the lime currently used in mortars is hydrated slaked lime.

Personal contributions

Carrying out an interdisciplinary study on the development of the study area in the context of sustainable urban regeneration and the use of new lime-based mortar compositions for rehabilitation works on historic monuments.

Development of interest maps on the main aspects of our study area, namely the Administrative Territorial Unit of Ovidiu:

1.Map with the location of the Ovidiu Local Authority

2.Map with the administrative territorial boundary of Ovidiu

3.Map containing the digital terrain model for the Ovidiu TAU

4. Two maps of the geological zoning of Ovidiu, as well as a detail of the geology in the vicinity of Lake Siutghiol.

5.Bathymetric map of Lake Siutghiol

6.Vegetation map of the Ovidiu Local Authority area

7.Map of the development area of Ovidiu

Elaboration in a 3D modelling program of the three-dimensional model for the Castrum Roman Castle of Ovidiu.

Taking a number of 7 mortar samples from 4 different areas of the archaeological site of Ovidiu, to be analysed in terms of physical and chemical characteristics in order to develop new compatible mortar compositions.

Processing of the samples taken for testing. Following the processing of the mortar samples, 3 specimens were obtained for mechanical testing and 7 samples for chemical and mineralogical analysis. On the 3 specimens marked A, B and C, bulk density, water absorption and compressive strength were determined, while on the 7 specimens marked A-G, XRD, XRF, SEM-EDX and TGA-ATD were performed.

Interpretation of the data obtained from the testing of the 7 Roman mortar specimens, further information used to prepare new lime-based mortar compositions.

Making 9 mortar compositions of which a classical cement-based mortar composition and 8 lime-based mortar compositions in different forms as follows:

1. R1 - Cement-based mortar composition

2. R2 - Mortar composition based on slaked lime paste

3. R3 - Mortar composition based on lump unhardened lime

4. R4 - Hydrated slaked lime based mortar composition in which 5% of the aggregate mass has been replaced by waste obtained by grinding mortars taken from the Roman castle.

5.R5 - Hydrated slaked lime based mortar composition in which 10% of the aggregate mass has been replaced by waste obtained by grinding mortars from the Roman quarry.

6. R6 - Hydrated slaked lime mortar composition in which 15% of the aggregate mass has been replaced by waste from the grinding of mortars from the Roman castrum.

7.R4' - Mortar composition based on unhardened lime lumps in which 5% of the aggregate mass has been replaced by waste obtained by grinding mortars taken from the Roman castle.

8.R5' - Mortar composition based on lump lime in which 10% of the aggregate mass has been replaced by waste obtained by grinding mortars taken from the Roman castle.

9. R6' - Mortar composition based on lump lime in which 15% of the aggregate mass has been replaced by waste obtained by grinding mortars taken from the Roman castle.

For each type of composition, 3 patterns of 3 specimens were warped and tested at different time intervals from the time of casting. R1 mortars were tested at 7, 14 and 28 days and R2-R6' mortars at 30, 60 and 90 days from the time of pouring respectively. Cement-based mortars were analysed only for their physical-mechanical properties, while all lime-based mortars were analysed both physically and chemically to determine their chemical and mineralogical composition.

A test report was also made for each of the 81 resulting specimens, indicating their composition, size, bulk density and compressive strength, which are presented in the appendices.

Following the bulk density tests, all the results were centralised in tables for each composition, then, for a better understanding and interpretation, a graph was made for each pattern of 3 specimens. The bulk densities of all the mortars were within the normal values for each type. For the lime-based mortars, the bulk density values are very close to the values obtained from the tests carried out on the mortars taken from the Roman Castle, which indicates that from this point of view, all 8 lime-based mortar compositions, scored from R2 to R6', can be used as a material for restoration.

The working procedure in the above paragraph was also applied to the results obtained from the compressive strength tests. The data were centralised both in tables for each composition and in graphs for each pattern. In the case of the compressive strength we found variations in compressive strength according to the type of composition. These variations were due to the presence of unslaked lime (both that which was taken into account for the recipe and that in the Roman mortar, in the case of compositions with the addition of waste) and were detailed in Chapter

7. The results taken into account for comparison with those obtained on Roman mortars were those of compositions R2, R3, R4, R5, R6, R4', R5' and R6' recorded 90 days after casting, as specified by the standards in force, and these showed the following aspects:

- In terms of SR EN 998-2:2011 - Specification of mortars for masonry. Part 2: Mortars for masonry, our mortars meeting the criteria for classification in strength class M1 are R2, R3, R4 and R5 mortars, whose average compressive strength exceeds 1 N/mm2;
- From the point of view of the average value of the compressive strength (0.6 N/mm2) obtained on the mortars used at the Roman Castrum, the average values of all 8 R2-R6' compositions exceed that value;

From a chemical and mineralogical point of view, the samples were subjected to several types of tests (XRD, SEM-EDX, TGA-ATD) from which we were able to obtain essential information on their structure, as well as images of the crystal structure of the samples tested.

Analyzing the samples in terms of mineralogical composition by XRD, it was found that the samples are similar, quartz being the predominant mineralogical phase, followed by calcite. This may indicate a conventional mortar composition, with calcite as binder and quartz as skeleton.

SEM-EDX analysis showed that the structure of the mortars made in the laboratory is similar to that of Roman mortars, both having a mixture of large and small granules, characterized by a well-defined matrix. In terms of EDX analysis, the chemical elements found in each specimen are highlighted by the EDX spectra recorded on the mortar samples. Specific maxima of each studied element (Ca, Mg, Si and O) as well as intensity variations that are probably attributable to local inhomogeneities were found in both studied mortar categories.

From the thermal analysis the mass loss values of each sample subjected to gradual heating up to 1000°C were extracted. Following the comparative analysis of the range 660-860°C, where strong endothermic processes can be attributed to the decomposition of carbonates, we observed a significant difference between the percentage of mass loss of Roman mortars and new mortars, explained by the quantitatively higher presence of carbonates in Roman mortars exposed to environmental factors for almost 2000 years, as a consequence the mass loss was also higher.

Also, following the terminal analysis, from the results obtained we made a graph on the distribution of the CO_2/H_2O ratio, a ratio that indicates the level of hydraulicity of the mortars, and from the graph we can see a difference between the mortars taken from Castrul Roman and those made in the laboratory, from the point of view of the percentage of carbon dioxide present, while from the point of view of the CO_2/H_2O ratio, it can be seen that the values are in the same range for both categories of mortars, which confirms what was said above about the presence of carbonation in the samples exposed to environmental factors.

We can conclude by saying that all the 8 mortar compositions made in the laboratory were chemically and mineralogically very similar in structure to the mortars from the Roman Castle studied, the only difference being the percentage of carbon dioxide, while from the point of view of mechanical properties, all 8 compositions had an average compressive strength higher than the average strength value recorded on the old mortars, but only compositions R2, R3, R4 and R5 exceeded the threshold of 1 N/mm2, required by the standards in force for class M1 masonry mortars.

Future directions for research

The author proposes the following topics for future research:

1. Update the urban development maps of the study area with new information and create an easily accessible database to enter new data on urban regeneration.
2. Analyse the effects of unbound lime in lime-based mortar compositions with higher mixing water and follow the evolution of their properties over a period longer than 90 days.
3. Determination of the substrate adhesion values of hydrated slaked lime and un slaked lime mortars, a property of particular importance in the field of masonry mortars.
4. Development of mortar compositions based on slaked lime and un slaked lime using sea sand as an aggregate, to simulate the conditions of the Roman period, when Lake Siutghiol was a bay of the Black Sea.
5. Study of the literature on the architectural details of Roman fortifications in order to model in detail the Roman Castrum and other historical monument constructions in the archaeological sites in the area.
6. Detailed study of the self-healing properties of mortars, due to the presence of non-hydrated unbound lime granules, which, once cracks appear and come into contact with water, start the hydration reaction leading to crack closure. In this regard, some eatages have already been made using 3D modelling software to create unique patterns of the dimensions of our mortar prisms, which were then 3D printed in the laboratory of the

Faculty of Construction Constanta. In these patterns, 2 prisms of mortar based on unburnt lime were inserted which were previously broken and put in place. The prisms supported by the patterns were submerged in water and left for 30 days, after which they were removed from the water and it was observed that the cracks had closed.

Of course, in order to study the phenomenon in detail, it will be necessary to make a much larger number of lime-based mortar prisms and also to follow them more closely at much smaller intervals using specialised equipment (electron microscope).

Selective bobliography

1. Bajenaru, C.: OBSERVAȚII RECENTE CU PRIVIRE LA FORTIFICAȚIA DE TIP QUADRIBURGIUM DE LA OVIDIU = Recent Observations About the Early Byzantine Quadriburgium-Type Fort of Ovidiu. Pontica 2002-2003. (2003).

2. Bergamonti, L. et al.: The 20th Century Wall Paintings in the Chapel of the Fallen in Parma Cathedral (Italy): Scientific Investigations for a Correct Conservation Project. Applied Sciences. 13, 12, 7235 (2023). https://doi.org/10.3390/app13127235.

3. Bucovală, M., Papuc, G.: Cercetările arheologice de la Ovidiu, Jud. Constanţa / Archäologische Forschungen (Munizipium Konstanza). Materiale şi cercetări arheologice. 14, 1, 342–347 (1980). https://doi.org/10.3406/mcarh.1980.1565.

4. Chanson, H.: Some aspects of the hydraulic design of Roman aqueducts Certains aspects de la conception hydraulique des aqueducs romains. Houille Blanche. 6–7, 43–58 (2002).

5. Dilaria, S. et al.: Volcanic Pozzolan from the Phlegraean Fields in the Structural Mortars of the Roman Temple of Nora (Sardinia). Heritage. 6, 1, 567–586 (2023). https://doi.org/10.3390/heritage6010030.

6. Elsen, J.: Microscopy of historic mortars—a review. Cement and Concrete Research. 36, 8, 1416–1424 (2006). https://doi.org/10.1016/j.cemconres.2005.12.006.

7. Fabre, G. et al.: L'Aqueduc de Nîmes et le ponts du Gard : Archéologie. Géosystème. Histoire. CNRS Editions, Paris (2000).

8. Fabre, G.: The Pont du Gard: Water and the Roman town. Presses du CNRS, Paris (1992).

9. Hodge, A.T.: Roman Aqueducts and Water Supply. Bristol Classical Press, London (2002).

10. Hughes, J.J.: Mortars in historic buildings: a review of the conservation, technical and scientific literature / by John J. Hughes and Jan Válek. Historic Scotland, Edinburgh (2003).

11. Kirilovica, I., Karpe, M.: Chemical and physical investigations of historic mortars in St. John's Church (Cesis, Latvia). Presented at the The 13th international scientific conference "Modern Building Materials, Structures and Techniques" , Vilnius Gediminas Technical University December 3 (2019). https://doi.org/10.3846/mbmst.2019.034.

12. Mociu, N.C. et al.: Highlighting the Characteristics of Roman Mortars from Ovidiu's Quadriburgium Archaeological Site, Romania. Buildings. 13, 3, 672 (2023). https://doi.org/10.3390/buildings13030672.

13. Montesano, G. et al.: Ancient Roman Mortars from Anfiteatro Flavio (Pozzuoli, Southern Italy): A Mineralogical, Petrographic and Chemical Study. Coatings. 12, 11, 1712 (2022). https://doi.org/10.3390/coatings12111712.

14. Moropoulou, A. et al.: Composite Materials in Ancient Structures. Cement and Concrete Composites. 27, 295–300 (2005). https://doi.org/10.1016/j.cemconcomp.2004.02.018.

15. Navarro-Mendoza, E.G. et al.: Physical and Mechanical Characterization of Lime Pastes and Mortars for Use in Restoration. Heritage. 6, 3, 2582–2600 (2023). https://doi.org/10.3390/heritage6030136.

16. Netea, A.G. et al.: Materiale de construcţii şi chimie aplicată. U.T. Press, Cluj-Napoca (2010).

17. Pollio, M.V.: Vitruvius. The Ten Books on Architecture: Translated by Morris Hicky Morgan. Adamant Media Corporation (2005).

18. Rispoli, C. et al.: Ancient Roman Mortars from Villa del Capo di Sorrento: A Multi-Analytical Approach to Define Microstructural and Compositional Features. Minerals. 11, 5, 469 (2021). https://doi.org/10.3390/min11050469.

19. Roberts, P.W., Sykes, H. eds: Urban regeneration: a handbook. SAGE, London ; Thousand Oaks, Calif (2000).

20. Santos, A.R. et al.: Characterization and Assessment of Performance of Innovative Lime Mortars for Conservation of Building Heritage: Paimogo's Fort, a Case Study. Applied Sciences. 13, 8, 4679 (2023). https://doi.org/10.3390/app13084679.

21. Silva, A.S. et al.: Characterization of Historical Mortars from Alentejo's Religious Buildings. International Journal of Architectural Heritage. 4, 2, 138–154 (2010). https://doi.org/10.1080/15583050903046322.

22. Silva, B.A. et al.: Influence of Water Content and Mixing Conditions on the Properties of Lime-Based Materials. Buildings. 13, 6, 1530 (2023). https://doi.org/10.3390/buildings13061530.

23. Válek, J. et al. eds: Historic Mortars: Characterisation, Assessment and Repair. Springer Netherlands, Dordrecht (2012). https://doi.org/10.1007/978-94-007-4635-0.

24. Zhang, S. et al.: Study on the Mechanical Properties and Durability of Hydraulic Lime Mortars Based on Limestone and Potassium Feldspar. Applied Sciences. 13, 4, 2412 (2023). https://doi.org/10.3390/app13042412.

25. 52 Pontica 3 (1970) M. BUCOVALĂ – Descoperiri noi în zona suburbană a Tomisului.pdf, https://drive.google.com/file/d/0BwmOVzh5qKnCV2JYb3ota1EwTUU/view?usp=drive_open&usp=embed_facebook, last accessed 2023/03/19.

26. 314 Pontica 12 (1979) M. BOTZAN – Observaţii din secolul trecut asupra unor construcţii antice din Dobrogea.pdf, https://drive.google.com/file/d/0BwmOVzh5qKnCVWhVMWtkbW1rX2s/view?usp=drive_open&pli=1&usp=embed_facebook, last accessed 2023/03/19.

27. 396 Pontica 15 (1982) GHEORGHE PAPUC – Despre apeductele Tomisului.pdf, https://drive.google.com/file/d/0BwmOVzh5qKnCOTNnS3JacE5GZms/view?usp=drive_open&usp=embed_facebook, last accessed 2023/03/19.

28. LacusCurtius • Cato On Agriculture — Sections 1-52, https://penelope.uchicago.edu/Thayer/E/Roman/Texts/Cato/De_Agricultura/A*.html, last accessed 2023/06/20.

29. Primăria | Orașului Ovidiu, https://primariaovidiu.ro/, last accessed 2023/06/29.

30. Renovarea Parisului de către Haussmanns, https://wikicro.icu/wiki/Haussmann%27s_renovation_of_Paris, last accessed 2022/11/08.

31. ROCK - Patrimoniul cultural care conduce viitorul urban, https://rockproject.eu/about, last accessed 2022/11/08.

32. Specificaţie a mortarelor pentru zidărie. Partea 1: Mortare pentru tencuire şi gletuire, https://magazin.asro.ro/ro/standard/186707, last accessed 2023/06/29.

33. Specificaţie a mortarelor pentru zidărie. Partea 2: Mortare pentru zidărie, https://magazin.asro.ro/ro/standard/186709, last accessed 2023/06/29.

34. Strategia Orasului Ovidiu PDF | PDF, https://ro.scribd.com/document/444571521/STRATEGIA-ORASULUI-OVIDIU-pdf, last accessed 2023/06/29.