

The mortar at the masonry bridges

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ABSTRACT: Through the years the constructors have made their constructions with many different materials, however stone and wood had been the two more frequently used. Both of them are used with little pieces, and at the work it is necessary to joint them. The stones sometimes are joined without any material, but in this case the blocks of stone must be done with special care. The most cases is used another material, softly, named mortar, between the blocks. Those mortars had similar characteristics trough the years, but also different ones. In this document is shown how it is possible to investigate the compositions of the mortars in order to know the age of the constructions where the mortar is. We present two techniques to know the composition of mortars. The techniques are the X Ray Diffraction and the X Ray Fluorescence. The X Ray Diffraction let know the main compounds. The second one show us all the chemical compounds.

1 INTRODUCTION

Among the centuries, builders of masonry bridges have employed different solutions to joint the voissures. The most usual one is to put another material different from the stones, more soft between each two voissures. This material is known as the mortar. However the quality of the mortar has been changing among the time. At roman time, as we can see at “The ten books of the architecture” by Marco Vitrubio Polión (35 – 25 b. C.), mortar was made with a mixture of lime and sand, in a frequent proportion of one part of lime and three parts of sand. Sometimes builders have made its joints without any material. This kind of joint is called “bond to bond joint”. In order to be possible to make a joint like this it is necessary the voissures to be made with a special precision. In other case, the surface where the contact between two voissures takes place are not regular, and there are high local stresses. So if the work on the voissures is not too much good it is necessary to put a mortar on the contact surface. Another alternative to joint two voissures has been the union with wood or the union with pieces of iron.

In this point, if the mortar had similar construction aspects associated to some centuries we can try to investigate the composition of mortars and then make relations between this composition and the age of the construction. Because of that idea we are going to study two techniques to investigate de composition of mortars. However, first, we are going to present how this composition has been changing among the time, and later we will present both techniques.

2 THE COMPOSITION OF MORTARS

2.1 Roman and Egyptian joints

Traditionally is accepted that the most ancients mortars are very soft and they were made with limestones (CaSO_4). It is also known the use of hemihydrated gypsum at the pyramid of Keops

(year 2600 b.C.) and anhidrita not soluble (over cooked gypsum) in the joints of the Amon Temple at Karnak. In this last case the mortar wasn't CaCO_3 if not CaSO_3 .

On Roman times, mortar was, as it is called on "Then books of Arquitectural" by Marco Vitrubio Polión (25 b.C. – 35), a moisture of lime and sand, with one part of lime and three parts of sand, or two parts of lime with five parts of sand. The lime mortars had been used through many centuries. To make them it was necessary to make first the lime and afterwards to burn off it.



Figure 1 : Joint at Kom Ombo Temple (Egypt)

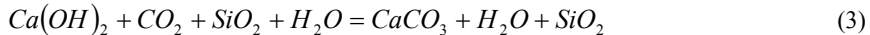
The lime is made with limestones and high temperatures, over 1000°C . The reaction is showed at (1).



In a second reaction, it's added water to the CaO , and it's obtained burn off lime. See equation (2).



In this point if we finally add sand and more water the $\text{Ca}(\text{OH})_2$ reaction with the CO_2 in the atmosphere and we obtain the desired lime mortar. In this process the reaction is indicated at (3).



2.2 Medieval mortars

On Medieval times on say that the mortars are made with some kind of clay, and they are of a bad quality. The clay is a sedimentary rock constituted basically by minerals of silica. The main silicates that contains are the silicates of alumina and magnesium. Their very variable colour depending on the impurities that contain, thus, for example, if they present sulphurs of iron is used to dominating the grey colour. If they possess impurities of organic matter presents blue or black colours, and if they contain oxides of iron the tones are brown or greenish. They present also affinity by the water, and its porosity is very high, but the size of pore is so little that impedes the circulation of the water through their mass. The clays proceed of it give-composition by alteration of the aluminumsilicates. Because of it origin are moved by the currents of water producing sedimentations, often far from its origin. In these sedimentations they can be contaminated, for example, with grains of quartz, giving rise to sandy clays, or well with carbonates of calcium, giving rise to loams. Normal composition of clay is shown in Table 1.

2.3 Actual mortars

Modern cements are developed from 19th century, combining the cooking at high temperatures of limestone and clay. Vicat (1818), and Joseph Aspdin (1824) are names connected with the

history of the modern cements. The base of the cements Portland, their clinkers, is obtained burning to the fusion artificial mixtures of limestones and clays until all their components are combined. From time to time other components can be added like they are the natural puzolanes, the flying ashes, the smoke of silica or the limestone powder..

Table 1 : Normal composition of clay

Sílice (SiO ₂)	31 – 41 %
Aluminio (Al)	40 – 48 %
Hierro (Fe)	0,11 – 0,77 %
Titanio (Ti)	0,13 – 0,47 %
Calcio (Ca)	0,05 – 0,13 %
Sodio y Potasio (Na y K)	0,25 – 0,85 %
Magnesio (Mg)	0,05 %

3 RESEARCH TECHNIQUES

3.1 *The X Ray Fluorescence Technique*

This laboratory technique is used when it is necessary to know the exactly chemical composition of a material, ever solid, dust or liquid material. If a normal sample is used to contrast it is possible to guess the quantity of each component.

There are two levels of analyzes. The first one searches for the mayor components, those who are present in a quantity upper than 0,1 %. In this phase we can found elements as Al₂O₃, P₂O₅, K₂O, CaO, SiO₂, TiO₂, MnO₂, Fe₂O₃, MgO, Na₂O

The second level is called as determination of minor elements. In this phase we can found V, Cr, Co, Ni, Cu, Zn, Ba, Nb, Rb, Sr, Y, Zr, U, Th, Pb, S.

To determinate the major compounds we need only 2 g. of material. However to determinate the minor elements we need 10 g. of sample.

3.2 *The X Ray Diffraction Technique*

The X Ray Diffraction Technique is an analytical technique that let obtain the diffraction spectra with high resolution. This information can be used to determinate, in a big kind of materials, through the analytical method of Rietveld profile, the crystalline structure, the existence of texture, residual tensions, fatigue, etc. Although, this information is necessary for later studies with others techniques as assemblies of neutrons and sincrotrón radiation.

In this case it is employed an X-ray diffraction apparatus model Seifert XRD 3000 that permits to obtain diffraction spectra with high resolution. It can get diffraction diagrams in the angular range of (1°-164°), to study thin sheets.

The preparation of the samples, whose size should be of 2 g, requires, in the first place, its grinding, second its sifting, and third the assembly to the analysis place. In the outputs the letters s (syn), l (low), i (intermediate), or (ordered) and x (without specifying) refer to the importance of the peaks obtained in the diagrams, by decreasing order of importance.

4 SAMPLES ANALYSED

To verify the suitability of the methods of trial it had been taken samples in thirteen masonry bridges dated between the centuries X and XIX. We have taken samples at vaults, cutwaters and spandrells. The first problem to resolve is to distinguish taking samples between the ancient mortars and the most recent mortars. For that, it is necessary to search at those parts of the masonry that assure a greater originality of the primitive construction (to see figure 2). The sample should be taken with the major care to assure to be not contaminated with other materials. Subsequently the sample is crushed, sifted and dried, as can be observed in the figure 3.

Both employed techniques provide numerical outputs of results as they can be appreciated in the tables 2 and 3. The table 2 indicates the totality of the results of the fourteen samples practiced. The table 3 provides the numerical output of the X-rays diffraction technique of the sam-

ple of Salas bridge. The X-rays Diffraction technique provides besides graphic outputs like the type of it indicated in the figure 4, for the same Salas bridge mentioned.



Figure 2 : Taking samples.

Table 2 : Numeric X Ray Fluorescence Output

Sample	-SiO2-	-CaO-	-Al2O3-	-Fe2O3-	-MnO-	-MgO-	L.O.I	Total
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Palacios Sierra	69,16	12,05	2,70	1,46	0,07	0,42	12,84	99,64
Castrovido	34,27	31,37	2,33	0,89	0,03	1,21	28,49	99,43
Salas	53,88	18,25	2,39	1,30	0,03	0,43	21,93	99,14
Barbadillo	58,56	19,65	1,60	0,92	0,02	0,18	18,23	99,99
Pielago	60,48	18,20	2,45	0,92	0,02	0,23	15,90	99,19
Quintanilla	49,34	20,22	6,71	2,13	0,04	0,59	18,85	99,84
Quintanilla A	48,52	20,24	6,02	2,43	0,04	0,60	19,99	99,95
Lerma 06-07	80,77	6,39	2,58	1,31	0,02	0,32	6,97	99,35
Lerma 06-05	19,02	41,50	1,30	0,59	0,01	0,28	35,88	99,12
Tordomar	63,55	14,61	3,36	1,11	0,02	0,36	14,75	99,31
Talamanca	63,51	17,10	2,24	0,66	0,02	0,27	15,20	99,98
Escuderos	49,38	24,50	2,20	0,76	0,02	0,49	21,50	99,93
Peral de Arlanza	56,93	16,79	4,27	1,59	0,03	1,09	17,28	99,74
Palenzuela	28,45	32,50	1,07	0,49	0,01	1,49	34,80	99,10

Table 3 : Numeric X Ray Diffraction Output

Reference Code	Compound Name	Chemical Formula	Displacement [°2Th.]
00-005-0586	Calcite, syn	Ca C O ₃	0,000
00-046-1045	Quartz, syn	Si O ₂	0,000
00-043-0697	Calcite, magnesian	(Ca , Mg) C O ₃	0,000
00-007-0042	Muscovite-3\ITM\RG	(K , Na) (Al , Mg , Fe) ₂ (Si _{3,1} Al _{0,9}) O ₁₀ (O H) ₂	0,000
00-018-0276	Margarite-2\ITM#\1\RG	Ca Al ₂ (Si ₂ Al ₂) O ₁₀ (O H) ₂	0,000

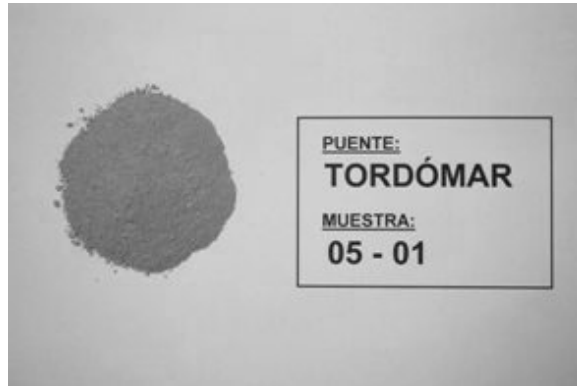


Figure 3 : Processed sample.

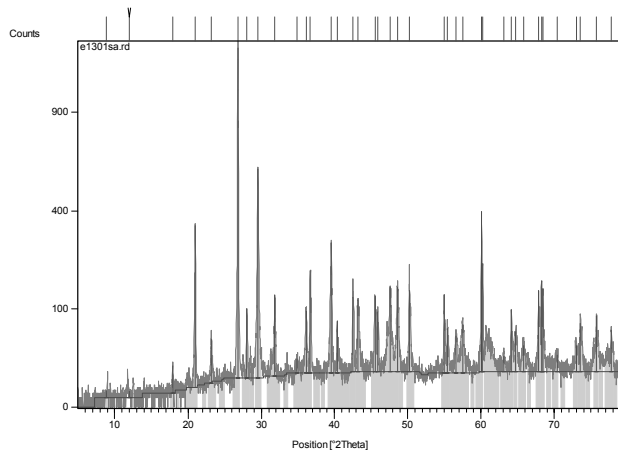


Figure 4 : X Ray Diffraction Output.

5 SOME CONCLUSIONS

All the data had been processed and the relations among the main oxides of the different samples have been compared. With regard to the trials of diffraction a matrix of impact has been carried out and where the main minerals detected have been characterized. The results obtained are indicated respectively in the tables 4 and 5.

From the analysis of showed tables, and from the assembly of the employed methodology, it can be obtained certain conclusions indicated subsequently.

The analysis of the mortars in the masonry bridges is a novel technique that gives valuable information by itself, and also that permits to know the composition of the same mortars, and to compare diverse samples, being able to ratify or to refute generalized theories, but not too much contrasted, on the evolution of the mortars through the years. For an adequate validation of the method of dating bridges, it will be necessary to have a great database, which those data presented are a first embryo. With that extensive database, it will be possible to obtain information not only about the origins of a bridge, but also about possible subsequent works in different zones and times.

Table 4 : X Ray Fluorescence Analysis

Bridge	Century	Sample	Oxides ratio		
			SiO ₂ /Al ₂ O ₃	CaO/Al ₂ O ₃	Fe ₂ O ₃ /Al ₂ O ₃
Tordómar	X	05.01	18,91	4,35	0,33
Castrovido	XII	14.01	14,71	13,46	0,38
Palacios de la Sierra	XIII	16.01	25,61	4,46	0,54
Barbadillo del Mercado	end.XIII	12.01	36,60	12,28	0,58
Palenzuela	XVI	01.01	26,59	30,37	0,46
Peral de Arlanza	XVI	02.01	13,33	3,93	0,37
Escuderos	XVI	03.01	22,45	11,14	0,35
Escuderos	XVI	03.02	19,84	9,48	0,32
Talamanca	XVI	04.01	28,35	7,63	0,29
Lerma	endXVI	06.02	8,58	1,38	0,11
Lerma	end.XVI	06.05	14,63	31,92	0,45
Lerma	endXVI	06.07	31,31	2,48	0,51
Salas de los Infantes	XIX	13.01	22,54	7,64	0,54
Quintanilla del Agua	XIX	07.01	7,35	3,01	0,32
Quintanilla del Agua	XIX	07.02	8,06	3,36	0,40
Pielágo Negro	XIX	10.01	24,69	7,43	0,38

Table 5: X Ray Diffraction Analysis

Bridge	Mineral compoused															
	Quartz (1)	Calcite (2)	Calcite, magnesian (3)	Microcline (4)	Albite (5)	Halite (6)	Halite, potassian (7)	Gypsum	Silica	Ankerite	Orthoclase	Muscovite	Muscovite-2\ITM#\1RG	Muscovite-3\ITTRG	Margarite-2\ITM#\1RG	Lepidolite-3\ITTRG
Tordómar		x							x				x			
Castrovido	s	s		x						x					x	
Palacios Sierra	s	s									x					
Barbadillo del Mercado		s,x		x					x							
Palenzuela	s	s				s		x								
Peral de Arlanza		s		i					x							
Escuderos	s	s										x				
Escuderos	s	s					s									x
Talamanca		x		i					x							
Lerma	l	s		i	o											
Lerma	s	s	x													
Lerma	s	s						x								
Salas de los Infantes	s	s	x											x	x	
Quintanilla del Agua	s	s,x,x		i												
Quintanilla del Agua	s	s														x
Pielágo Negro	s	s	x									x				

One of the key aspects to improve is to take samples, with special attention to the tools. As improved methods are suggested to scrape with small tools of drilling and reels of steel. At the same time it must be necessary to use several techniques base on vertical work and with all the safety measures to work in the middle of the river.

Also it is fundamental to identify, with every accuracy, the point in which the sample has been taken, because in a same bridge we can find out different zones of different ages.

With relation to the results of the X-Rays Fluorescence trials, it has been carried out, a comparative with the relations among the oxides of calcium silicon, iron and aluminium (Al). In general, it is observed greater relations lime/alumina ($\text{CaO}/\text{Al}_2\text{O}_3$) and silica/alumina ($\text{SiO}/\text{Al}_2\text{O}_3$) in the oldest mortars, while the iron/alumina oxide relation ($\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$) is maintained practically constant through the years. In this moment, with the quantitative results obtained not more conclusions can be obtained.

It can be accepted that the technique of analysis is validated, and also some improvement methods are proposed. In the future, it will be interesting to enlarge in great measure the number of samples and to proceed to an statistical study of the results.

With regard to the X-Rays Diffraction trials, it has been verified the presence of calcium and silicon oxides, in all the samples, just as it was to expect. also are observed other components less important whose meaning only will be able to be valued adequate with a more extensive sample of data.

With respect to the techniques of analysis, both techniques are considered adequate. We can say, also, that in the case of the X-Rays Fluorescence, it isn't considered necessary the decision to obtain minor elements, because of they don't contribute especially to give significant information, enlarging, on a great measure, the size of samples, and also the price and time of the trial. Finally, it is important to stand out that this technique of trials is absolutely comparable to the old constructions building mortars.

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