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Methodology and validation of a hot hydrochloric acid attack for the characterization of ancient mortars

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Abstract

A method for the analysis of the chemical composition of ancient mortars is proposed. The use of the hot hydrochloric acid attack to carry out a separation of the binder and the aggregate is discussed. Different types of mortars of Pamplona Cathedral are analyzed. Traditional chemical methods and atomic emission spectroscopy are employed. The mineralogical studies are carried out using X-ray diffraction. Statistical methods are employed in order to establish a comparison between the different attacks.

Keywords: Calcium-silicate-hydrate; Characterization; Aggregate; CaO; Mortar

The investigation of the chemical composition of ancient mortars represents a fundamental aspect of the characterization of these materials. The chemical analysis of the soluble fraction and the insoluble residue resulting from the attack of the mortar with hydrochloric acid using certain reaction conditions allows us to know, with some limitations, the chemical compositions of the aggregate and the binder, which correspond to the insoluble residue and the soluble fraction, respectively.

The different conditions of the acid attack to the mortar (concerning hydrochloric acid concentration, time, temperature, and mechanical stirring during the decomposition reaction) intend to achieve a separation of the binder (and its impurities) and the aggregate (and its impurities) as completely as possible, as proposed in the literature. The conditions chosen for the attack in a rapid approximate analysis to separate the soluble (binding material) and insoluble (aggregate) fractions (with the objective of using it in restoration) must take into account the following considerations:

1. It is convenient to establish an attack method valid to analyze as many types of mortars as possible [1–5].
2. The method should be valid in establishing the hydraulic effect of the mortars.

The proposed method allows analyses of lime mortars, gypsum and lime mortars, and gypsum mortars with sand of siliceous nature, but it is not useful for mortars with limestone sand. This study was carried out due to the controversy generated among different authors, especially concerning the attack procedure [6–11].

1. Materials and methods

The samples of the mortars came from the inside of Pamplona Cathedral (1394–1512), which is of gothic style. Seven representative samples of the different types of mortars identified, corresponding to defined architectural zones, were chosen in a previous study [12]. These samples are lime mortars with siliceous aggregates. In order to validate the results obtained, twelve more samples of mortars from this temple were chosen randomly with the aim of duplicating the comparisons performed.

The sampling procedure for mortars was carried out by taking a part of the mortars with a chisel and throwing away the external portion of the joints, with the aim of obtaining nonaltered material. The sample ground in an agate mortar was dried in a heater until constant weight was achieved and then 1 g of sample was taken for its subsequent analysis.

A titration with ethylenediaminetetraacetic acid (EDTA) (using murexide and eBT (eriochrome black T) as indicators) was used for the analysis of calcium and magnesium in the soluble fraction. The contents of soluble silica, Fe, and Al were determined by atomic emission spectroscopy with inductively coupled plasma (ICP) (Jobin Ybon JY 38S Plus Sequential, Instruments SA, France). When the amounts of

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Table 1
Chemical analysis of the soluble fraction hydrochloric acid attack at room temperature

Sample	SiO_2[a] (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)
1	0.35	32.31	1.77	0.38	0.27	0.039	0.077
2	2.56	35.63	2.64	0.25	0.22	0.034	0.039
3	0.75	34.40	2.86	0.38	0.50	0.072	0.081
4	0.67	35.98	2.67	0.32	0.40	0.142	0.132
5	0.65	36.60	1.89	0.32	0.45	0.110	0.185
6	0.93	35.05	2.20	0.42	0.40	0.030	0.094
7	0.32	30.04	0.86	0.20	0.19	0.048	0.074

Percentages related to original dry mortar.

[a] Acid-soluble silica.

Fe_2O_3 and Al_2O_3 were higher than 1%, the determinations were carried out by titrations using barium diphenylaminosulphonate and ditizone as indicators. Sodium and potassium were determined by flame emission atomic spectroscopy (Perkin Elmer 460, Perkin Elmer, Überlingen, Germany). The contents of elements after an alkaline fusion of the samples were determined by traditional chemical methods. The mineralogical studies were carried out using a Siemens D-500 (Karlsruhe, Germany) Kristalloflex 810 X-ray powder diffractometer.

2. Results and discussion

The following experimental conditions for the attack of mortars were taken from the literature [9,11]: attack with 1:5 volume ratio HCl (2 M), room temperature, and mechanical stirring for 30 min. The results of the analysis of the soluble fraction after the attack of the samples in these conditions are summarized in Table 1.

It can be observed that the percentages of acid soluble SiO_2, which indicates the existence of hydraulicity in the mixture [4,10], present low values. The results of the study of the insoluble residue resulting from this attack, which was carried out after dissolution with an alkaline flux (sodium carbonate-borax), are presented in Table 2. A remarkable presence of CaO as well as an important calcination loss were observed. This fact may give evidence of an incomplete attack of the sample with hydrochloric acid in the conditions employed, which leaves calcium carbonate undissolved in the binding fraction.

Table 2
Chemical analysis of the insoluble residue obtained after hydrochloric attack at room temperature

Sample	Loss[a] (%)	SiO_2[b] (%)	CaO (%)	MgO (%)	R_2O_3[c] (%)	SO_4^{2-} (%)	Na_2O (%)	K_2O (%)
1	5.37	80.48	1.95	0.98	10.11	0.30	0.78	0.15
2	6.84	76.01	5.58	1.01	10.08	0.31	0.67	0.43
3	8.28	73.74	6.74	0.70	10.80	0.28	0.73	1.01
4	7.95	81.33	1.38	0.98	8.22	0.22	0.34	0.22
5	6.93	81.11	1.89	0.99	8.24	0.36	0.30	0.18
6	7.16	75.13	5.02	0.96	10.79	0.25	0.51	0.18
7	5.01	81.22	1.43	1.02	10.37	0.77	0.55	0.17

Sodium carbonate - borax alkaline flux.

Percentages related to the sample of dry insoluble residue.

[a] Calcination loss at 975–1000°C.

[b] Total silica in the sample.

[c] R_2O_3 referred to % Fe, Al, and Ti oxides.

In addition, as was stated in previous studies [6,11], the attack with HCl (1:5) at room temperature is not useful for plaster mortars and lime-plaster mortars because an important fraction of the calcium sulphate phases remains undissolved. These facts are evidence of the need for establishing new experimental conditions for the attack.

A previous study [9] concluded that the attack of the sample must be carried out using very diluted HCl to increase the solubility of the compounds and to limit the formation of colloidal silica. In fact, acid concentrations in the range of 20–25% are frequently used in specialized investigations. In this matter, lower concentrations (1:9, for example) do not provide an acid with enough medium to achieve a complete dissolution, especially considering that the length of the attack must be reduced as well. On the other hand, the use of higher concentrations of acid (1:1, for example) do not guarantee that colloidal silica is not formed. In this investigation, it was considered that the use of HCl (1:5) fulfills the requirements related to acid concentration.

Regarding temperature, the aforementioned considerations suggest the convenience of a hot attack with HCl (1:5) for no more than half an hour in order to avoid excessively long processes for an approximate analysis. Therefore, a method to attack the mortars for separating the aggregate and the binder was proposed: attack with HCl (1:5), digestion in boiling water bath for 30 min, and subsequent mechanical stirring of the resulting suspension for 5 min.

Tables 3 and 4 summarize the results of the chemical analysis of the soluble fraction and the insoluble residue resulting from the attack of the samples using the method proposed. Table 5 presents the percentage of insoluble residue after the cold and hot attacks of the different samples.

It was observed that CaO is not present in the residue as a macrochemical component; this fact gives evidence of a complete dissolution of $CaCO_3$ in the sample. This is not evidenced when the treatment is carried out at room temperature. In addition, a decrease in the calcination loss was observed and confirms the dissolution of calcium carbonate.

Table 3
Chemical analysis of the soluble fraction hot hydrochloric acid attack

Sample	SiO_2[a] (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)
1	0.50	32.67	2.71	4.34	0.66	0.035	0.098
2	0.57	37.20	2.23	3.23	0.56	0.037	0.062
3	0.71	35.42	3.24	3.21	0.75	0.045	0.052
4	0.55	36.90	2.40	2.98	0.60	0.151	0.138
5	0.62	38.41	2.28	2.86	0.70	0.114	0.191
6	0.89	36.65	0.96	3.46	0.79	0.048	0.125
7	0.37	31.23	1.70	6.92	0.69	0.031	0.095

Percentages related to original dry mortar.

[a] Acid-soluble silica.

Table 4
Chemical analysis of the insoluble residue obtained after hot hydrochloric acid attack

Sample	Loss[a] (%)	SiO_2[b] (%)	CaO (%)	MgO (%)	R_2O_3[c] (5)	SO_3 (%)	Na_2O (%)	K_2O (%)
1	1.91	85.78	–	1.19	8.79	0.57	1.09	1.29
2	3.31	84.31	–	2.02	9.11	0.61	0.60	0.27
3	5.34	82.57	–	0.81	9.98	0.40	0.65	1.20
4	2.80	85.19	–	1.84	8.05	0.66	0.72	0.61
5	2.73	85.66	–	1.58	8.13	0.64	0.70	0.56
6	4.21	83.27	–	1.37	8.85	0.56	0.89	0.85
7	2.00	88.16	–	1.26	7.01	0.72	0.47	0.73

Sodium carbonate - borax alkaline flux.
Percentages related to the sample of dry insoluble residue.
[a] Calcination loss at 975–1000°C.
[b] Total silica in the sample.
[c] R_2O_3 refers to % Fe, Al, and Ti oxides.

The comparison of the values of the components present in the soluble fraction obtained using hot and cold attacks was carried out using the Wilcoxon test because it is a nonparametric test (that is, chosen when the total number of samples is lower than 10, or when the previous normality test results significant) and it allows comparison of two dependent samples.

There are significant differences ($p = 0.018$) in the determinations of CaO (it experiences a 0.4–1.8% increase in most of the samples analyzed by the hot method). The cold method seems to be unable to solubilize calcium carbonate completely, as was seen in the analysis of the insoluble residue (Table 6).

Taking into account all the facts mentioned above, it is possible that the cold method fails to solubilize the binding fraction completely, and leaves part of it in the insoluble residue. This hypothesis is reinforced with the significant differences observed in the contents of Fe and Al ($p = 0.018$ and $p = 0.0176$, respectively) that correspond partly to the impurities of the binding fraction and also to hydraulic silicates that could not be dissolved after the treatment at room temperature. The results obtained with the 12 samples randomly selected (with the aim of comparing and validating the results of the representative samples) present a complete correspondence, with the exception of the differences in Na_2O (in the limit of the statistical significance) and K_2O, which does not have a clear explanation until now (Table 6).

Table 5
Results of percentage of insoluble residue in the samples after the attacks with cold and hot HCl

	Sample						
	1	2	3	4	5	6	7
IR (%) cold attack	39.69	27.93	36.45	26.03	26.10	32.68	46.71
IR (%) hot attack	35.31	26.26	25.72	21.89	19.89	27.97	45.94

Percentages related to original dry mortar.

Table 6
Results of the statistical comparison of the soluble fraction cold and hot attacks representative and randomly selected samples (Wilcoxon test)

	Representative samples		Randomly selected samples	
Variable	Associate probability	Statistical significance	Associate probability	Statistical significance
Soluble SiO_2	0.4982	n.s.	0.0871	n.s.
CaO	0.0180	*	0.0019	**
MgO	0.7353	n.s.	0.4445	n.s.
Fe_2O_3	0.0180	*	0.0001	***
Al_2O_3	0.0176	*	0.0001	***
Na_2O	0.9325	n.s.	0.0461	*
K_2O	0.1747	n.s.	0.0024	*

n.s. = no significance.
Statistical significance: * $p < 0.05$ (significant differences), ** $p < 0.01$ (very significant differences), *** $p < 0.001$ (highly significant differences).

However, it could be possible that the hot method was so drastic that it dissolved part of the aggregate fraction, but this does not seem probable due to the short length of the attack. In principle, a reaction time limited to half an hour would avoid the decomposition of clayey sands. Regarding this matter, the solubilization of Fe and Al oxides has already been revealed in the literature as a problem of cold attacks. Some studies have established a reaction time of 16 h with HCl to ensure the dissolution of these oxides [9,11].

To clarify this situation, the results of the global macrochemical analysis of the components in the samples (Table 7) were compared in cold and hot attacks with HCl. For this purpose, the value of total silica obtained in the complete analysis was compared with that of the insoluble residue obtained in both hot and cold acid attacks (Table 8). The comparison was performed using the Friedman test (nonparametric test for three or more samples with two criteria without repetition) and the two-by-two comparisons were carried out using the Wilcoxon test. In general, the attack with hot diluted acid proposed is neither as drastic as the complete analysis nor as mild as that carried out in cold acid, which does not dissolve the sample completely.

Table 7
Complete chemical analysis of the samples

Sample	Loss[a] (%)	SiO_2[b] (%)	CaO (%)	MgO (%)	R_2O_3[c] (%)	SO_4^{2-} (%)	Na_2O (%)	K_2O (%)
1	27.48	29.37	32.98	2.49	5.63	0.81	0.28	0.55
2	32.27	22.18	37.56	2.49	4.79	0.63	0.26	0.47
3	31.11	24.95	35.96	3.28	4.17	0.52	0.31	0.53
4	34.50	19.75	36.90	3.48	3.98	0.69	0.28	0.45
5	34.01	19.11	38.42	4.08	3.55	0.65	0.17	0.42
6	30.43	23.66	37.42	0.98	5.95	0.78	0.19	0.59
7	23.35	39.13	26.34	2.12	7.23	0.82	0.22	0.66

Sodium carbonate - borax alkaline flux.
Percentages related to original dry mortar.
[a] Calcination loss at 975–1000°C.
[b] Total silica in the sample.
[c] R_2O_3 refers to % Fe, Al, and Ti oxides.

Table 8
Results of the statistical comparison of the samples cold and hot hydrochloric attacks and alkaline flux analysis

	Cold-hot-alkaline flux analysis comparison (Friedman's test)		Hot-alkaline flux analysis (Wilcoxon's test)		Cold-alkaline flux analysis (Wilcoxon's test)	
Variable	Associate probability	Statistical significance	Associate probability	Statistical significance	Associate probability	Statistical significance
SiO_2	0.0009	***	0.0180	*	0.0180	*
CaO	0.0131	*	0.3454	n.s.	0.2367	n.s.
MgO	0.1801	n.s.	0.0630	n.s.	0.1763	n.s.
R_2O_3	0.0009	***	0.0180	*	0.0180	*
Na_2O	0.0038	***	0.0180	*	0.0178	*
K_2O	0.0021	***	0.0180	*	0.0180	*

n.s. = no significance.
Statistical significance: * $p < 0.05$ (significant differences), ** $p < 0.01$ (very significant differences), *** $p < 0.001$ (highly significant differences).

1. The first parameter that leads to this conclusion is the insoluble residue. The higher values were observed with the cold treatment, followed by those of the hot treatment, and the lowest were found in the complete analysis (total silica). All the two-by-two comparisons of the treatments give rise to significant differences ($p = 0.018$ in all cases). This may indicate that the hot attack is not drastic enough to attack the aggregate fraction because the value obtained is significantly different from the value of total silica in the complete analysis (the insoluble residue was expected to be silica such as α-quartz, nonhydraulic silicates, and clays) [11,13–15]. It implies that this treatment does not dissolve those components of the aggregate that are more susceptible of being attacked than α-quartz (nonhydraulic silicates and clays). As mentioned previously, the significant differences with respect to the cold attack show that the last does not dissolve the binding fraction.
2. The results obtained in the comparison of R_2O_3 point out similar considerations. The two-by-two comparisons of the R_2O_3 values indicate significant differences ($p= 0.018$ in all cases). The highest values correspond to the complete analysis (including nonhydraulic silicates and clays) followed by the hot treatment. Finally, the lowest value corresponds to the cold attack. Therefore, the aforementioned explanation can be also applied in this case.
3. The existence of significant differences ($p = 0.018$ each case) in the contents of sodium and potassium between the complete analysis and the attack with hot HCl supports the hypothesis that there is no significant attack to the aggregate fraction. Na and K are also included as cations within the lattices of nonhydraulic silicates and clays.

The study of the compositions of the insoluble residue obtained by both cold and hot acid attacks also allows establishment of some considerations. The results were compared using Wilcoxon's test and they are shown in Table 9.

1. It has already been pointed out that CaO disappears as a macrochemical component of the insoluble residue after the hot attack. The significant differences observed in the calcination loss and CaO allow evidence of and quantification of an incomplete attack of calcium carbonate with cold HCl during half an hour.
2. With regard to the values obtained for MgO, sulphates, alkalines, and silica present in the insoluble residue, which are higher in hot attacks, it seems that the method employed has no influence on them (as was also observed in the soluble fraction). The significant differences observed ($p = 0.018$) can be due to an increase in percentage terms caused by the adjustment of the rest of variables due to the loss of CaO. Probably the method has no influence on the dissolution processes of these components present in the insoluble residue.
3. It must be pointed out that in spite of these variations in percentages, a significant decrease ($p = 0.018$) of R_2O_3 content in the insoluble residue was detected after a hot attack. This means that a significant part (related to the binding fraction and hydraulic silicates) passed to the soluble fraction.

The insoluble residue resulting from both attacks was analyzed by X-ray diffractometry. The results obtained were compared with data from the ASTM powder diffraction file. Nonhydraulic silicates that exhibit diffraction peaks were studied and no differences were found in types or quantities of mica

Table 9
Results of the statistical comparison of the insoluble residue cold and hot attacks representative samples

Variable	Associate probability	Statistical significance	Cold-hot tendency
Calcination loss	0.0180	*	↓
SiO_2	0.0180	*	↑
CaO	0.0180	*	↓
MgO	0.0180	*	↑
R_2O_3	0.0180	*	↓
SO_3	0.0280	*	↑
Na_2O	0.1747	n.s.	↑
K_2O	0.0280	*	↑

n.s. = no significance.
Statistical significance: * $p < 0.05$ (significant differences).

derivatives and others silicates [muscovite, $(K,Na)(Al,Mg,Fe)_2(Si_{8,1}Al_{0,9})O_{10}(OH)_2$; anorthite, $CaAl_2Si_2O_8$; albite, $NaAlSi_3O_8$; glassy feldspar, $Na_{0,61}K_{0,39}\ AlSi_3O_8$; augite, $(Ca,Mg,Fe)SiO_3$; oligoclase, $0,83NaAlSi_3O_8\ 0,16CaAl_2Si_2O_8$; parawollastonite, $CaSiO_3$; amphiboles, and others]. Slight variations were detected in clays of the smectite group and also in kaolinites $(Al_2(OH)_4Si_2O_5)$. Tobermorite (hydraulic silicate $Ca_5(Si_60_{18}H_2) \cdot 8H_2O$) was not found within the insoluble residue of the attacks.

The fact that nonhydraulic silicates do not experience alterations also confirms that there is no significant alteration in the aggregate fraction. If this attack had taken place, these compounds present in the aggregate would have passed to solution.

3. Conclusions

After a comparative analysis of the method for the attack of mortars with diluted (1:5) HCl both in cold and hot conditions for use in a rapid analysis of restoration with the aim of dissolving the binder, it was found that the hot attack (digestion in boiling water bath for 30 min and subsequent mechanical stirring of the resulting suspension for 5 min) was more effective than the attack at room temperature for dissolving the binding fraction. There was no evidence of any attack on the aggregate fraction with the hot method.

Significant variations in the contents of Fe and Al oxides were observed. These oxides can be partially associated to the binding fraction and also to certain hydraulic silicates that are not dissolved in a cold attack. The hot attack is also valid for a great number of different types of mortars, except for those types that present limestone aggregate, due to the fact that the chemical differentiation with the ligant phase is impossible.

References

[1] A.E. Charola, Study of hydrated cement pastes of aged concretes from Acropolis monuments, Symposium International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, 1981, pp. 207–217.

[2] G. Alessandrini, Gli intonaci nelledilizia storica: Metodologie analitiche per la caratterizzazione chimica e fisica, L'intonaco: storia, cultura e tecnologia, Atti dil Convegno di Studi, Bressanone, L.P.E., Padova, 1985, pp. 147–166.

[3] A.E. Charola, M. Dupas, R.P. Sheryll, G.G. Freund, Characterization of ancient mortars: Chemical and instrumental methods, in: L. Parrini (Ed.), Proceedings of the International Symposium Scientific Methodologies Applied to Works of Art, Florence, Italy, May 1984, Milan: Montedison Progetto Cultura, Arcadia, 1986, pp. 28–33.

[4] F.X. Deloye, Le calcul minéralogique. Application aux monuments anciens, Bull liaison Labo P et Ch 175 (1991) 59–65.

[5] B. Schouenborg, J.E. Lindqvist, M. Sandström, K. Sandin, E. Sidmar, Analysis of old lime plaster and mortar from southern Sweden, SP Swedish National Testing and Research Institute Building Technology SP Report, vol. 34, 1993, pp.1–25.

[6] H. Jedrzejwska, Old mortars in Poland, a new method of investigation, Studies in Conservation 5 (1960) 132–138.

[7] M. Frizot, Mortiers et enduits peints antiques-étude technique et archéologique, Université de Dijon, Centre de Recherches sur les Techniques Gréco-Romains, 1975, pp. 57–137.

[8] F.X. Deloye, G. Maire, M.J. Buisson, Analyse des bétons durcis à partir d'une attaque nitrique, Bull liaison Labo P et Ch 104 (1979) 61–66.

[9] M. Dupas, L'analyse des mortiers et enduits des peintures murales et des bâtiments anciens, Symposium International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, 1981, pp. 281–296.

[10] F.X. Deloye, L'analyse du béton durci. Le béton hydraulique, Presses de l'Ecole Nationale des Ponts et Chaussées, Paris, 1982, pp. 531–541.

[11] F. Puertas, M.T. Blanco-Varela, M. Martínez, F. Acción, G. Alvarez, Methodology of analysis of stones and mortars in monuments, in: D. Rodrigues (Ed.), 7th Congress International on Deterioration and Conservation of Stone, Lisbon, 1992, pp. 763–770.

[12] J.I. Alvarez, A. Martín, P.J. García Casado, Méthodologie employée dans la caractérisation de mortiers de la cathédrale de Pampelune (Espagne), in: J. Riederer (Ed.), 8th Congress International on Deterioration and Conservation of Stone, Berlin, Vol. 3, 1996, pp. 1457–1470.

[13] M. Frizot, L'analyse des mortiers antiques; problèmes et resultats, Mortars, Cements and Grouts used in the Conservation of Historic Buildings, Symposium International Centre for the Study of the Preservation and the Restoration of Cultural Property, Rome, 1981, pp. 331–339.

[14] H.Y. Ghorab, J. Ragai, A. Antar, Surface and bulk properties of ancient egyptian mortars. Part I: X-ray diffraction studies, Cem Concr Res 16 (1986) 813–822.

[15] F. Gutiérrez-Solana, M. Jauregui, R. Bohigas, P. Sarabia, Análisis de morteros medievales de dos castillos de Cantabria/España, Materiales de Construcción 39 (213) (1989) 37–45.