

# METHODOLOGY AND VALIDATION OF A HOT HYDROCHLORIC ACID ATTACK FOR THE CHARACTERIZATION OF ANCIENT MORTARS

J.I. Alvarez, A. Martín, P.J. García Casado, I. Navarro and A. Zornoza  
Department of Chemistry and Soil Science, University of Navarra  
31.080, Pamplona (Spain)

## ABSTRACT

A method for the analysis of the chemical composition of ancient mortars is proposed. The use of the hot hydrochloric acid attack in order 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 have been carried out using X-Ray Diffraction. Statistical methods are employed in order to establish a comparison between the different attacks.

## INTRODUCTION

The investigation of the chemical composition of ancient mortars represents a fundamental aspect in 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 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, which are proposed in the literature, intend to achieve a separation of the binder (and its impurities) and the aggregate (and its impurities) as complete as possible. The conditions for the attack to be used in a rapid approximate analysis to separate the soluble (binding material) and insoluble (aggregate) fractions (with the objective of using it in restoration) must be chosen taking into account the following considerations:

- 1- It is convenient to establish an attack method valid to analyze as many types of mortars as possible (1,2,3,4,5).
- 2- The method should be valid to establish the hydraulic effect of the mortars.

The proposed method allows to analyse lime mortars, gypsum and lime mortars, and gypsum mortars with sand of siliceous nature, but it is unuseful for mortars with

limestone sand. This study has been carried out due to the controversy generated among different authors, specially concerning the attack procedure (6,7,8,9,10,11).

## MATERIALS AND METHODS

The samples of the mortars come from the inside of Pamplona Cathedral (1394-1512), that is of gothic style. Seven representative samples of the different types of mortars identified, corresponding to defined architectural zones, have been 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 have been chosen randomly with the aim of duplicating the comparisons performed.

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

A titration with EDTA (using murexide and nET as indicators) has been used for the analysis of calcium and magnesium in the soluble fraction. The contents of soluble silica, Fe and Al have been determined by atomic emission spectroscopy with inductively coupled plasma (ICP) (Jobin Yvon JY 38S Plus Sequential). When the amounts of Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> 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). The contents of elements after an alkaline fusion of the samples were determined by traditional chemical methods. The mineralogical studies have been carried out using a Siemens D-500 Kristalloflex 810 X ray powder diffractometer.

## RESULTS AND DISCUSSION

The following experimental conditions for the attack of mortars have been extracted from the bibliography (9,11): attack with 1:5 volume ratio HCl (2M), room temperature and mechanical stirring during 30 minutes.

The results of the analysis of the soluble fraction after the attack of the samples in these conditions are summarized in Table I.

TABLE I. CHEMICAL ANALYSIS OF THE SOLUBLE FRACTION. HYDROCHLORIC ACID ATTACK AT ROOM TEMPERATURE

Sample	SiO <sub>2</sub> * (%)	CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
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. \* Acid soluble silica

It can be observed that the percentages of acid soluble  $\text{SiO}_2$ , which indicate 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 II.

A remarkable presence of CaO as well as an important calcination loss have been observed. This fact may evidence an incomplete attack of the sample with hydrochloric acid in the conditions employed, which leaves calcium carbonate undissolved in the binding fraction.

In addition, as it has been 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.

TABLE II. CHEMICAL ANALYSIS OF THE INSOLUBLE RESIDUE OBTAINED AFTER HYDROCHLORIC ACID ATTACK AT ROOM TEMPERATURE (SODIUM CARBONATE-BORAX ALKALINE FLUX).

Sample	Loss* (%)	$\text{SiO}_2$ # (%)	CaO (%)	MgO (%)	$\text{R}_2\text{O}_3$ § (%)	$\text{SO}_4^{2-}$ (%)	$\text{Na}_2\text{O}$ (%)	$\text{K}_2\text{O}$ (%)
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

Percentages related to the sample of dry insoluble residue. \* Calcination loss at 975-1000°C. # Total silica in the sample. §  $\text{R}_2\text{O}_3$  referred to % Fe, Al and Ti oxides.

These facts evidence the need of establishing new experimental conditions for the attack.

A previous study (9) concluded that the attack of the sample must be carried out using very dilute HCl, so as to increase the solubility of the compounds and 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 enough medium to achieve a complete dissolution, specially 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 has been considered that the use of HCl (1:5) fulfils the requirements related to acid concentration.

Regarding temperature, the aforementioned considerations suggest the convenience of a hot attack with HCl (1:5) during 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 has been proposed: attack with

HCl (1:5), digestion in boiling water bath during 30 minutes and subsequent mechanical stirring of the resulting suspension during five minutes.

Tables III and IV 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 V presents the percentage of insoluble residue after the cold and hot attacks of the different samples.

TABLE III. CHEMICAL ANALYSIS OF THE SOLUBLE FRACTION. HOT HYDROCHLORIC ACID ATTACK.

Sample	SiO <sub>2</sub> <sup>*</sup> (%)	CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
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. \* Acid soluble silica

TABLE IV. CHEMICAL ANALYSIS OF THE INSOLUBLE RESIDUE OBTAINED AFTER HOT HYDROCHLORIC ACID ATTACK (SODIUM CARBONATE-BORAX ALKALINE FLUX).

Sample	Loss <sup>*</sup> (%)	SiO <sub>2</sub> <sup>#</sup> (%)	CaO (%)	MgO (%)	R <sub>2</sub> O <sub>3</sub> <sup>§</sup> (%)	SO <sub>3</sub> (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
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

Percentages related to the sample of dry insoluble residue. \* Calcination loss at 975-1000°C. # Total silica in the sample. § R<sub>2</sub>O<sub>3</sub> referred to % Fe, Al and Ti oxides.

TABLE V. 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

It has been observed that CaO is not present in the residue as a macrochemical component, this fact evidence a complete dissolution of CaCO<sub>3</sub> in the sample, this is not evidenced when the treatment is carried out at room temperature. In addition, a decrease in the calcination loss has been observed and it confirms the dissolution of calcium carbonate.

The comparison of the values of the components present in the soluble fraction obtained using hot and cold attacks (Wilcoxon test) allows to establish several considerations:

TABLE V. RESULTS OF THE STATISTICAL COMPARISON OF THE SOLUBLE FRACTION: COLD AND HOT ATTACKS. REPRESENTATIVE AND RANDOMLY SELECTED SAMPLES (WILCOXON TEST).

<i>variable</i>	<b>representative samples</b>		<b>randomly selected samples</b>	
	<i>associate probability</i>	<i>statistical significance</i>	<i>associate probability</i>	<i>statistical significance</i>
soluble SiO <sub>2</sub>	0.4982	n.s.	0.0871	n.s.
CaO	0.0180	*	0.0019	**
MgO	0.7353	n.s.	0.4445	n.s.
Fe <sub>2</sub> O <sub>3</sub>	0.0180	*	0.0001	***
Al <sub>2</sub> O <sub>3</sub>	0.0176	*	0.0001	***
Na <sub>2</sub> O	0.9325	n.s.	0.0461	*
K <sub>2</sub> O	0.1747	n.s.	0.0024	*

n.s.: no significance

There are significant differences ( $p=0.018$ ) in the determinations of CaO (it experience a 2-2.5% increase in most of the samples analyzed by the hot method). The cold method seems to be unable to solubilize calcium carbonate completely, as it has been evidenced in the analysis of the insoluble residue.

Taking into account all the above mentioned, it can be possible that the cold method fails to solubilize the binding fraction completely and it 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 which could not be dissolved after the treatment at room temperature. The results obtained with the 12 samples randomly selected present a complete correspondence, with the exception of the differences in Na<sub>2</sub>O (in the limit of the statistical significance) and K<sub>2</sub>O, which does not have a clear explanation up to now.

However, it could be possible that the hot method was so drastic that it dissolved part of the aggregate fraction, but it 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 as a problem of cold attacks in the bibliography. Some

studies have established a reaction time of 16 hours with HCl to ensure the dissolution of these oxides (9,11).

In order to clarify this situation, the results of the global macrochemical analysis of the components in the samples have been compared in cold and hot attacks with HCl. For this purpose, the value of total silica obtained in the complete analysis has been compared with that of the insoluble residue obtained in both hot and cold acid attacks. (Table VII). The comparison has been performed using the Friedman test and the two by two comparisons have been 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 VI. COMPLETE CHEMICAL ANALYSIS OF THE SAMPLES (SODIUM CARBONATE-BORAX ALKALINE FLUX).

Sample	Loss* (%)	SiO <sub>2</sub> <sup>#</sup> (%)	CaO (%)	MgO (%)	R <sub>2</sub> O <sub>3</sub> <sup>§</sup> (%)	SO <sub>4</sub> <sup>2-</sup> (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)
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	29.78	38.36	24.63	1.98	4.81	0.30	0.15	0.47
7	23.35	39.13	26.34	2.12	7.23	0.82	0.22	0.66

\* Calcination loss at 975-1000°C. # Total silica in the sample. § R<sub>2</sub>O<sub>3</sub> referred to % Fe, Al and Ti oxides.

TABLE VII. RESULTS OF THE STATISTICAL COMPARISON OF THE SAMPLES: COLD AND HOT HYDROCHLORIC ATTACKS AND ALKALINE FLUX ANALYSIS.

variable	cold-hot-alkaline flux analysis comparison (Friedman's test)		hot-alkaline flux analysis (Wilcoxon's test)		cold-alkaline flux analysis (Wilcoxon's test)	
	associate probability	statistical significance	associate probability	statistical significance	associate probability	statistical significance
SiO <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	0.0009	***	0.0180	*	0.0180	*
Na <sub>2</sub> O	0.0038	***	0.0180	*	0.0178	*
K <sub>2</sub> O	0.0021	***	0.0180	*	0.0180	*

n.s.: no significance

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  $\alpha$ -quartz, non-hydraulic silicates and clays) (11,13,14,15), it implies that this treatment does not dissolve those components of the aggregate that are more susceptible of being attacked than  $\alpha$ -quartz, these are non-hydraulic silicates and clays. As it was said before, the significant differences with respect to the cold attack show that the last does not dissolve the binding fraction.

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 ( $p=0.0018$  in all cases). The highest values correspond to the complete analysis (it includes non-hydraulic silicates and clays) followed by the hot treatment and finally, the lowest value corresponds to the cold attack. Therefore, the aforementioned explanation can be also applied in this case.

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 non-hydraulic silicates and clays.

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

TABLE VIII. RESULTS OF THE STATISTICAL COMPARISON OF THE INSOLUBLE RESIDUE: COLD AND HOT ATTACKS. REPRESENTATIVE SAMPLES.

<i>variable</i>	<i>associate probability</i>	<i>statistical significance</i>	<i>cold-hot tendency</i>
Calcination loss	0.0180	*	↓
SiO <sub>2</sub>	0.0180	*	↑
CaO	0.0180	*	↓
MgO	0.0180	*	↑
R <sub>2</sub> O <sub>3</sub>	0.0180	*	↓
SO <sub>3</sub>	0.0280	*	↑
Na <sub>2</sub> O	0.1747	n.s.	↑
K <sub>2</sub> O	0.0280	*	↑

n.s.: no significance

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 to evidence and quantify an incomplete attack of calcium carbonate with cold HCl during half an hour.

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 it was also observed in the soluble fraction). The significant differences observed ( $p=0.0018$ ) can be due to an increase, in percentage terms, caused by the adjustment of the rest of variables due to the loss of CaO and, probably, the method has no influence on the dissolution processes of these components present in the insoluble residue.

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 has been detected after a hot attack. This means that a significant part (related to the binding fraction and hydraulic silicates) has passed to the soluble fraction.

The insoluble residue resulting from both attacks has been analyzed by X-Ray diffractometry. The results obtained were compared with data from the ASTM powder diffraction file. Non-hydraulic silicates that exhibit diffraction peaks have been studied and no differences were found in types or quantities of mica 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...). Slight variations have been detected in clays of the smectite group and also in kaolinites  $(Al_2(OH)_4Si_2O_5)$ . Tobermorite (hydraulic silicate  $Ca_5(Si_6O_{18}H_2).8H_2O$ ) was not found within the insoluble residue of the attacks.

The fact that non-hydraulic 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.

## CONCLUSIONS

After a comparative analysis of the method for the attack of mortars with diluted (1:5) HCl both in cold and hot conditions in order to use it in a rapid analysis for restoration with the aim of dissolving the binder, it was found that the hot attack (digestion in boiling water bath during 30 minutes and subsequent mechanical stirring of the resulting suspension during five minutes) is more effective than the attack at room temperature for dissolving the binding fraction. The possibility of an attack to the aggregate fraction with the hot method can be dismissed.

Significant variations in the contents of Fe and Al oxides have been 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.



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