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Replicating the chemical composition of the binder for restoration of historic mortars as an optimization problem

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Abstract. The present study aims to show how the problem of reproducing, as closely as possible, binders of historic mortars by mixing raw materials which are commercially available, can be formulated as a linear optimization problem. The study points out that by mixing five standard raw materials (end-members) it is possible to obtain mortar binders with the almost same chemical compositions of those determined on the historic and archaeological mortar samples studied in some recent scientific papers. An advanced function of the Microsoft Excel spreadsheet, the Solver add-in, was used for the calculation of the right amount of each raw material to be mixed for producing the new binders. This approach could be useful to provide an optimal solution in the process of restoration of ancient monuments, where it is necessary to replace the historic mortars with new highly compatible repair mortars.

Keywords: mortar; concrete; binder; aggregate; lump; mixing; optimization problem; excel; solver; restoration

1. Introduction

In recent years, many studies have been published on the importance of reproducing compatible repair mortars for the restoration of historic and archaeological buildings (Hassan *et al*. 2001, Binda *et al*. 2003, Maravelaki-Kalaitzakia *et al*. 2005, Van Balen *et al*. 2005, Crisci and Miriello 2006, Lanas *et al*. 2006, Beck and Al-Mukhtar 2008, Varas *et al*. 2008, Goldsworthy and Min 2009, TC 203-RHM 2009, Klisińska-Kopacz *et al*. 2010, Miriello *et al*. 2010a, Schueremans *et al*. 2011). Many of these works show that the production of compatible repair mortars can be made only after a multidisciplinary study whose primary purpose is a detailed chemical and

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mineralogical characterization of the old mortars. In general, a repair mortar is suitable for a restoration purpose when it has an aesthetic, chemical, mineralogical, mechanical and physical compatibility with the substrate on which its application is expected (Schueremans *et al*. 2011). Generally speaking, mortars are mixtures of a binder (mainly lime putty or hydraulic lime), an aggregate (usually river sand) and water. This recipe is supposedly simple, but, in actual fact, the historic tradition of the repair mortars has highlighted the existence of several recipes (Arcolao 2001, Crisci and Miriello 2006, Miriello *et al.* 2010b). The aggregate fraction may have a very complex mineralogical composition. For example, if the aggregate is composed of marble sand, it is unlikely that chemical reactions may occur between the binder and the aggregate. On the contrary, if the mortar contains natural or artificial pozzolanic materials, such as natural volcanic pozzolans, diatomaceous earths, opaline rocks, and crushed pottery fragments, this can produce significant changes in the chemical and mineralogical composition of the binder (McCarter and Tran 1996, Sánchez de Rojas and Frías 1996, Liebig and Althaus 1998, Ubbrìaco and Tasselli 1998, Franzini *et al*. 1999, Sánchez *et al*. 1999, Franzini *et al*. 2000a, 2000b, Biernacki *et al*. 2001, Roszczynialski 2002, Moropoulou *et al*. 2004).

Furthermore, the high variability of the chemical, mineralogical and petrographic compositions of the historic mortars, even in the same building, suggests that each sample has a peculiar feature (Güleç and Tulun 1997, Moropoulou *et al*. 2000, Crisci *et al*. 2004, Lezzerini 2005, Meir *et al*. 2005, Anastasiou *et al*. 2006, Miriello and Crisci 2006, Riccardi *et al*. 2007, Barba *et al*. 2009, Miriello *et al*. 2010a, 2010b, Miriello *et al*. 2011a, 2011b, Miriello *et al*. in press).

This means that before choosing the most appropriate analytical techniques to study the mortars, each case study should be evaluated individually. Of course, the best way to produce mortars compatible with the ancient ones would be to find all the original raw-materials used in the mixture. Subsequently, the same raw materials could be used to produce the new mortars. The source of raw materials cannot always be identified exactly, due to lack of time, financial reasons, or merely because the old quarries used for quarrying the raw materials are no longer accessible. In these circumstances, common commercial products such as non-hydraulic lime putty, hydraulic lime and various types of aggregates may be used to restore the old mortars. This is when several complications arise. Is it possible to find commercial products that have the same chemical and mineralogical composition of the components used to produce the original historic mortars (lime and aggregates)? If we are lucky, the answer is 'yes'. In fact, we are more likely to find commercial products with a composition which is similar to that of the original components, but in several occasions, we do not find any suitable commercial products.

The present study aims to give a significant contribution on the above-mentioned topic. In particular, generalizing the question as a linear optimization problem, it will try to demonstrate that it is possible to calculate the percentages of raw materials to be mixed for producing chemically compatible binders in the restoration of historic and archaeological mortars, by mixing raw materials commercially available.

Some examples of optimal solutions obtained through the use of the Microsoft Excel optimizer Solver on literature data, are presented. This idea could have an important impact on the world of restoration and it may help, at least in part, to solve the problem of the chemical compatibility of the binder.

2. Formalization of the optimization problem

Let *m* be the number of available end-members (i.e., raw materials of known composition), and $\left(\alpha_{1j}, \alpha_{2j}, \ldots, \alpha_{nj}\right)$ the chemical composition (mass fraction) of the j^o end-members. The chemical composition of the end-members is representable by the following $m \times n$ matrix

$$A = \begin{pmatrix} \alpha_{11}, & \ldots & \alpha_{1m} \\ \ldots & \ldots & \ldots \\ \alpha_{n1}, & \ldots & \alpha_{nm} \end{pmatrix} \tag{1}$$

whose α_{ij} element is the mass fraction of the i^o chemical element for the j^o end-member, with $\sum_{i=1}^{n} \alpha_{ij} = 1$ for each j. Mixing $p = (p_1, p_2, \ldots, p_m)^T$ amount (weight) of end-members, a new mixture of weight

$$p_{tot} = \sum_{j=1}^{m} p_j \tag{2}$$

is obtained, where the weight of the i^o chemical element is

$$\gamma_i = \sum_{j=1}^{m} \alpha_{ij} p_j \tag{3}$$

Dividing (3) by p_{tot} we obtain

$$y_i = \sum_{j=1}^{m} \alpha_{ij} x_j \tag{4}$$

where $x_j = \dfrac{p_j}{p_{tot}}$ is the fraction of the j^o end-member used in the preparation of the new mixture, and $y_i = \dfrac{\gamma_i}{p_{tot}}$ the resulting mass fraction of the i^o chemical element in the new mixture.

Therefore, if

$$Y = \left(y_1, \ldots, y_n\right)^T \tag{5}$$

is the chemical composition of the mixture to be obtained with m available end-members, the percentages $X = (x_1,...,x_m)^T$ of end-members to be used is the solution of the following linear system

$$A \times X = Y \tag{6}$$

Note that, to ensure the physical sense of the solution, the following constraints must hold

$$\sum_{j=1}^{m} x_j = 1 \tag{7}$$

$$0 \le x_j \le 1, \quad \forall j \tag{8}$$

The problem under consideration is therefore

$$\begin{cases} A \times X = Y \\ \sum_{j=1}^{m} x_j = 1 \\ 0 \le x_j \le 1 \end{cases} \tag{9}$$

Note that, in general, the equation system (9) does not allow an exact solution, but it is possible to find an optimal solution X_{opt} which minimizes, for example, the square difference Δ^2 between real values (Y_R) and simulated ones (Y_S)

$$\Delta = \left| Y_R - Y_S \right|^2 = \sum_{i=1}^{n} \left(Y_{i_R} - Y_{i_S} \right)^2 \tag{10}$$

3. Materials and methods

To evaluate the possibility of obtaining lime binders with a chemical composition close to that of ancient binders by mixing suitable components, we have taken into consideration the chemical data reported in some recent papers which have fully studied the binder of the mortars from several historic buildings (Franzini *et al.* 2000a, Franzini *et al.* 2000b, Miriello 2005, Riccardi *et al.* 2007, Villasenor and Price 2008, Miriello *et al.* 2011a). The selected samples are characterized by air-hardening and hydraulic binders. The CaO content of the samples ranges from about 50 to 100% by weight. The chemical compositions of both raw materials (Table 1) and historic binders (Table 2) are reported in an anhydrous state and normalized so that the sum of their components is 100 (wt %). In Table 1, it is possible to observe Vesuvio pozzolan and diatomite, as end-members. Their presence might seem strange, since they are not lime binders; however, their presence is intentional, because, historically, natural pozzolanic materials were intentionally added to the mixtures to improve the performance of binders. Of course, we could use two hydraulic limes instead of Vesuvio pozzolan and diatomite, but this would not change the efficacy of the model previously described.

The anhydrous chemical compositions (wt %) of the raw materials shown in Table 1 represent the value of the matrix (1). In more details, pure lime, magnesian lime, NHL 3.5 hydraulic lime (El-Turki *et. al*. 2007), diatomite (Yilmaz and Ediz 2008), and volcanic ash from the Vesuvio Monte Somma (Campania, Italy), with the chemical composition determined by Miriello *et al.* (2010a), were used as end-members. Similarly, Table 2 contains the values of the vector (5).

A solution of the system (9), for the data of Table 1 and Table 2 was obtained with the optimization tool Solver.

Solver is a Microsoft Office Excel add-in program based on the code of non linear optimization "GRG2" (Generalized Reduced Gradient) developed by Leon Lasdon (University of Texas) and Allan Waren (Cleveland State University) that can be added to a primary program for solving a nonlinear equation, a system of linear/nonlinear equations, and optimization problems (Fylstra *et al*. 1998). The same algorithm was recently used in the archaeometric field to simulate the mixtures of some historic bricks and to define their provenance (Miriello and Crisci 2007).

The optimization was performed using the Newton method and the default setting of the Solver tool (Fletcher 1987).

Table 1 Chemical compositions of the selected raw materials used for reproducing mortar binders with chemical composition like those of some historic and archaeological binders. TiO_2, MnO and $P_2O_5 < 0.01$ wt %. 1 = NHL 3.5 by El Turky *et al.* 2007; 2 = Diatomite by Ylmaz and Ediz 2008; 3 = Vesuvio pozzolan by Miriello *et al*. 2010a

Wt%	SiO_2	AI_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Sum
Pure calcitic lime					100			100
Hydraulic lime-NHL 3.5[1]	13.25	4.80	1.89	1.89	76.86	0.14	1.17	100
Diatomite[2]	93.72	0.66	1.34	1.04	1.27	1.00	0.90	100
Pure dolomitic lime				41.82	41.82			100
Vesuvio pozzolan[3]	54.79	19.97	8.72	1.68	1.68	6.15	4.19	100

Table 2 Major and minor chemical components of some historic and archaeological mortar binders (R) and chemical compositions of the simulated binders (S) obtained using Microsoft Excel optimizer Solver for mixing the raw materials of Table 1

Literature	Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Sum
Franzini *et al.* 2000a	6/65-5_R	43.25	8.37	0.90	1.28	45.56	0.17	0.47	100
	6/65-5_S	42.43	5.70	2.68	1.61	44.83	1.24	1.51	100
	1A/85-2_R	41.58	5.64	0.66	0.72	51.07		0.33	100
	1A/85-2_S	40.91	3.60	1.82	1.40	50.46	0.71	1.10	100

Table 2 Continued

Franzini *et al*. 2000b	LTm(17)_R	39.78	5.46	0.79	0.90	52.22	0.39	0.46	100
	Ltm(17)_S	39.26	3.83	1.90	1.34	51.73	0.82	1.12	100
	LTc(28)_R	39.39	5.45	0.93	1.03	52.31	0.41	0.48	100
	LTc(28)_S	38.91	3.95	1.94	1.41	51.86	0.78	1.15	100
Riccard *et al*. 2007	AM 1_R	36.92	3.58	0.66	0.51	58.20		0.13	100
	AM 1_S	36.46	2.22	1.25	0.98	57.78	0.54	0.77	100
	AM 11_R	29.59	5.41	0.82	0.82	62.99		0.37	100
	AM 11_S	29.05	3.76	1.74	1.36	62.47	0.58	1.04	100
Villasenor and Price 2008	6_R	11.00	3.00	1.00	17.00	68.00			100
	6_S	10.84	2.60	1.07	16.85	67.86	0.12	0.66	100
	16_R	11.00	2.00	1.00	15.00	71.00			100
	16_S	10.91	1.84	0.79	14.92	70.92	0.12	0.50	100
Miriello 2005	MRl2p3_R	16.94	2.42	1.94	1.53	71.83	3.96	1.38	100
	MRl2p3_S	17.44	4.14	1.88	1.99	72.30	1.33	0.92	100
	MRl4p7_R	18.76	2.90	1.97	2.44	72.11	0.61	1.21	100
	MRl4p7_S	18.87	3.31	1.50	2.54	72.22	0.74	0.82	100
Miriello *et al*. 2011a	M1_B1_R	11.39	4.44	1.20	1.38	79.62	1.37	0.60	100
	M1_B1_S	11.29	4.04	1.76	1.29	79.55	1.22	0.85	100
	M6_B1_R	13.51	4.04	0.48	1.57	78.77	0.94	0.69	100
	M6_B1_S	13.39	3.48	1.50	1.46	78.67	0.69	0.81	100
Villasenor and Price, 2008	8_R	6.93		0.99	8.91	83.17			100
	8_S	6.99	0.34	0.22	8.96	83.21	0.16	0.12	100
	10cp_R	1.98	0.99	0.99	11.88	84.16			100
	10cp_S	2.24	0.82	0.35	11.96	84.24	0.21	0.18	100
Miriello *et al*. 20011a	M7_B1_R	6.88	2.48	0.65	1.80	86.57	1.26	0.36	100
	M7_B1_S	6.88	2.43	1.06	1.80	86.57	0.75	0.51	100
	M8_B1_R	6.57	2.52	0.68	1.61	86.72	1.37	0.53	100
	M8_B1_S	6.73	2.45	1.07	1.68	86.81	0.75	0.51	100
Franzini *et al*. 2000a	ARA 101_R	4.50	1.31	0.79	0.72	91.90	0.39	0.39	100
	ARA 101_S	4.53	1.43	0.63	0.75	91.92	0.43	0.31	100
	ARA 94_R	3.31	1.49	0.40	1.31	92.67	0.67	0.15	100
	ARA 94_S	3.47	1.26	0.55	1.36	92.70	0.39	0.27	100
Franzini *et al*. 2000a	MP 114_R	2.16	0.83	0.22	0.92	94.84	0.57	0.46	100
	MP 114_S	2.36	0.86	0.38	1.02	94.94	0.26	0.18	100
	MP 111_R	0.36	0.36	0.11	0.91	97.44	0.48	0.34	100
	MP 111_S	0.76	0.28	0.12	1.09	97.60	0.09	0.06	100

4. Results and discussions

By solving the optimization problem (9) it was possible to calculate -for each real sample- the best percentage of selected raw materials to be mixed in order to obtain a binder fraction that is chemically compatible with that of the mortar to be restored. Fig. 1 and Table 3 show the results obtained by using the Solver advanced function for linear optimization, in which it is possible to see the mixtures of the end-members that can be used for producing binders which are compatible with those of the historic mortars. It is interesting to highlight that the combination of these raw materials produces binders that have a chemical composition close to that of the real samples (Table 2).

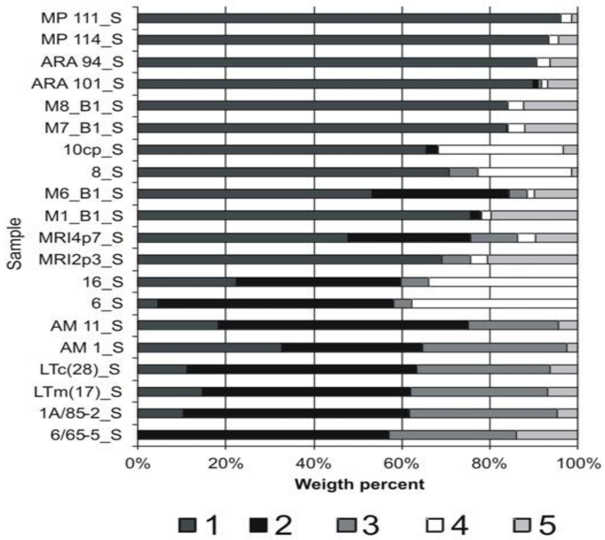

Fig. 1 The best binder recipes to obtain chemically compatible binders as calculated using Microsoft Excel Solver add-in. 1=Lime; 2=Hydraulic lime - NHL 3.5 by El Turki *et al*. 2007; 3=Diatomite by Ylmaz and Ediz 2008; 4=Magnesian lime; 5=Vesuvio pozzolan by Miriello *et al*. 2010a

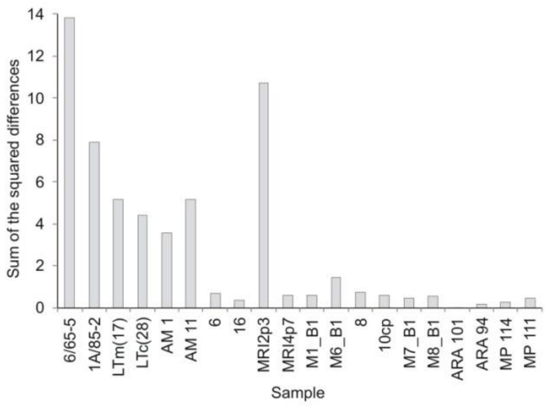

Fig. 2 Sum of the squared differences between real and simulated chemical compositions of the mortar binders

Table 3 Percentages of selected raw materials to be used for reproducing mortar binders with a chemically compatible recipe in respect to some historic and archaeological ones. 1=Lime; 2=Hydraulic lime - NHL 3.5 by El Turki *et al*. 2007, 3=Diatomite by Ylmaz and Ediz 2008, 4=Magnesian lime, 5=Vesuvio pozzolan by Miriello *et al*. 2010a

Simulated sample	1	2	3	4	5	Sum
6/65-5_S		57.03	29.12		13.85	100
1A/85-2_S	10.26	51.47	33.71		4.56	100
LTm(17)_S	14.56	47.44	31.24		6.76	100
LTc(28)_S	11.24	51.99	30.51		6.26	100
AM 1_S	32.80	31.81	33.01		2.38	100
AM 11_S	18.36	56.79	20.32		4.53	100
6_S	4.62	53.61	3.99	37.78		100

Table 3 Continued

16_S	22.39	37.43	6.35	33.83		100
MRI2p3_S	69.10		6.63	3.77	20.50	100
MRI4p7_S	47.82	27.87	10.62	4.16	9.53	100
M1_B1_S	75.76	2.09	0.21	2.20	19.74	100
M6_B1_S	53.33	31.11	4.16	1.60	9.80	100
8_S	70.73		6.60	21.20	1.47	100
10cp_S	65.45	2.81		28.33	3.41	100
M7_B1_S	83.80		0.24	3.81	12.15	100
M8_B1_S	84.19			3.53	12.28	100
ARA 101_S	89.73	1.35	0.66	1.44	6.82	100
ARA 94_S	90.68			2.99	6.33	100
MP 114_S	93.41			2.28	4.31	100
MP 111_S	96.08			2.54	1.38	100

Table 4 Squared differences between chemical components of real (R) and simulated (S) mortar binders

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	Sum
6/65-5	0.67	7.15	3.15	0.11	0.53	1.15	1.08	13.84
1A/85-2	0.45	4.15	1.35	0.46	0.38	0.51	0.59	7.89
LTm(17)	0.27	2.65	1.24	0.19	0.22	0.18	0.43	5.18
LTc(28)	0.23	2.26	1.01	0.14	0.19	0.14	0.44	4.41
AM 1	0.22	1.85	0.35	0.23	0.18	0.3	0.41	3.54
AM 11	0.29	2.71	0.85	0.29	0.25	0.33	0.44	5.16
6	0.02	0.16		0.02	0.02	0.01	0.44	0.67
16	0.01	0.03	0.04	0.01	0.01	0.01	0.25	0.36
MRI2p3	0.25	2.95		0.21	0.21	6.91	0.21	10.74
MRI4p7	0.01	0.17	0.22	0.01	0.01	0.02	0.15	0.59
M1_B1	0.01	0.16	0.32	0.01	0.01	0.02	0.06	0.59
M6_B1	0.01	0.32	1.04	0.01	0.01	0.06	0.01	1.46
8		0.11	0.6			0.03	0.01	0.75
10cp	0.07	0.03	0.41	0.01	0.01	0.05	0.03	0.61
M7_B1			0.17			0.26	0.02	0.45
M8_B1	0.02		0.15	0.01	0.01	0.38		0.57
ARA 101		0.01	0.03				0.01	0.05
ARA 94	0.03	0.05	0.02			0.08	0.01	0.19
MP 114	0.04		0.02	0.01	0.01	0.09	0.08	0.25
MP 111	0.16	0.01		0.03	0.03	0.16	0.08	0.47
Min	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.05
Max	0.67	7.15	3.15	0.46	0.53	6.91	1.08	13.84
Mean	0.14	1.24	0.55	0.09	0.10	0.53	0.24	2.89
Dev.st.	0.18	1.91	0.76	0.13	0.15	1.52	0.28	3.93
Median	0.04	0.16	0.27	0.01	0.01	0.12	0.12	0.64

The data in Table 4 show that the maximum squared differences between the chemical compositions of the simulated binders (S) and the chemical compositions of the real binders (R) are 7.15 for Al_2O_3, 6.91 for Na_2O, 1.08 K_2O and less than 1 for all other chemical elements. Considering all the major chemical components (Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO and Fe_2O_3), the sums of the squared differences (last column of Table 4 and Fig. 2) range from 0.05 (sample ARA 101) to 13.84 (sample 6/65-5), with a mean and relative standard deviation value of 1.84 ± 2.32, excluding 6/65-5 and MRI2p3 samples which show high squared differences for Al_2O_3 and

Na_2O, respectively.

The results point out that by using optimization techniques, it is possible to reproduce binders which are very similar to the historic ones, starting from components already available as raw materials. The restorer should simply be aware of the chemical composition of the binder to be restored. This chemical composition could be obtained from a previous diagnostic study on the binder of the historic mortar (e.g., by SEM-EDS analysis).

Data collected starting from the chemical compositions of mortar binders reported by several authors (Franzini *et al.* 2000a, Franzini *et al.* 2000b, Miriello 2005, Riccardi *et al.* 2007, Villasenor and Price 2008, Miriello e*t al.* 2011a) point out that the mixtures of the selected raw materials can be used for producing binder recipes with chemical compositions close to those of the real samples (Table 2).

5. Conclusions

We have demonstrated that it is theoretically possible to reproduce the chemical composition of historic mortar binders by mixing selected materials potentially available, generalizing the question as a linear optimization problem and obtaining optimal solutions through the use of the Microsoft Excel optimizer Solver.

Despite the high compositional variability of raw materials potentially usable to produce the historic binder, the strength of our idea concerns the possibility of recreating the entire chemical variability (but not the mineralogical variability) of the historic binder independently from the raw materials used historically to make the binder, by using the same end-members.

Of course, this would not solve all the problems of compositional compatibility. Its use would have both advantages and disadvantages. Among the possible advantages, we have the possibility of obtaining new binders by mixing products traditionally used for producing historic mortars. Furthermore the use of traditional raw materials as end-members may help to partially meet the mineralogical compatibility of the binder. Of course, the use of this optimization approach to mix selected materials is based on the knowledge of the chemical composition of the historic binder, so before proceeding with the production of a historic binder, an accurate compositional characterization of the historic mortar is necessary.

Producing compatible binders does not mean making totally compatible mortars, but this could be a first step to solve, at least partially, compatibility problems. The method could be improved in the near future by using other raw materials than those herewith proposed, and the chemical compatibility may be improved by including in the calculation not only the major elements, but also some trace elements, for example Sr and Ba obtained by LA-ICP-MS analysis of the historic binders.

We hope that this approach can be useful in the restoration of ancient monuments, a field where currently the problem of compatibility of the historic binders is treated confusedly.

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