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The mortar of the "Leaning Tower" of Pisa: the product of a medieval technique for preparing high-strength mortars

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Abstract: Thirty mortar samples from the "Leaning Tower" of Pisa were examined. The specimens include mortars from both the first (1173-1178) and second (1272-1278) stages of Tower's construction. The mineralogical, petrographical, chemical and physical data collected on the bulk mortar and its binder show that the famous "Leaning Tower" of Pisa was built through the constant use of a high-quality hydraulic mortar (average compressive strength about 16 N/mm^2; average binder SiO_2 content about 29 %) as the binding agent for the "infill" masonry. Although a great deal of variability exists in the values of each measured property, even amongst samples from the same stage of construction, the averaged values for the foundations and the above-ground structures erected during the two distinct construction stages are highly uniform. The most conspicuous differences lie in the sand content and granulometry, which are respectively greatest and coarsest in the foundation mortars. Chemical and mineralogical data suggest that the Tower mortar was prepared by mixing slaked lime, obtained from an almost pure limestone, with sand from Arno and Serchio Rivers alluvium and a diatomaceous earth, probably quarried at Mt. Amiata, about 180 km to the south of Pisa. It is estimated that the construction of the Tower from the foundations to the top of the 7th storey (the belfry, added to the main structure only around 1365, is not considered here) required the use of about 1400 tons of slaked lime (assuming 60% water content), 1350 tons of sand and 400 tons of diatomite.

Key-words: "Leaning Tower of Pisa", mortar, binder, lumps, hydraulic character, formulation procedure.

1. Introduction

The "Leaning Tower" of Pisa is a medieval eight-storey structure (total height: 58.36 m), made up of a hollow cylinder (external diameter: 15.5 m; height: 47.24 m), surrounded by 6 loggias (from the 2nd to the 7th storey) and topped by the belfry (= 8th storey; external diameter 12.7 m; height: 7.21 m). It rests on a ring-shaped foundation with an external diameter of 19.58 m and a height of 3.91 m. The masonry structure was constructed using the "infill" technique: two stone walls facing a concrete core made of stone fragments, gravel and sand, cemented with a lime mortar. The construction of the Tower began in 1173 and progressed steadily until about the middle of the 4th storey; in 1178 the work was suspended, to be resumed only a century later, in 1272. This second stage ended in 1278, at the top of the 7th storey. Only between 1360 and 1370 was the belfry finally added to the Tower. Full details on the historical, architectural and structural features of the monument, as well as the make up and mechanical properties of the subsoil is provided in the Report of Minister of Public Works (Ministero Lavori Pubblici, 1971).

In 1990 growing concern over the possibility of an almost instantaneous structural collapse of the Tower compelled the Italian Government to set up the "International Committee for Safeguarding the Leaning Tower of Pisa". This Committee began its works by promoting a number of multidisciplinary studies in the fields of art history and restoration, structural and geotechnical engineering and so forth. In particular, the Committee deemed investigations of the masonry structure's

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Table 1. Studied samples. The alphanumeric identifier of each sample contains the following data: the original identification mark assigned to the core, slash, the year it was bored, hyphen, the position of the sample in the core.

n	mark	H(m)	L(m)	φ(°)
	Second construction stage (1272-78)			
1	6/65-5	46.90	6.10	155
2	6bis/65-11	45.36	5.25	335
3	4/65-12	32.53	5.36	3
4	5/65-22	32.03	5.81	3
5	8/65-6	27.72	7.48	0
	First building stage (1173-78) Above ground structures			
6	3/65-8	21.30	4.85	183
7	3B/85-1	13.78	4.77	0
8	3C/85-1	13.78	4.77	265
9	2/65-6	8.41	4.47	183
10	1/65-6	7.95	4.57	3
11	1A/85-1	0.84	5.85	104
12	1A/85-2	0.84	4.52	104
13	1B/85-1	0.84	6.13	3
14	1B/85-2	0.84	4.22	3
15	1C/85-1	0.84	4.54	266
16	1C/85-2	0.84	4.32	266
	Foundations			
17	7/65-2b	-0.94	8.00	355
18	7/65-4	-1.14	7.97	355
19	12/95-1	-1.44	4.05	165
20	AF8/85-1	-1.89	6.33	12
21	16/95-1	-2.09	5.73	225
22	AF8/85-2	-2.15	5.74	12
23	1/95-1	-2.21	5.84	0
24	5/95-1	-2.21	5.85	60
25	15/95-2	-2.29	6.06	210
26	23/95-1	-2.79	7.55	330
27	7/95-1	-2.81	7.39	90
28	20/95-1	-2.83	7.66	285
29	13BIS/95-1	-3.08	8.10	180
30	AF8/85-3	-3.33	3.09	12

H and L: distances from the top of the foundations and from the central axis of the Tower. φ: azimuth measured counterclockwise from the north.

materials as an absolute prerequisite to understanding the monument's "state of health" and properly managing its definitive stabilization, reinforcement and restoration. Within the framework of such studies, the Department of Earth Sciences of the University of Pisa was entrusted with a comprehensive characterization of the Tower masonry's concrete. The present article refers to obtained results, focused particularly on assessing the chemical, mineralogical and physical parameters of the mortar, identifying the techniques and the raw materials employed in its preparation and determining the sources from which these materials were drawn.

2. Studied samples

Twenty-four cores, bored through both the Tower's infill masonry and its foundations, were available and 30 samples (Table 1) were selected. The cores are made up of stone fragments cemented by an unaltered, white to off-white coloured mortar. The adhesion between mortar and stone fragments is fairly good. The mortar's texture is heterogeneous due to the presence of subspherical, almost sand free, snow-white lumps (up to 10 % by volume; diameter from 0.5 to 5 mm). The mortar was laid uniformly; shrinkage cracks are rare and small. All selected samples present similar macroscopic features with the exception of no. 1, which is light and has a very low aggregate content, and no. 18, which is hard and heavy, with a bluish-grey tint. The average mortar content results to be 32.4 % by volume (Lezzerini, 1997), as assessed on the nine cores of the "/65" series.

The study was also extended to some samples representative of the raw materials presumed to have been employed in the mortar's preparation.

3. Experimental and data processing

Details on experimental procedures and data processing are given in the Appendix. The data collected are presented herein as mean values with relative variability ranges computed on five sample groups. The first group (I) includes all the samples except 1 and 18. Groups II, III and IV consist, respectively, of 4 samples from the 2nd construction stage (from 2 to 5), 11 samples from the above ground 1st stage (from 6 to 16), and 13 samples from the foundations (from 17 to 30, excluding sample 18). Group V includes 6 samples from cores 1A/85, 1B/85, and 1C/85 (from 11 to 16). Since it is believed that construction was carried out through the successive addition of courses corresponding to the thickness of one facing stone, Group V mortars, bored at the same level, must be considered as coming from the same period of construction. The data for the largely

Table 2. Simplified modal compositions of the aggregate. Average values and variation ranges.

	Sample groups					Sample	
	I	II	III	IV	V	1	18
Quartz	45.17	45.05	48.70	42.22	47.07	38.12	39.62
	36.1 – 54.3	38.1 – 54.3	43.1 – 52.0	36.1 – 52.1	43.1 – 51.7		
Feldspars	22.05	24.31	23.51	20.12	25.41	20.94	18.85
	16.0 – 31.5	16.5 – 31.5	18.4 – 31.4	16.0 – 26.8	21.0 – 31.4		
Calcite	11.91	10.76	9.79	14.06	9.81	15.16	15.75
	7.7 – 21.7	8.1 – 15.2	7.7 – 14.2	8.2 – 21.7	7.7 – 13.1		
Others	20.87	19.88	18.00	23.60	17.71	25.78	25.78
	11.6 – 28.5	11.6 – 25.8	13.6 – 23.4	18.6 – 28.5	14.5 – 22.9		

Group I: all the samples excluded 1 and 18. Group II: samples from 2 to 5
Group III: samples from 6 to 16. Group IV:samples from 17 to 30, 18 excluded
Group V: samples from 11 to 16

anomalous samples no. 1 and 18 are reported separately.

The original measurements on all the samples can be viewed at the Internet site: http://www.dst.unipi.it/min

4. Results and discussion

4.1. Mineralogical and petrographical data

The aggregate grains have medium to medium-high sphericity, sub-angular to sub-rounded shape and smooth surface morphology, sometimes with slight corrosion. In order of decreasing abundance, they are: mono- or polycrystalline quartz; feldspars (oligoclase prevailing over K-feldspar); lithic fragments with carbonate and siliceous sedimentary rocks prevailing on minor amounts of igneous (acid volcanites and ophiolites) and metamorphic rocks (marble and phyllites); calcite; phyllosilicates; heavy minerals (garnet, epidote, titanite, tourmaline, zircon). No residue of natural or artificial pozzolanic materials was observed neither by scanning electron microscopy.

Table 2 reports the modal composition (volume percentages) of the aggregate as determined by thin-section study. Both the single carbonate grains and carbonate rock fragments are grouped in the "Calcite" class. The fineness modulus is given in Table 6. The aggregate composition, expressed as quartz (including chert), feldspar and lithic fragments (including carbonates), is shown in Fig. 1. The classification fields of Tucker (1981) permit classifying the aggregates as intermediate between lithic and arkosic sands. The fineness modulus varies widely. The average value appears to increase from the Tower's top to its foundations.

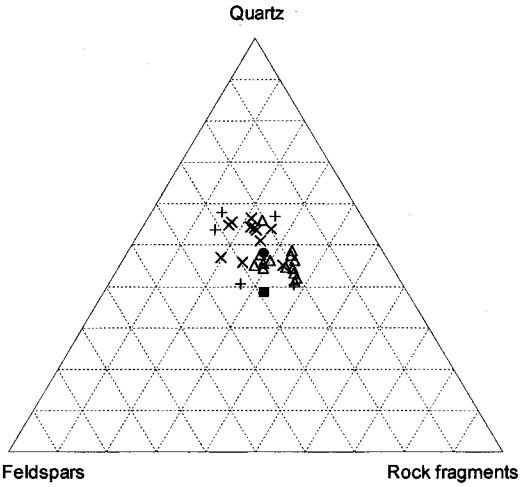

Fig. 1. Aggregate modal composition. + samples from 1 to 5; × samples from 6 to 16; blank triangle = samples from 17 to 30; filled circles = Arno River sand; filled squares = Serchio River sand.

Table 3. Chemical composition (wt.%) and aggregate content (X_a) of bulk mortar samples. Average values and variation ranges.

	Sample groups					Sample	
	I	II	III	IV	V	1	18
H_2O^+	3.09 2.1 – 4.2	3.66 2.8 – 4.2	2.70 2.1 – 3.9	3.24 2.1 – 4.1	2.91 2.3 – 3.9	5.50	4.84
CO_2	11.22 6.5 – 19.3	15.70 10.6 – 19.3	11.34 8.7 – 13.9	9.74 6.5 – 15.2	11.56 9.8 – 13.9	17.00	10.91
Na_2O	0.92 0.4 – 1.8	0.60 0.4 – 1.02	1.06 0.6 – 1.8	0.91 0.7 – 1.1	0.92 0.6 – 1.2	0.23	0.65
MgO	1.58 1.3 – 2.0	1.52 1.3 – 2.0	1.53 1.3 – 1.8	1.64 1.4 – 1.9	1.45 1.3 – 1.7	2.20	1.72
Al_2O_3	6.45 4.8 – 8.2	5.86 4.8 – 6.9	7.00 5.7 – 8.2	6.17 5.6 – 6.8	7.45 6.4 – 8.2	6.23	5.25
SiO_2	52.84 37.1 – 61.8	45.34 37.1 – 57.6	52.97 44.5 – 61.8	55.03 44.9 – 61.5	50.94 44.5 – 54.4	39.53	38.74
SO_3	0.33 0.06 – 0.69	0.34 0.31 – 0.38	0.31 0.21 – 0.63	0.34 0.06 – 0.69	0.29 0.21 – 0.35	0.36	0.44
K_2O	1.30 0.9 – 1.7	1.05 0.9 – 1.3	1.40 1.1 – 1.7	1.30 1.2 – 1.4	1.39 1.1 – 1.7	0.84	0.85
CaO	19.81 12.7 – 30.5	23.71 16.0 – 30.5	19.28 12.7 – 26.6	19.06 14.6 – 24.4	20.73 16.8 – 26.6	25.57	33.51
Fe_2O_3	2.10 1.5 – 2.8	1.84 1.5 – 2.4	2.05 1.8 – 2.4	2.22 1.9 – 2.8	2.00 1.8 – 2.2	2.18	2.67
SiO_2 + CaO	72.64 66.0 – 77.2	69.04 66.0 – 73.6	72.25 70.7 – 74.5	74.08 68.9 – 77.2	71.67 70.7 – 72.8	65.10	72.25
CaO excess	5.53 1.6 – 9.7	3.73 2.0 – 6.0	4.84 1.6 – 9.3	6.66 2.9 – 9.7	6.02 2.7 – 9.3	3.93	19.63
X_a (x 100)	59.06 23.5 – 76.8	46.95 23.5 – 73.1	56.91 39.8 – 72.0	64.60 44.7 – 76.8	53.57 39.8 – 72.0	28.70	35.20

The binder shows a non-uniform texture due to the presence of lumps, which in thin section appear as patches devoid of aggregate grains. Both intergranular binder and lumps consist of a finely (from micro- to crypto-) crystallized carbonate matrix sometimes exhibiting aggregate polarization. Only in a small number of lumps may the calcite crystals attain dimensions of 10 μm. XRPD analysis of the lumps reveals calcite to be the dominant constituent, with minor amounts of aragonite and vaterite and, sometimes, traces of gypsum and dolomite. Tobermorite traces have been detected in some lumps from foundations. These can be explained as likely due to contamination from cement injections carried out on the first half of this century (Ministero Lavori Pubblici, 1971).

4.2. Chemical data

Table 3 reports the mortar's chemical composition; minor components such as P_2O_5 (average content 0.05%), TiO_2 (0.21 %) and MnO (0.10 %) have been omitted. The essential chemical features of mortars are as follows:

Table 4. Average SEM chemical analyses of the intergranular binder and lumps and calculated average chemical compositions of binder and aggregate.

	SEM microanalysis data						Computed data		
	Intergranular binder (n = 17)			Lumps (n = 17)			Binder (n = 28)		Aggregate (n = 28)
	Aver. (wt.%)	$(\sigma_1)_j$	$(\sigma_2)_j$	Aver. (wt.%)	$(\sigma_1)_j$	$(\sigma_2)_j$	Aver. (wt.%)	$(\sigma_1)_j$	Aver. (wt.%)
H_2O^+	---			---			7.30	2.76	0.50
CO_2	---			---			18.63	6.62	5.39
Na_2O	0.39	0.38	0.24	0.35	0.61	0.14	0.30	0.26	1.37
MgO	0.90	0.39	0.41	0.98	0.74	0.32	0.75	0.38	2.19
Al_2O_3	5.44	0.92	0.85	5.56	1.70	0.55	3.98	0.88	8.28
SiO_2	39.61	7.46	5.86	39.78	12.80	2.76	28.77	7.27	69.70
K_2O	0.46	0.35	0.16	0.79	0.30	0.13	0.35	0.22	2.04
CaO	51.98	7.68	6.57	51.80	14.66	3.06	38.21	3.71	6.85
Fe_2O_3	0.79	0.39	0.39	0.38	0.29	0.17	0.68	0.28	3.16
Alk / Al	0.210			0.199			0.220		0.539
Alk / FM	0.696			0.747			0.632		0.934
Al / Si	0.162			0.164			0.163		0.140

n = number of samples; Alk = molar (Na + K); Al = molar Al; FM = molar (Fe + Mg); Si = molar Si

- SiO_2 and CaO are the most abundant components, they are inversely correlated and their sum exhibits only small variations. The average value of CaO diminish from the Tower's top to its foundations, whereas that of SiO_2 increase. Samples no. 1 and 18 exhibit anomalous amounts of the above components;
- the CaO/CO_2 weight ratio consistently exceeds that of pure $CaCO_3$. The CaO excess (second-last line in Table 3) increases from top to foundations and it is anomalously high in sample 18 (19.63%);
- the H_2O^+ content of mortars (average value 3.09 %) is too high to be explained by the value assumed for the aggregate (0.5 %). Hence, the greater part of water comes from the binder;
- the SO_3 content is generally low in all samples (<0.35 %). This component is probably present in the mortar as gypsum formed by the percolation and infiltration into the infill of polluted rainwater containing sulphuric acid (Camuffo, 1999).

A total of 133 SEM analyses were carried out on the intergranular binder of all 30 samples, and 62 analyses on the lumps from 17 samples. From the data obtained, no substantial chemical variation results from top to foundation. Table 4 reports the average values obtained on the seventeen samples for which both binder (84) and lumps analyses are available (lacking samples: no. 1, 5, 7, 10, 13, 14, 16, 17, 18, 20, 25, 28, 30). The average concentrations (columns 2 and 5) show that the intergranular binder and lumps have nearly the same composition, except for the Fe_2O_3 content, which is lower in lumps than in the intergranular binder. Since the mobility of iron in a basic environment is very low, the higher iron content of the intergranular binder is probably due to contamination by iron hydroxides coming from the aggregate.

The standard deviation values $(\sigma)_{i,j}$, computed for each sample (i) and chemical component (j), are higher than expected from instrumental errors, suggesting that the binder and lumps are somewhat inhomogeneous within each sample. The standard deviation values $(\sigma_1)_j$, calculated, for each chemical component, over the entire dataset, reveal that the composition of both intergranular binder and lumps vary from sample to sample. The average values $(\sigma_2)_j$ of the standard deviations $(\sigma)_{i,j}$ are smaller than the $(\sigma_1)_j$ values suggesting greater infra-sample homogeneity.

The last three columns in Table 4 show the average composition of binder and aggregate, for Group I samples, calculated through solution of system (1) (see Appendix) (last line of Table 3 reports the X_a values).

Table 5. Computed normative analyses of the intergranular binder and simplified chemical composition of its amorphous phase.

Samples	Normative analysis				Composition (wt.%) of the amorphous phase				
	Calcite	Magnesite	Gypsum	Amorphous Phase	H_2O^+	Al_2O_3	SiO_2	CaO	Fe_2O_3
Group I	40.48 5.9 – 63.4	1.43 0.1 – 3.1	1.89 0.3 – 4.0	56.19 34.1 – 88.8	12.78 6.6 – 23.0	7.39 5.3 – 10.9	52.56 37.8 – 69.8	25.94 10.6 – 40.5	1.33 0.3 – 4.0
1	45.61	1.74	1.10	51.55	14.23	11.66	60.24	12.61	1.26
18	26.46	2.26	1.46	69.82	9.98	7.87	32.92	45.92	3.31

4.3. Mineralogy and chemistry of the binder

The chemical data highlight that the Tower's mortar binder is very variable and presents hydraulic features, *i.e.* high silica contents with minor quantities of alumina and ferric iron. XRPD analyses, however, reveal only the presence of calcite, with minor amounts of aragonite, vaterite and, sometimes, traces of gypsum and dolomite, suggesting that the binder must be in large part made up of an amorphous silicate phase.

The amounts and the chemical composition of the non-carbonate amorphous phase have been obtained by computing the binder normative analyses under the assumptions that all Mg is present as magnesite and all SO_3 as gypsum (mortar SO_3 has been attributed entirely to the binder). The chemical compositions of this phase, recomputed to 100 % after deduction of minor components (Na_2O and K_2O), are reported in Table 5 and plotted, as molecular percentages, in the triangle diagram CaO – H_2O – (Si + Al + Fe) of Fig. 2, where the variability fields of C-S-H (I) and C-S-H (II) compounds (Taylor, 1972) are also provided. The binder's non-carbonate amorphous phase appears to be richer in hydraulic components than the C-S-H compounds. Using the C-S-H notation (with S = Si + Al + Fe molar percentages), the composition of this phase results to be 0.34-1.10 : 1 : 0.34-1.56, with a mean composition of 0.48 : 1 : 0.74. Sample 18, contaminated by cement, shows the lowest S content and plots in the C-S-H (I) field.

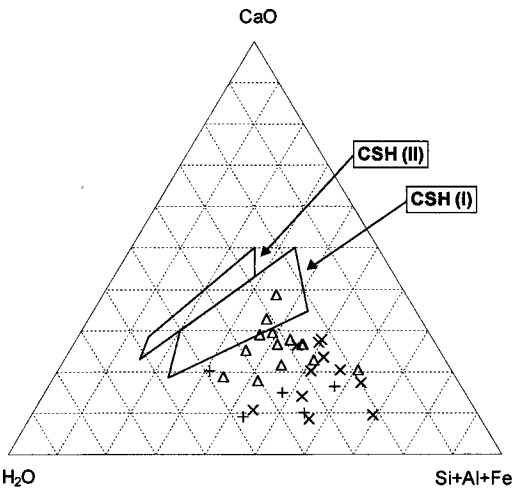

Fig. 2. Chemical composition, expressed as molar percentages, of the binder amorphous phase. CSH (I) and CSH (II): compositional variation fields of C-S-H compounds (from Taylor, 1972); + samples from 1 to 5; × samples from 6 to 16; blank triangles = samples from 17 to 30.

The mineralogical and chemical data reveal that the binder can be described as a mixture of crystalline carbonates (essentially calcite) and a C-S-H like amorphous phase in widely varying proportions: from about 1:15 (sample 26) to about 2:1 (sample 2).

4.4. Physical properties

The measured and calculated values of the physical properties of mortars and their binders are reported in Table 6. The mean mortar bulk density (γ_m) increases slightly from top to foundations, in agreement with the increase of aggregate content. The relation $|\gamma_m = 0.0104$ (aggregate volume %) + 1.122| explains about 60% of the observed variation on 28 samples. Sample 1 and 18 have largely anomalous γ_m values.

Table 6. Physical properties of mortar and its binder. Average values and variation ranges.

	Sample groups I	II	III	IV	V	Samples 1	18
			MORTAR				
γ_m (g/cm^3)	1.61 1.48 – 1.80	1.53 1.48 – 1.55	1.60 1.49 – 1.80	1.64 1.54 – 1.71	1.57 1.49 – 1.66	1.09	2.19
G_m (g/cm^3)	2.619 2.58 – 2.66	2.610 2.58 – 2.63	2.615 2.60 – 2.63	2.626 2.60 – 2.66	2.615 2.60 – 2.63	2.56	2.72
W_w (wt.%)	22.13 16.5 – 26.9	24.55 21.3 – 26.9	21.69 16.5 – 26.6	21.77 19.6 – 25.8	23.33 19.6 – 26.6	51.8	7.6
C_c	0.550 0.33 – 0.84	0.650 0.54 – 0.78	0.603 0.36 – 0.84	0.460 0.33 – 0.80	0.674 0.36 – 0.84	0.98	0.06
P (vol%)	38.6 31.6 – 43.3	41.6 40.7 – 43.3	38.7 31.6 – 43.3	37.6 34.5 – 41.4	40.0 36.2 – 43.3	57.4	19.5
SI (%)	92 79 – 100	90 82 – 96	90 79 – 99	95 87 – 100	91 79 – 99	98	96
σ (N/mm^2)	15.9 8.6 – 23.1	14.7 13.3 – 16.7	16.6 13.1 – 19.2	15.7 8.6 – 23.1	16.6 13.1 – 19.2	10.8	31.3
M_f	2.13 1.37 – 2.62	1.62 1.37 – 1.75	1.97 1.43 – 2.57	2.42 2.18 – 2.62	1.75 1.43 – 2.05	1.43	2.85
			BINDER				
γ_b (g/cm^3)	1.012 0.65 – 1.33	1.080 0.74 – 1.31	1.049 0.82 – 1.33	0.960 1.65 – 1.23	1.065 0.89 – 1.33	0.88	2.01
G_b (g/cm^3)	2.565 2.43 – 2.65	2.569 2.53 – 2.60	2.561 2.51 – 2.60	2.567 2.43 – 2.65	2.571 2.55 – 2.60	2.52	2.75
G_{am} (g/cm^3)	2.452 2.20 – 2.65	2.381 2.33 – 2.47	2.439 2.33 – 2.52	2.485 2.20 – 2.65	2.465 2.42 – 2.52	2.37	2.77

γ = bulk density; G = absolute density; $_m$ = mortar; $_b$ = binder; $_{am}$ = binder amorphous phase
W_w = imbibition capacity; C_c = capillary coefficient; P = porosity; SI = saturation index
σ = uniaxial load strength; M_f = aggregate fineness modulus

The absolute density of the amorphous binder phase (G_{am}) can be computed from the γ_b and G_b values and the weights of the non-carbonate phase as defined in Table 5. Although the values of this parameter are probably affected by a certain degree of uncertainty, they point out that the binder amorphous phase is relatively light, in accordance with the low density of C-S-H phases (from 2.22 to 2.35 g/cm^3; Taylor, 1972).

The capillary water imbibition coefficient (C_c), imbibition capacity (W_w), porosity (P) and saturation index (SI) for the different sample groups vary widely and overlap wholly or partially, revealing substantial physical homogeneity among samples from the two construction stages. The average C_c values decrease from the Tower's top to its foundations, indicating a lower rate of water movement for the samples from this latter

Table 7. Chemical composition of raw materials (wt.%).

	H_2O^+	CO_2	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Alk/Al	Alk/FM	Al/Si
						Limestones						
1	43.11*		0.02	1.26	0.26	0.74	0.09	54.39	0.15	0.501	0.077	0.414
2	41.43*		0.10	0.79	0.76	4.72	0.22	51.94	0.52	0.530	0.303	0.189
3	38.26*		0.08	1.14	2.01	9.00	0.73	47.66	0.94	0.459	0.451	0.263
						Siliceous earths						
4	5.76	0.13	0.38	1.39	14.33	69.56	2.28	0.52	4.69	0.216	0.653	0.242
5	6.86*		1.60	1.42	17.96	60.83	4.81	1.64	4.23	0.437	1.75	0.349
6	7.19	4.07	0.43	2.62	9.39	64.34	1.61	5.18	4.57	0.262	0.395	0.172
						River sands						
7	1.29	5.73	1.64	1.74	7.60	66.89	1.87	10.62	2.27	0.622	1.29	0.134
8	2.59	3.20	1.81	3.62	12.69	62.85	2.47	6.19	3.91	0.446	0.800	0.237

* LOI Alk = molar (Na+K); Al = molar Al; FM = molar (Fe + Mg); Si = molar Si
1 – S.Giuliano marble; 2 – gray cherty limestone; 3 – brown cherty limestone; 4 - Mt. Amiata diatomite; 5 – Montopoli diatomite; 6 – Gabbro siliceous earth; 7 – Arno River sand; 8 – Serchio River sand
1 - Franzini & Lezzerini (1998); 2 and 3 - Franzini & Lezzerini (1999); 4, 5, 6, 7 and 8 - Lezzerini (1997)

portion. Samples 1 and 18 exhibit highly anomalous values for all these parameters.

Although the measured uniaxial compression data are limited by their low accuracy, they appear consistent with the hydraulic nature of the Tower's mortars. The measured values agree with those reported for cylindrical specimens, 4.2 cm in diameter and about 8 cm long, bored through the Tower's concrete (from 41 to 248 kg/mm^2; Ministero Lavori Pubblici, 1971). As for some other properties, sample 18 shows anomalous values.

4.5. Raw materials employed in mortar preparation

The low-grade metamorphic limestones known as "San Giuliano marble" and "Calcare selcifero" (cherty limestone) (Rau & Tongiorgi, 1974) were easily available (Franzini, 1993) at the time of the Tower's construction and represent, most likely, the source materials used to produce the lime. The chemical compositions of "San Giuliano marble" and "Calcare selcifero" (Franzini & Lezzerini, 1999, in press) are reported in Table 7.

"San Giuliano marble" yields an almost pure white slaked lime with good plasticity, whereas the cherty limestone gives rise to a low-plasticity brownish slaked lime. The bright white colour of the Tower's mortar binder leads to the conclusion that the marble was used. The cherty limestone must be ruled out as the parent material for direct production of a hydraulic lime. Apart from the unsuitable properties mentioned above, this material has, in fact, a higher (K+Na)/Al atomic ratio (0.46 to 0.53) than the binder (0.22) and a silica content (from 5 to 9 %) incompatible with the average 29 % silica measured in the binders.

Assuming the marble to be the source of the slaked lime, our data indicate that some material was added to the mortar to increase the binder's silica content. The added material has to react with the slaked lime so to be no longer observable in the binder even at a SEM scale. Franzini *et al.* (1999) have suggested that such material must have contained amorphous hydrated silica (highly soluble in a basic environment) with a high specific surface (high reaction rate). Present study tests proved that opaline-silica frustules of diatoms dissolve in slaked lime in half an hour, leaving no detectable residue, and that a mixture of slaked lime and Mt. Amiata diatomite (20 % by weight) produces a very light, hard material.

Within a reasonable distance from Pisa, three sites are known where suitable materials outcrop: a diatomaceous earth at Montopoli, ~30 km to the west; a diatomaceous earth at Mt. Amiata, ~180 km

to the south; a siliceous earth in the vicinity of Gabbro, ~30 km to the south. The chemical composition of these silica-rich materials is reported in Table 7.

The Montopoli diatomite can be excluded having too high alkali content and too high alkali/Al atomic ratio. Regarding the Mt. Amiata diatomite it is known (Clerici, 1903) that good deposits existed which also produced the renowned coloured earths (sienna, red ochre, *etc.*) widely employed in medieval painting. Today, all the old known diatomite deposits on Mt. Amiata have been wholly exhausted. The sample analysed comes from the S. Fiora deposit, which was exploited until 30 years ago. There are no reports that the Gabbro siliceous earth outcroppings have ever been exploited. The ternary diagram (CaO + MgO) – (H_2O + CO_2) – (SiO_2 + Al_2O_3 + Fe_2O_3) in Fig. 3 shows that the binder compositions of the Tower mortars may be interpreted as a mixture of slaked lime, obtained from San Giuliano marble, and Mt. Amiata diatomite or Gabbro siliceous earth. Obviously, such conclusions cannot exclude the possibility that a diatomite from other farther sites (from Lazio deposits, for example) was employed.

Table 8 reports the modal composition of mortar aggregate and the data from Gandolfi & Paganelli (1975). The Arno sands clearly show a better correspondence to the mortar aggregate. A similar indication is obtained comparing the computed chemical composition of the aggregate (Table 4) with the average composition of current sands from the Arno and Serchio Rivers (Table 7). However, it cannot be excluded that the sand used was a natural mixture of sands carried by both the rivers, as suggested by the contemporaneous presence of chert and serpentine fragments in the mortar. In fact, during the Middle Ages, the geomorphological situation of Pisa was very different from that existing today (Della Rocca *et al.*, 1987) and the Serchio River flowed into the Arno River just west of the city (Tolaini, 1992).

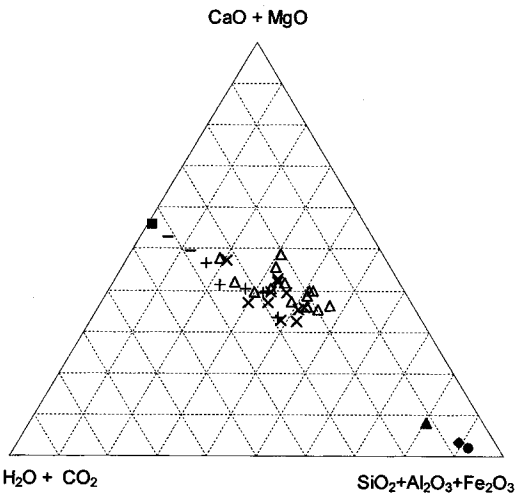

Fig. 3. Chemical compositions of the whole binder compared with those of materials probably employed for its preparation (wt.%). + = samples from 1 to 5; × = samples from 6 to 16; blank triangles = samples from 17 to 30; filled square = San Giuliano marble; – cherty limestone; filled circle = Mt. Amiata diatomite; filled rombus: Montopoli diatomite; filled triangle = Gabbro siliceous earth.

4.6. The quantities of raw materials employed

The sample heterogeneity allows only a rough quantitative estimate of the raw materials used to make the Tower's mortars. The estimate is based

Table 8. Modal compositions of mortar aggregate and Arno and Serchio Rivers sands.

	Quartz	Feldspars	Chert	Serpentine	Carbonate rocks	Other rocks	Other Minerals
Mortar aggregate	44.9	22.0	2.8	2.0	17.7	8.9	1.7
Arno River sand*	44.4	22.2	---	1.2	16.0	8.6	7.6
Serchio River sand*	29.6	22.8	4.2	---	10.2	10.6	22.6

* Recomputed from data reported by Gandolfi and Paganelli (1975) for their samples 9F and 12F.

Table 9. Quantitative estimate of Tower concrete and its components.

	Concrete	Mortar		Binder	
	Vol. (m^3)	Vol. (m^3)	Weight (tons)	whole binder (tons)	silica component (tons)
IV-VII storey	1380	447	684	363	104
I-IV storey	2540	823	1317	571	164
Foundations	780	253	415	143	41
Total	4700	1523	2416	1077	309

on the assumption that the mortars were prepared by mixing Arno and Serchio Rivers sand and slaked lime from San Giuliano marble, with the addition of minor quantities of a diatomaceous earth.

From data on the Tower's architecture (Ministero Lavori Pubblici, 1971), assuming a thickness of 20 cm for the stone facings, the total volume of the infill concrete from the foundations up to the 7th storey has been calculated to be 4700 m^3; 1523 m^3 (32.4 %) are accounted for by the mortar and 3177 m^3 by rock fragments. Using the mortar bulk densities (γ_m values) reported in Table 6 and the X_a values from Table 3, the total volume (m^3) and weight (tons) of mortar and binder employed in the Tower construction have been estimated and are reported in Table 9, together with an estimate of the SiO_2 (tons) necessary to prepare the binder. It appears that to build the infill of the masonry structure from foundations up to the 7th storey, about 3200 m^3 of rock fragments and 1350 tons of Arno and Serchio Rivers sand were employed; about 800 tons of San Giuliano marble were ignited to produce the lime and about 400 tons of diatomite added to the mixture.

5. Conclusions

The data collected in this study show that the construction of the famous "Leaning Tower" of Pisa involved the constant use of high-quality (average compression strength of about 16 N/mm^2) hydraulic mortar as the binding agent for the masonry infill.

The hydraulic characteristics of the binder cannot be "natural", *i.e.* derived from a lime produced by igniting marly limestone. In fact, the binder of the Tower mortar is white in colour, has a very high, variable silica content (from 13% to 41%) and values of the ratios Al_2O_3/SiO_2 and K_2O/Al_2O_3 which are incompatible with clay materials. Nor can they be explained as due to a reaction between lime and added natural or artificial pozzolanic materials whose presence was never observed, either by SEM. We conclude therefore that the hydraulic character of the binder is due to mixture of a slaked lime with a highly siliceous and strongly reactive material characterized by a very high specific surface, like a diatomaceous earth, whose pozzolanic activity has long been well known. Diatom frustules react very rapidly with lime (they dissolve completely in about half an hour) to produce gel materials containing calcium oxide, silica and water, much like the C-S-H cement compounds. The presence of C-S-H like compounds is confirmed by the low computed absolute density of binder (2.565 g/cm^3). Identified sources for the diatomite are the deposits of Mt. Amiata (Grosseto, Italy). However, available data do not permit excluding other Italian regions (Lazio) or even more distant areas.

The aggregate's chemical and mineralogical composition is similar to that of the sands currently found in the Arno River or, more likely, to natural mixtures of Arno and Serchio Rivers sands.

The average mortar characteristics are rather constant throughout the three sample groups corresponding both to the different historical stages of construction (Group II: 1272-1278; Groups III and IV: 1173-1178) and to the monument's different structural units (Group III: above ground structures; Group IV: foundations). On the whole, only minor variation has been observed from the monument's foundations to the top of its 7th storey: on average the aggregate granulometry and hydraulic character diminish, while the binder weight % increases.

Samples 1 and 18, which were to be considered anomalous on the basis of macroscopic features alone, can be explained in terms of their composition and physical properties. The former is a mortar with a large amount of a highly hydraulic binder and very little aggregate content; it is roughly comparable to a mega-lump. Sample 18 is a mortar heavily contaminated by the cement injected into the Tower's foundations during the years 1933-35.

The substantial uniformity of the mortar characteristics in the different sample groups implies that the technique of mortar preparation remained constant for a full century. The finding throughout the samples of homogeneous intergranular binder and lumps indicates that slaked lime and diatomite were very carefully mixed: such a result can be achieved by stirring diatomite in the water to be added to the lime and sand mixture to obtain a workable mortar.

The large variations in composition among the different samples, also observed between samples within the same Group V, suggest that only small quantities of mortar were prepared at a time. In fact, the addition of diatomite reduces the duration of a lime mortar's workability to just a few hours.

The total quantity of mortar in the Tower's infill concrete from foundations to the 7^{th} storey has been estimated to be about 2400 tons: about 1350 tons of sand, 400 tons of diatomite, 1400 tons of slaked lime (with 60 % of water) were employed in its preparation.

It is astonishing that such an unusual building strategy was utilized at the end of the XII century and then taken up again without modification after a full century, producing almost indistinguishable mortars in the two different stages of construction of the "Leaning Tower". Equally astonishing is the fact that, at least from preliminary results (Lezzerini, 1997), no example of this technique, adopted for over a century in Pisa, has been found in Lucca's Middle Ages building, although this last city is not more than twenty kilometers from Pisa.

Appendix

A parallelepiped, a slice, some fragments and a finely ground (under 20 μm) powder were obtained from each sample. Bulk density, water imbibition by capillarity and uniaxial load strength were measured on the parallelepipeds. Thin polished uncovered sections were prepared from the slices for optical microscope study, after which the sections were metallized for SEM analyses. The powder was used for XRF and XRPD measurements and determination of absolute density, L.O.I., CO_2 and SO_3 content. Sandy residue was obtained, by acid attack with dilute HCl (1N), from the fragments.

Aggregate qualitative mineralogical and modal composition was obtained from XRPD data and optical microscopy. Aggregate granulometry was measured by sieving the sandy HCl-insoluble residue through sieves with 2, 1, 0.5, 0.25, 0.125 and 0.063 mm openings and has been expressed through the fineness modulus (M_f) (Head, 1992).

Mortar bulk sample analyses were performed by XRF (Franzini *et al.*, 1975). CO_2 concentration was determined by a gasometric technique (Leone *et al.*, 1988). The difference between the LOI and the CO_2 content was entirely ascribed to H_2O^+. SO_3 contents were derived by weighing the $BaSO_4$ precipitated from the filtered solution obtained during preparation of the HCl-insoluble residue (UNI 8520/11, 1985). The chemical composition of mortar intergranular binder and lumps were derived (EDAX 2.0 program, Edax Intern., 1995) from microanalysis data (X-ray energy dispersive system EDAX PV 9760/77 on a Philips XL30 SEM) after ZAF correction (Mikledust *et al.*, 1978). The chemical composition (including CO_2 and H_2O^+) and weight percentages of both binder and aggregate were derived by combining the SEM data with the modal aggregate composition and XRF bulk sample analyses (Franzini *et al.*, in press). The equation system describing the chemical composition of a mortar:

$$|(C_i)_m = X_a(C_i)_a + X_b(C_i)_b | i = 1,n \qquad (1)$$

where the subscripts refer to mortar (m), aggregate (a) and binder (b), the C_i are the weight percentages of each chemical component, and X_a and X_b (with $X_b = 1 - X_a$) are the weight fractions of aggregate and binder, respectively, was solved by selecting the subset of equations relative to the H_2O, CO_2 and CaO components. $(CaO)_a$ and $(CO_2)_a$ contents were estimated by the modal percentage of carbonates (almost entirely represented by calcite); the small amount of CaO contained in the plagioclases of the aggregate was neglected. The $(H_2O)_a$ content was assumed as 0.5 % for all samples. In fact, the only appreciable hydrated minerals in the aggregate are micas and chlorites, and their total amount is always below 10 %. The

X_a computed values are reported in the last line of Table 3.

Mortar bulk density (γ_m) was computed as the ratio between the weight of the dry sample and its volume, as measured by means of a hydrostatic balance on a water-saturated sample. Mortar absolute density (G_m) was measured by a pycnometer. The binder bulk (γ_b) and absolute (G_b) densities were calculated as $\gamma_b = X_b\gamma_m G_a / (G_a - X_a\gamma_m)$ and $G_b = X_b G_m G_a / (G_a - X_a G_m)$, respectively. The aggregate absolute density (Ga) was derived from aggregate modal data assigning a density of 2.71 g/cm^3 to calcite and an average density of 2.65 g/cm^3 to the other components.

The mortar capillary water imbibition was measured according to NORMAL Recommendations 7/81 (1981) and 11/85 (1985). We also provide the water imbibition capacity at saturation (W_w), expressed as weight % of the sample dry mass, and the capillary coefficient (C_c), *i.e.* the initial angular slope of the curve describing the capillary water uptake (g/cm^2) against the square root of time (hours). Mortar porosity (P) and saturation index (SI) were computed, respectively, as $P = 100\ (1 - \gamma_m/G_m)$ and $SI = 100\ (W_w\gamma_m /P)$.

The uniaxial load strength was measured with a Zwick UTM 148670 gauge on cubic specimens of varying dimensions. Neither the ASTM (cubic samples with two-inch edges - ASTM C170-90, 1990) nor UNI (cubic samples with 7.1 or 10 cm edges - UNI 9724/3, 1990) recommendations were followed; the measures are therefore to be considered as suffering from low accuracy.

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