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Physicochemical and Pozzolanic Properties of the Bricks Used in Certain Historic Buildings in Anatolia

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ABSTRACT:

In this study, the pozzolanic and physicochemical properties of the bricks used in a number of historic buildings built between the second and ninth centuries were investigated. To test this assumption, samples were taken from certain historic buildings dating back to the Roman Empire, Byzantine Empire or Ottoman Empire in order to conduct ICP analyses, chemical analyses and XRD-based mineralogical analyses. To study the pozzolanic properties of the bricks, lime mortars were prepared in accordance with the TS 25 and ASTM C 593-05 standards. These analyses indicate that to some extent all the bricks sampled contain pozzolanic properties. These findings indicate that these bricks were fired at low temperatures in kilns.

Keywords: Historic building, brick, lime mortar, pozzolanic activity, physicochemical and mechanical characterization.

1. INTRODUCTION

Throughout history bricks have always been an important construction and detail material for countless buildings serving a variety of functions [1]. Many historic buildings around the world were either built of bricks or decorated with bricks, or their supplementary walls, arches, domes or vaults were built of bricks, with the result that bricks became an indispensable building material. Furthermore, artificial pozzolan made of crushed brick fragments or powders was used as an additive for lime mortars to develop a high-quality binding material.

When lime is added to clay fired at different temperatures in a kiln, or into crushed brick or roof tile powder which is nothing but fired clay, a hydraulic binding material is the result. Firing powder brick at 600 to 900°C to produce artificial pozzolan and to mix the same with lime, especially fat lime, is a process invented during ancient times in both the East and the West. Called Cocciopesto in the Roman Empire and Horasan in this country and the Far East, this ground and sieved brick or roof tile powder dates back to ancient times. Mortars prepared of this material is also called by the same name. This material is called Homra in Egypt and Surkhi in India [2]. Both the Romans and the Byzantines added either volcanic ash i.e. natural pozzolan or an artificial pozzolan such as crushed bricks and roof tiles directly to mortar. This process produced hydraulic mortars which were used for the building of various structures which still survive today [3-5]. Since the time of the Romans, the use of calcined clays such as pozzolanic mixture for cement has been known. The use of calcined kaolinite clay (metakaolin) as a pozzolanic additive for modern cement and concrete has become very popular in recent years [6].

Clays which are the raw components of soil-based materials such as bricks, roof tiles, etc. are a kind of aluminum silicate system containing Al_2O_3 and SiO_2 compounds, and are generally a mixture of various minerals including quartz and feldspar. When fired at certain temperatures, these clays will develop different

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pozzolanic properties depending on the actual firing temperature and the minerals they contain [7,8]. Such temperatures degrade the structures of the clay's minerals to such an extent that amorphous compounds appear that results in the clay developing pozzolanic properties. When the amorphous crystals forming as a result of this calcination process react with lime, hydrate calcium aluminate silicates will be produced; while kaolin clays will turn into metakaolin under sufficient temperatures. The fact that metakaolin reacts with lime to produce hydrate calcium and alumina silicate ensured it to be considered a good artificial pozzolan [9].

Temperature is a factor that plays a major role in the structure of the hydrate compounds forming as a result of the calcination of clay, and calcination appears to be a very important parameter [10]. Furthermore, the mineral structures of clay also play a decisive role in its pozzolanic activity. Various studies were conducted on the pozzolanic properties developed by clays depending on the calcination temperatures at which they are fired, and various temperature ranges were suggested. Literature shows that the best pozzolanic activity is takes place at 550 to 850^{o}C [5, 6, 11, 12, 13].

For centuries, bricks were manufactured by firing clay at lower temperatures in primitive kilns using low calorie fuels. The low temperatures in question ensure that the bricks develop pozzolanic properties, with reactive structures leading to good surface adhesion to mortar [13]. Therefore, in terms of their mechanical properties this adherence improves the performance of systems such as walls, vaults and arches. On the other hand, crushed or powder bricks with pozzalonic properties ensure that lime-based mortar have hydraulic characteristics and better cohesion.

Although the firing temperatures of bricks are important in terms of the pozzolanic properties they would develop, a study [8], on pozzolanic activities of samples taken from various historic bricks calcined at temperatures from 600 to 900°C found no pozzolanic effect on these before mentioned samples. This finding does not verify the view that bricks fired at low temperatures and used in historical buildings would necessarily have pozzolanic properties. The same study also focused on the pozzolanic properties of kaolin clay and of new bricks fired at a temperature from 650 to 750°C. It was found out that the samples taken from new bricks did not have pozzolanic properties, but kaolin clay had such properties. As a result of these observations, it was concluded that bricks will not have pozzolanic properties unless they are fired at a temperature below 900°C and unless they contain clay minerals in amounts sufficient to develop such properties. Unlike the results obtained from this study, samples taken from some bricks fired at temperatures above 900°C in various European countries were found to have pozzolanic properties [14].

In conclusion, it is understood that firing temperature is a very important factor in terms of the properties of bricks. The brick firing techniques employed in ancient times were developed using empirical information based on time-honored traditions and customs. A scientific explanation of the effect of temperature on the properties of bricks was not attempted until the 1900s.

2. EXPERIMENTAL STUDY AND METHOD

This study examined the pozzolanic properties of samples taken from historical structures built of brick by the Roman, Byzantine and Ottoman between the second and ninth centuries. General information about these structures is given in Table 1.

Of the structures described above, Yoros Castle, Amasra Castle, Kütahya Castle, Ottoman Cistern and Yedikule City Walls were built of a pinkish mortar containing crushed and powder brick as aggregate and artificial pozzolan. The same method was applied for the mill built of brick. Trabzon Castle, Roman Basilica and Ottoman Baths were built of a white-cream mortar not containing crushed or powder brick. Both types of mortar have hydraulic properties. It was assumed that the above mentioned pinkish mortar might owe its hydraulic properties to the pozzolan in question, so that a number of samples were taken from the walls of these buildings to examine their properties.

Table 1. Appearance, parent building and construction period of the sampled historical bricks (in chronological order)

Samples	Color	Texture	Dimensions	Construction Period	Region	The photo of the buildings
BAZ-I BAZ-II (basilica)	red, dark red, dark orange,	Smooth surface, hard, less porous, efflorescence	square, rectangle a=28/33	I-II	Amasra Roman	
KUL-I KUL-II KUL-III	light pink light red light salmon pink-	Smooth form	Square a=25/28 b=25/28	VIII-X	Istanbul Roman Byzantine	
KUT-I KUT-II KUT-III	yellowish white-creamy, light red, dark red	Rough surface, thin in middle, concave, with recesses and protrusions on one surface	square, rectangle a=23/32	VIII-X XIII-XIV	Kutahya Byzantine Ottoman	
AMAS-I AMAS-II (castle)	light red dark orange reddish	Some fine and medium size grain	square a=26/36 b=26/36	IX-XI	Amasra Roman/ Byzantine	
TR-I TR-II (castle)	red brown	One surface smooth, hard texture, porous, rough surfaces	Square a=28/34 b=28/34	X-XII	Trabzon Byzantine	
YOR-I YOR-II (castle)	Dark red Camel hair yellow	One surface semicircular, fine texture, hard, porous	square a=29/38 b=29/38	XIII-XIV	Istanbul Byzantine	
HİS-I HIS-II (castle)	dark salmon, dark red	Smooth surface, some having a shaped surface, porous in the middle, brittle	square a=25/38 b=23/33	XIII-XIV	Istanbul Ottoman	
HAM (bath)	orange, red brown, light red	Smooth form	square a=25/28 b=25/28	XVII	Istanbul Ottoman	
SAR-I SAR-II (cistern)	Light brown, reddish	Less porous, thin in middle, thick edges, textured surfaces	square a= 26/32 b= 26/32	XVII-XVIII	Istanbul Ottoman	
HAR (mill)	Light salmon pink-creamy	Porous, brittle, rough surface, one surface containing 6 inscriptions in Ottoman Turkish, blackish,	rectangle a= 23,5 b= 11,5	XVIII-XIX	Istanbul Ottoman	

2.1. Samples

The samples taken from the above mentioned buildings located in different regions of Turkey (Figure 1) and built in different eras were coded as follows: Ottoman Mill (HAR), Ottoman Baths (HAM), Byzantine Yoros Castle (YOR), Ottoman Anadolu Hisarı Castle (HIS), Roman/Byzantine Amasra Castle (AMAS), Byzantine Trabzon Castle (TR), Roman Basilica (BAZ), Ottoman Cistern (SAR), Kütahya Castle (KUT) and Yedikule City Walls (KUL). These buildings date back to the Roman, Byzantine and Ottoman eras. Three samples taken from Kütahya Castle and Yedikule City Walls, one sample from the Mill, and two samples taken from each of the remaining buildings i.e. total 20 brick samples were used for this study.

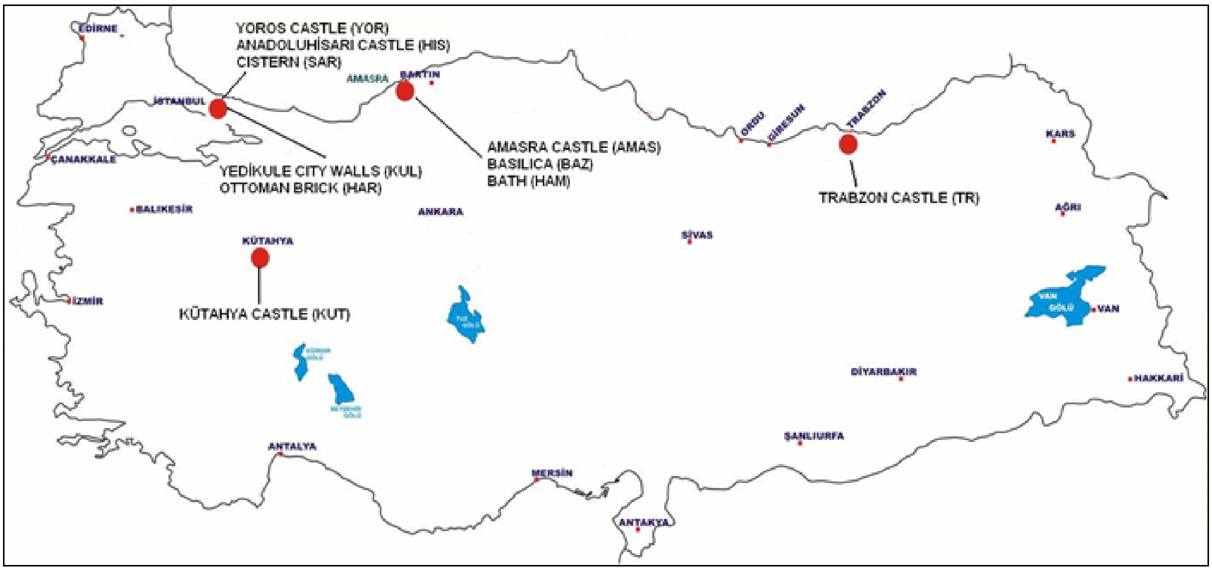

Figure 1. Location of Castels in Turkey

2.2. Experimental methods

A hypothetic-deductive method based on experimental study was employed for this paper. This method is based on a hypothesis promising the explanation or deduction of testable results, and comparing the results with relevant observations or the data obtained from experiments.

The brick samples were categorized into groups, mortar remnants and other foreign substances were cleaned off their surfaces before grinding them into powder form. Granulometric, physicochemical and XRD analyses were conducted on these powder samples. There after 20 lots of total 60 mortar samples containing lime binder were prepared by employing the method described in ASTM C 593-95 [15]and TS 25 [16]standards.

2.2.1. Chemical and physical analyses

Chemical compositions of the ground bricks were analyzed using Inductively Coupled Plasma Emission Spectroscopy ICP-ES (Acme Analytical Labs) after their 0.200 gram 125 micron under-sieve samples were dissolved by means of lithium metaborate ($LiBO_2$) fusion. General chemical contents of the samples were found as metal oxide (%), their other trace elements as element (ppm); results of the analyses conducted on both group of samples are shown in Table 3. Specific gravities of the samples were measured by La Chatelier balloon according to EN 1936 standard [17].

2.2.2. XRD analysis

General mineralogical composition of the powder bricks were found by conducting XRD analysis on 125 micron under-sieve samples using Philips X-Pert Pro X-Ray Diffractometer (XRD). These analyses were conducted on one sample of each building and three samples of Kutahya Castle.

2.2.3. Granulometric analysis of powder bricks

All samples were ground into powder form to meet ASTM C 593-95 [15] and ASTM C 618-03 [18] standards and were passed through standard 250, 125, 90, 63 and 45 micron mesh sieves before conducting granulometric analyses on them.

2.2.4. Mortar mixtures and experiment method

The amounts of the materials comprising the mixtures were measured in accordance with TS 25 standard [16], (Table 2), the mortars were prepared in standard molds 40 x 40 x 160 mm. The binder used for preparing the mortars consisted of 85% CaO and 5% MgO. The mortars were cured in accordance with the ASTM C 593-95 standard. 20 lots of a total of 60 units of lime mortar were produced for this experimental study. After these samples were produced, the molds were covered in accordance with the above mentioned standard, were let to rest for 24 hours, and were cured for 7 days in an autoclave at a regulated temperature of 54 ±2°C. Thereafter the samples were removed from the autoclave, were let to rest for 4 hours at T=23±2°C and RH= 90%, were weighed to measure their unit volume weights, and their ultrasound pulse velocity (UPV) were measured.

Table 2. Proportions of the components of the mortar produced according to the TS 25 Standard.

Materials	Weight (in gram)
Standard sand	1350
Slaked lime $Ca(OH)_2$ *(L)*	150
Pozzolan *(P)*	2x150x ($\delta P/\delta L$)*
Water	0.50 ($L+P$)

*δP= specific density of pozzolan,
δL= specific density of slaked lime

2.2.5. Mechanical tests and UPV Measurements
The mechanical tests were done by the AMSLER Type 6DB7F120 hydraulic press with a capacity of 6-60 kN in 1/4 loading speed. The prismatic samples were applied to flexural strength tests at first. Then on those pieces left out of the flexural strength tests, compressive and tensile splitting strength tests were applied. Compressive and flexural strength tests were done according to the Turkish Standard TS EN 1015-11 [19], while tensile splitting strength tests were done according to the Turkish Standard TS EN 12390-6 [20]. Ultrasound pulse velocity (UPV) measurements of all the mortars were determined according to the Standard EN 14579 [21]. Longitudinal measurements were taken by using PUNDIT (CNS Electronic Ltd.) non-destructive ultrasound equipment (transducer frequency with 54 kHz).

3. EXPERIMENTAL RESULTS and DISCUSSION

Results of analyses applied on samples and stated above shall be evaluated separately under associated headings.

3.1. Grain size distrubition of brick powders

Size distribution ratios and granulometric properties found by means of the granulometric analyses conducted on all the ground brick samples are shown in Figure 2.

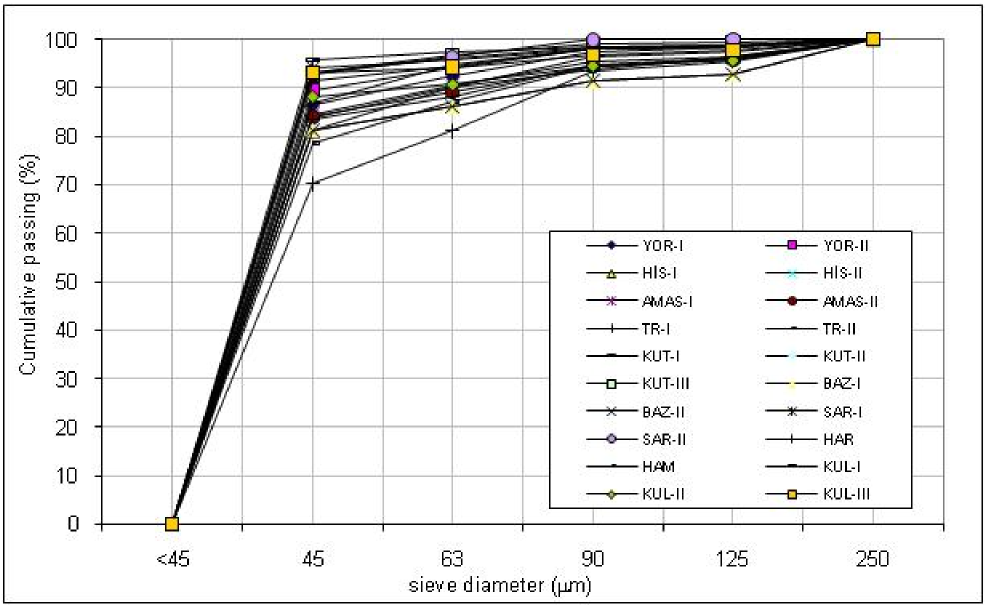

Figure 2. Granulometric distribution of ground brick samples

It is known that in addition to the chemical and physical properties of pozzolan materials, fineness is an important factor for pozzolanic activity. Various physicochemical characteristics influence pozzolanic reactivity such as: the glassy compounds content, the total and active silica content, the grain size distribution and the specific surface area. Granulometric distribution of all pozzolana materials is shown in Fig. 2. It is estimated that max. 34% of material will be retained on the 45μm sieve in ASTM C 618 03 standard, on the 600μm one in ASTM C 593-95 standard this amount will be max. 2% and, 30% of material will be retained on the 75μm sieve. As seen in Fig. 2, all samples provide this condition, and the granulometry curves of the ground brick samples are similar in general.

3.2. Assessment of chemical analysis results

Through ICP analyses, general chemical compositions of all samples were found as oxide (%), other trace elements in their contents were found as element (ppm); results of the analyses are shown in Table 3. Clays calcined in accordance with ASTM C 618-03 formed Class N pozzolans, and this standard requires the total ratio of their content of Al_2O_3, SiO_2 and Fe_2O_3 to be minimum 70%. The results of the analyses performed on the samples indicated that all except for one sample (KUT-III) meet the above mentioned requirement of minimum total content of oxide compounds. The ratio of the total content of these ingredients is 69.97% in the KUT-III sample and at the limit level. Some of the samples (YOR-II, TR-I, KUT-II, KUT-III, BAZIL-II, SAR-I, SAR-II and KULE-I,II,III) contain relatively higher CaO content, a fact indicating that they were made of clays having a high calcium content. Furthermore, loss on ignition of these samples is high. ASTM C 618-03 requires that loss in ignition should be maximum max 10%. Loss on ignition of the SAR-I and KUT-III samples is slightly higher than the above mentioned maximum limit.

For merging of pozzolans with $Ca(OH)_2$, the most important role is played by the reactive SiO_2 and Al_2O_3 compounds. Studies indicate that crystallized SiO_2 does not merge with lime. Therefore, the higher the amorphous silica content i.e. active silica content of a pozzolan, the higher the binding effect thereof. Furthermore, if chemical analysis reveals that the SiO_2 content of a pozzolan is high, that result is considered a significant indicator that the active silica content of that pozzolan might be high enough, but it is not final evidence proving that the material in question has pozzolanic properties [22]. For example, quartz minerals are not active in pozzolanic terms [23] Therefore, mechanical tests need to be conducted to find out whether or not a material have pozzolanic properties. Although all brick samples have oxide compounds high enough for such activity, their pozzolanic properties are different. The mechanical tests prove this conclusion.

Table 3. Chemical and physical analysis of brick powders used in lime paste preparation

samples	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	Cu	Ba	Zn	Ni	Co	Sr	Zr	Ce	Y	Nb	Sc	Ta	LOI	Sum	TOT/C	TOT/S	density
	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	g/	%	%	%	%	g/cm^3
YOR-I	64,51	16,75	8,89	1,49	1,06	0,73	2,65	1,21	0,18	0,27	0,016	165	391	244	80	<20	72	289	118	53	21	20	20	2	99,94	0,11	0,05	2,55
YOR-II	54,29	14,2	7,31	5,28	9,59	1,34	2,03	0,8	0,16	0,12	0,059	334	293	141	327	<20	259	166	45	26	11	18	<20	4,5	99,89	0,91	0,06	2,49
HIS-I	66,65	14,44	6,0	1,76	3,46	2,37	1,98	0,91	0,19	0,09	0,02	87	308	82	52	<20	183	216	65	28	8	16	<20	2	99,96	0,26	<0,02	2,43
HIS-II	63,89	15,01	6,74	1,91	3,52	1,67	2,17	1,01	0,21	0,11	0,023	418	360	171	91	<20	167	247	61	34	15	17	<20	3,5	99,94	0,75	<0,02	2,51
AMAS-I	62,44	15,16	5,62	1,24	3,75	1,98	3,63	0,79	0,12	0,06	0,009	129	435	103	40	<20	192	181	49	20	14	11	<20	5	99,97	0,6	0,09	2,62
AMAS-II	59,85	14,56	7,57	2,96	5,66	1,45	2,62	0,94	0,2	0,12	0,027	378	436	158	124	<20	211	184	65	27	19	17	<20	3,8	99,91	0,7	0,03	2,48
TR-I	60,24	13,11	6,48	2,42	9,15	0,78	1,26	0,92	0,32	0,1	0,032	209	582	107	45	<20	440	200	80	25	17	20	<20	4,9	99,92	0,52	0,03	2,53
TR-II	56,67	13,33	7,98	3,34	6,96	1,27	1,31	0,96	0,48	0,11	0,059	159	680	101	62	<20	479	177	72	24	16	27	<20	7,2	99,9	0,46	0,11	2,47
KUT-I	49,07	19,26	6,39	4,15	7,79	0,62	3,56	0,83	0,13	0,1	0,021	63	648	203	111	<20	186	181	85	29	19	20	<20	7,8	99,89	0,98	0,03	2,52
KUT-II	50,36	16,82	5,79	4,65	9,66	0,81	3,54	0,74	0,15	0,09	0,017	87	612	198	79	<20	176	179	74	29	15	17	<20	7,1	99.90	0.93	0.18	2,46
KUT-III	49,36	15,27	5,34	5,58	8,95	0,69	3,18	0,67	0,14	0,08	0,014	55	546	151	71	<20	173	171	68	27	15	15	<20	10,5	99,88	1,46	0,04	2,36
BAZ-I	59,64	14,67	7,17	3,14	5,73	1,47	2,65	0,93	0,20	0,12	0,03	363	443	155	128	<20	214	176	55	26	15	17	<20	4	99,9	0,76	0,03	2,49
BAZ-II	54,15	13,47	7,68	4,19	8,46	1,71	2,18	0,98	0,17	0,11	0,033	164	325	138	141	<20	249	133	42	22	19	19	<20	6,6	99,9	1,09	0,09	2,54
SAR-I	48,65	14,8	7,32	4,04	10,47	0,94	2,26	0,72	0,15	0,17	0,036	64	434	107	203	<20	382	133	53	26	13	20	<20	10,2	99,92	0,97	<0,02	2,58
SAR-II	49,25	15,53	7,76	4,28	9,18	0,95	2,47	0,75	0,18	0,19	0,035	78	430	113	229	<20	372	123	53	25	11	20	<20	9,2	99,9	0,75	0,1	2,63
HAR	67,65	14,2	6,08	1,77	3,42	2,39	1,97	0,88	0,18	0,09	0,021	83	307	79	55	<20	181	215	71	30	11	15	<20	1,2	99,96	0,12	0,09	2,43
HAM	60,66	16,14	5,25	1,44	3,5	2,07	4,27	0,81	0,16	0,13	0,008	126	723	75	27	<20	218	179	58	22	15	10	<20	5,3	99,94	0,96	<0,02	2,45
KUL-I	57,45	14,13	6,43	3,59	9,19	1,66	2,38	0,73	0,18	0,13	0,042	86	484	94	201	<20	273	154	54	26	12	18	<20	3,8	99,92	0,6	0,05	2,48
KUL-II	53,84	14,29	6,71	3,71	8,53	1,36	2,5	0,71	0,16	0,13	0,038	80	457	97	202	<20	228	144	50	27	13	19	<20	7,8	99,92	1,03	0,04	2,54
KUL-III	49,16	16,46	7,19	3,9	11,81	1,24	2,35	0,74	0,14	0,14	0,035	54	273	92	242	<20	322	132	41	24	12	20	<20	6,6	99,91	1,37	0,03	2,53

3.3. Pozzolanic activity and mechanical analysis

The pozzolanic activity depends on a number of factors, the most significant of which seem to be the chemical and mineralogical composition of the additive, amorphous phase content, the degree of hydration, specific surface area, content of $Ca(OH)_2$ in the paste, the admixture content and water to binder ratio in the material [24]. Values measured by means of the mechanical analysis are shown in Table 4.

Table 4. Mechanical properties of the mortars (for 7 days)

Samples	bulk density (g/cm^3)	UPV (ultrasound pulse velocity) (km/s)	E_d (modulus of elasticity) (kN/mm^2)	R_c (compressive strength) (N/mm^2)	R_f (flexure strength) (N/mm^2)	R_s (splitting tensile strength) (N/mm^2)
YOR-I	1,99	3,03	18,6	5,7	2,4	3,1
YOR-II	1,95	2,78	15,4	4,4	1,9	2,2
HİS-1	1,90	2,84	14,8	4,4	2,2	2,5
HİS-II	1,93	2,93	16,8	4,2	2,2	2,5
AMAS-I	1,97	3,08	19,1	5,5	2,7	3,1
AMAS-II	1,97	3,10	19,3	5,2	2,4	3,0
TR-I	1,95	2,94	17,2	4,9	2,3	2,6
TR-II	1,95	2,83	15,9	4,6	2,0	2,2
KUT-I	1,94	3,12	18,8	6,3	2,9	3,1
KUT-II	1,98	3,30	21,9	7,1	3,2	3,6
KUT-III	1,93	3,06	18,4	4,6	2,2	2,5
BAZ-I	1,95	3,03	18,4	5,4	2,3	2,8
BAZ-II	1,96	3,00	18,2	5,8	2,4	3,3
SAR-I	1,91	2,70	14,2	3,9	1,8	2,0
SAR-II	1,95	2,96	17,4	5,7	3,0	3,2
HAR	1,97	2,81	15,9	3,8	2,1	2,3
HAM	1,96	2,88	16,6	4,2	2,0	2,3
KUL-I	1,95	3,02	18,1	5,2	2,2	2,5
KUL-II	1,96	3,01	18,1	5,0	2,2	2,6
KUL-III	1,97	3,15	19,9	7,0	2,9	3,5

If hydrate lime is mixed with a material having pozzolanic properties, the resulting mortar will be expected to have higher mechanical strength. The mechanical tests conducted for this study indicate that all the samples except for one (SAR-I = 3.9 N/mm^2) have the minimum 4.1 N/mm^2 compressive strength (Rc) value required by ASTM C 593-95 standard. Another brick sampled from the same building (SAR-II= 5.7 N/mm^2) meets the requirement in question. The flexure strength (Rf) limit value of 1.0 N/mm^2 required by TS 25 standard has been met by all the samples (Fig. 3). This fact indicates that the bricks have pozzolanic properties in varies different ratios. It was discovered that different brick sampled from the Cistern has higher pozzolanic activity compared to the sample with a lower pozzolanic activity.(SAR-II= 5.7 N/mm^2). The fact that the lime mortar used in this building with its hydraulic characteristics contained in crushed and powder bricks indicates that the bricks have pozzolanic properties. Results of the mechanical tests indicate that all the mortar samples have pozzolanic properties in different ratios, so that this finding indicates that the powder bricks mostly contain amorphous minerals and that these minerals reacted with lime to produce calcium silicate and calcium alumina hydrates. This latter finding indicates that the bricks were fired at temperatures below 900 to 950^oC' in general. The differences between the pozzolanic activities of the samples arise from the mineral properties of the raw materials used for manufacturing the bricks.

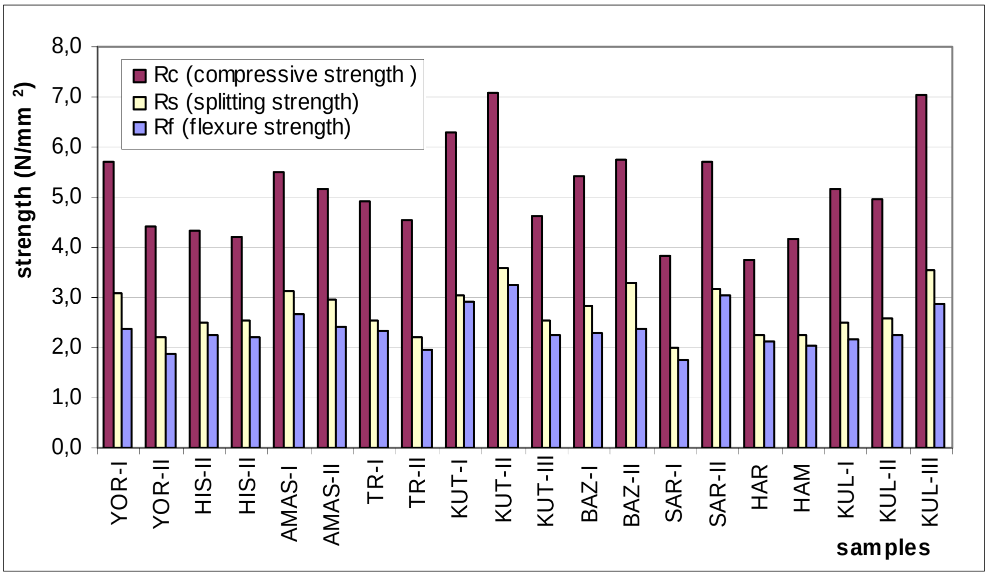

Figure 3. Mechanical properties of the lime mortars produced of powder brick

It is a known fact that one of the important parameters of pozzolanic activity is the chemical composition of raw material. The chemical analyses indicate that the total ratio of the Al_2O_3, SiO_2 and Fe_2O_3 contents of the HAR sample is as high as 87.93%, but its pozzolanic activity is lower (4.6 N/mm²) than those of certain samples having the same contents at lower amounts. It is the same for the YOR-I sample in which the total oxide ratio was measured to be 90.15% and compressive strength was 5.7 N/mm^2. On the second brick (YOR-II) sampled from the same building, compressive strength was measured to be 4.4 N/mm^2. These compounds are at the limit value (70.77%) on the SAR-I sample, and their activity value (3,9 N/mm^2) is similar to that of the HAR sample.

Although the pozzolanic activity and compressive strength values of the mortars produced from the YOR-II, HIS-I, TR-I and KUT-III samples are the same, the total ratios of their respective oxide compounds are different. Furthermore, the total oxide ratio of the KUT-II sample is relatively lower at 72.97%, but its compressive strength is as high as 7.1 N/mm^2; while the total oxide ratio of the HIS-I sample is 87.69%, but its compressive strength is lower at 4.4 N/mm^2. These findings do not indicate that the higher the total oxide content of a brick, the higher the pozzolanic activity thereof. What is important is the level of active compound contents, as the results prove. Furthermore, the types of the clays used for manufacturing the bricks are important too, because bricks manufactured of kaolin clay and calcined at lower temperatures have higher pozzolanic properties [8].

Ultrasound pulse velocity (UPV) and modulus of dynamic elasticity (Ed) of all the mortar samples were measured before conducting the mechanical tests, and relations between these values and pozzolanic activities were examined. UPV of all the samples varies between 2.7 and 3.3 km/s, their dynamic Ed varies between 14.2 and 21.9 kN/mm^2. Samples having high UPV values (for example YOR-I, AMAS-I, KUT-I, KUT-II, SAR-II, BAZ-II and KULE-III) have high pozzolanic activities, and the results of the mechanical tests indicate that the compressive, splitting and flexure strengths of these samples are higher. UPV and mechanical properties of the YOR-II, HIS-I, HAR and SAR-I samples having lower pozzolanic activities are also lower than those of the other samples. This finding indicates that there are good relationships between the UPV and mechanical properties of all the samples and that pozzolanic activity can be estimated by means of non-destructive methods. Small variations between the mechanical properties and the UPV values can be considered normal due to the anisotropic structure of the samples and that pozzolanic development of inner structures depends on different behavior of the mineral structures included in the samples.

3.4. Assesment of XRD analyses

Results of the XRD analyses indicate that all the brick samples are mainly composed of quartz and contains various clay minerals. Table 5 presents the mineralogical composition of the overall fraction of the bricks determined by XRD analysis.

Table 5. Mineralogical composition of the <125 μ fraction by XRD analysis

Samples	Q	A	An	At	H	L	G	M	P	S	I	Le	T	CaO	C	Ha	K	So
YOR-I	+++/+	-	-	-	-	++	-	-	+	-	-	-	-	-	-	-	++/+	-
HİS-II	+++/+	-	-	-	-	-	-	++	-	-	-	-	-	-	-	-	++/+	-
AMAS-I	+++	-	-	-	+	++	-	-	+	++/+	-	-	-	-	-	-	-	-
TR-II	+++	-	-	-	-	-	-	-	++	-	-	-	-	-	-	-	-	±
KUT-I	+++	-	++	-	++/+	-	-	-	-	-	-	-	-	+-	++	+	-	-
KUT-II	+++	++	-	-	±	-	-	-	-	-	-	-	-	-	++/+	-	-	-
KUT-III	+++	-	-	-	-	-	-	-	-	-	++/+	-	-	-	++	-	-	-
BAZ-I	+++/+	-	-	-	-	++/+	+ +	-	-	-	-	-	-	-	-	-	-	-
SAR-II	+++/+	-	-	-	-	-	-	-	-	-	++	-	-	++/+	+	-	++	-
HAM	+++/+	-	++	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HAR	+++	++	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-
KUL-III	+++	++	-	-	-	-	-	-	-	-	-	++/+	+	+	-	-	-	-

+++= high , ++=present, += low, ±= too low, - = undetected

Q: Quartz, A: albite, An: anorthoclas, At: Anortite, H: hematite, L: labradorite, G: Glaucophane, K: Cyanite, M: Microline, P: Pyroxene, S: Sanidine, I: Illite, Le: Lepidolite, T: Tourmaline, CaO: Calcium oxide, C: Calcite, So: Sodium silicate, Ha: Halloysite, O: Orthoferrosillite

The kyanite mineral found in HIS-II sample undergoes transformation above 1000°C and turns into mullite phase at 1200 to 1500°C [25, 26] (Fig. 4a). Furthermore, the fact that this sample contains microcline which is a type of alkali feldspar indicates that the brick was calcined at a temperature not exceeding 950°C, and this range was reached probably due to its low pozzolanic properties. A similar situation is present for the YOR-I sample in which kyanite peaks were found (Fig. 4b). Therefore, it can be assumed that these bricks, which are located in regions close to each other and date back to the Ottoman and Byzantine periods were built of similar raw materials employing similar technologies.

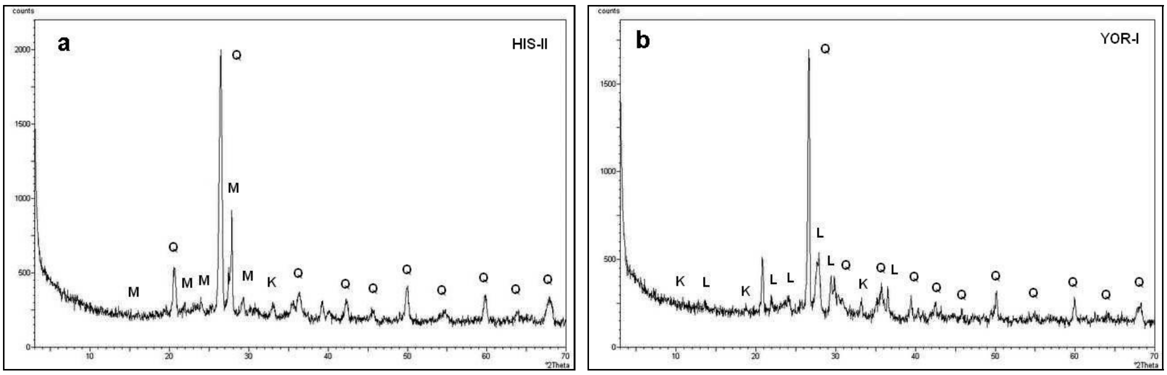

Figure 4. X-ray diffractions of (a) Anadolu Hisarı Castle (HIS) and (b) Yoros Castle (YOR) bricks. *(Q: Quartz, K: Cyanite, M: Microline, L: labradorite)*

The *CaO* and *illite* minerals found in the SAR-II brick might indicate that it was fired at a temperature between 800 and 950°C (Fig. 5a). The *CaO* peaks indicate that the calcite content of the raw material calcified or tended to turn into lime. Calcite starts decarbonizing at <800°C [27] and the structural re-organization is weak around 930°C [28]. Wild et al.[29] reported that X-ray analysis of the clay fired between 600 and 800°C showed substantial clay phase (illite) still remaining. Also, [7] indicated that optimum calcination temperature for illite is 930°C. Illite is present in the KUT-III sample (Fig. 5b), *CaO* mineral is present in the KUT-I sample (Fig. 6a), and the same is true for said samples. Maximum crystallization temperature of *lepidolite* mineral found in the KUL-III sample dating back to the Byzantian period is approximately 1060°C [30]. The presence of *lepidolite*, which is a mineral of the mica group such as muscovite, indicates that its calcination was low (Fig. 6b).

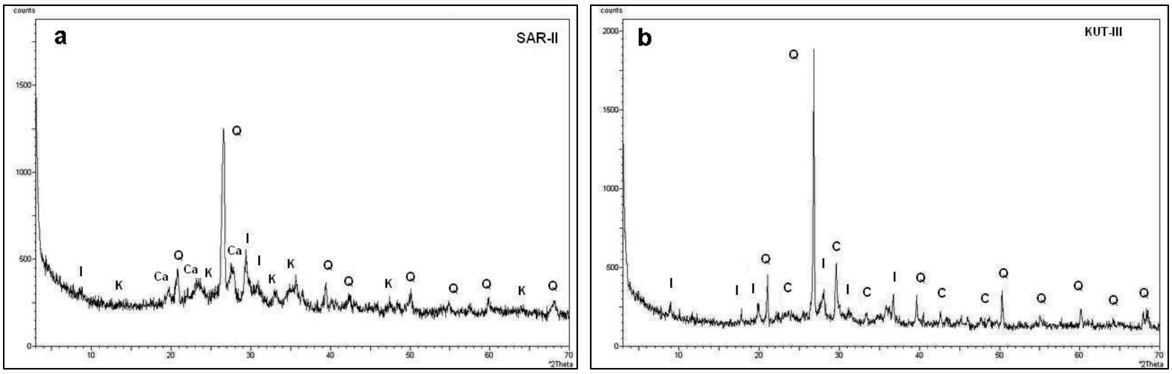

Figure 5. X-ray diffractions of (a) Ottoman Cistern (SAR) and (b) Kütahya Castle (KUT-III) bricks *(Q: Quartz, Ca: Calcium oxide, I: Illite, K: Cyanite, C: Calcite)*

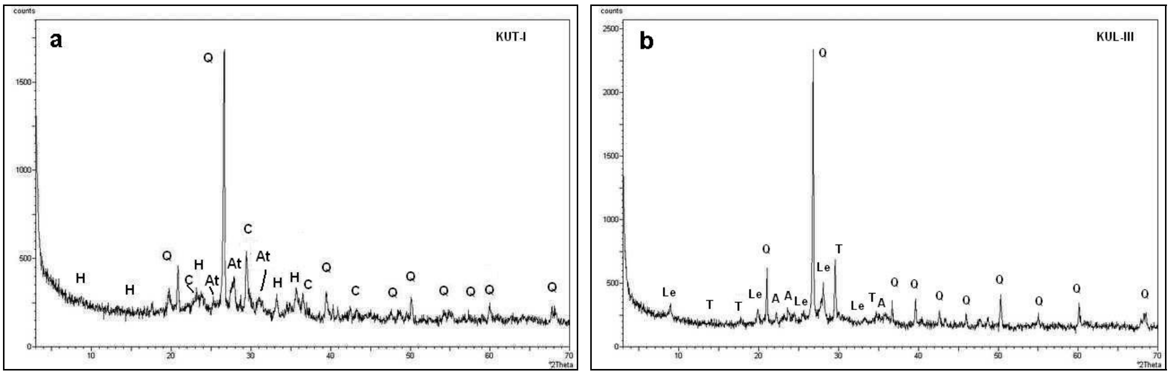

Figure 6. X-ray diffractions of (a) Kütahya Castle (KUT-I) and (b) Yedikule City Wall (KUL-III) bricks *(Q: Quartz, At: Anortite, A: albite, C: Calcite, H: hematite, Le: Lepidolite, T: Tourmaline)*

The feldspars of albite, anortite, anorthoclase, sanidine and microline found in the bricks modify in various ways depending on temperature [31], and melt at high temperatures to act some kind of cement. The albite peaks might indicate that the KUT-II and KUL-III bricks were fired at temperatures below 900^{o}C (Fig. 6b) (Fig. 7a), because albite minerals undergo phase change at temperatures above 900 to 1000^{o}C [28,32], begin crystallizing at 800^{o}C and undergo transformation at higher temperatures (≅1050^{o}C).

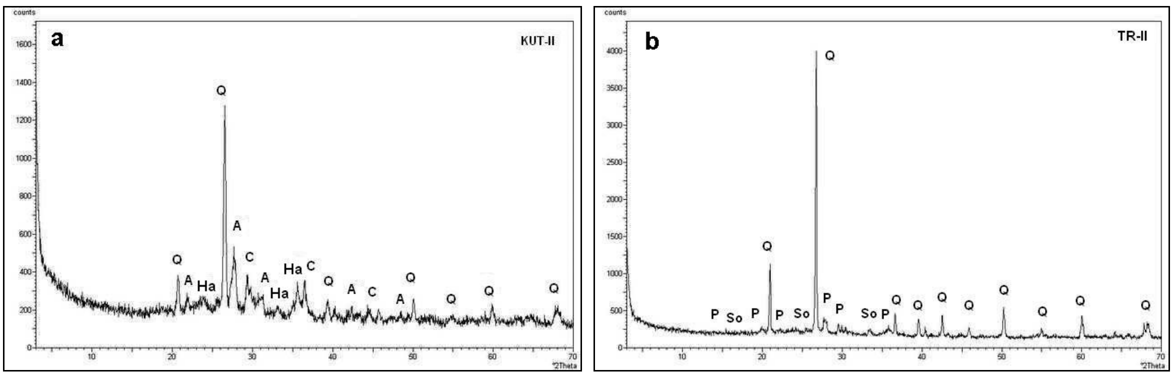

Figure 7. X-ray diffractions of (a) Kütahya Castle (KUT-II) and (b) Trabzon Castle (TR-II) bricks *(Q: Quartz, A: albite, Ha: Halloysite, C: Calcite, P: Pyroxene, So: Sodium silicate)*

The same mineral is present in low level in the HAR brick whose pozzolanic property is lower, and this fact might indicate that it was fired at a relatively higher temperature [33] (Fig. 8a). A study reports that the anortite mineral present in the HAM (Fig. 8b) brick has crystallized at approximately 1200^{o}C [34]. Therefore, it might be suggested that this brick was calcinated at a lower temperature. The same suggestion can also be made for the labradorite feldspar found in the BAZ-I brick sampled from the Roman Basilica (Fig. 9a).

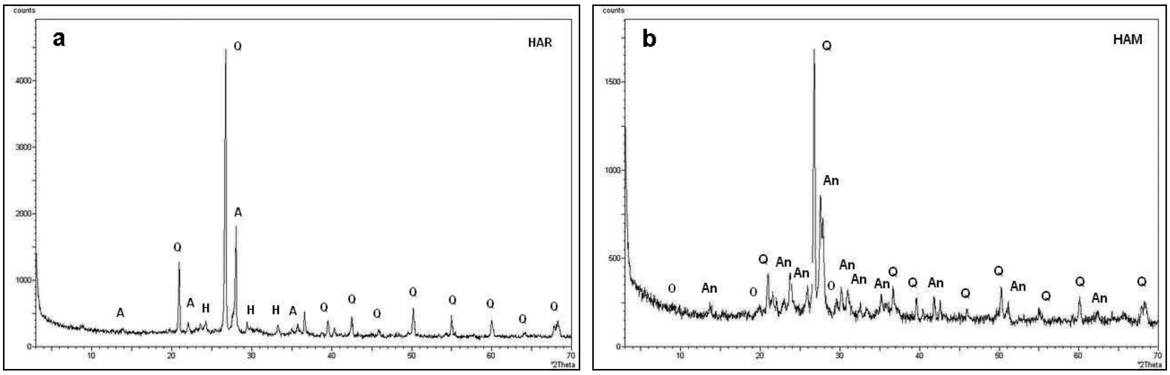

Figure 8. X-ray diffractions of (a) Mill brick (HAR) and (b) Ottoman Bath brick (HAM) *(Q: Quartz, A: albite, An: anorthoclas, L: labradorite, H: hematite, G: Glaucophane, O: Orthoferrosillite)*

The presence of sanidine mineral in the XRD peaks for the AMAS-I brick dating back to the Byzantium/Roman period indicates that it was fired at a temperature above 600°C, and the presence of hematite in the same indicates that this temperature was below 900 to 950°C (Fig. 9b). A study found that the clay component dehydroxylated to metakolin at 550°C and metastable sanidine formed from decomposition of the feldspar at about 600°C and dissolved at about 900°C [35]. The fact that these bricks have higher pozzolanic activity verifies this conclusion. All these feldspars have different pozzolanic properties depending on their mineral structures, and react with binding lime to produce tetracalcium aluminate hydrates [36]. The hematite (Fe_2O_3) peaks of the HAR and KUT-I bricks might suggest that they were fired at 900°C or a slightly higher temperature [37] (Fig. 6a, Fig. 8a). Furthermore, the presence of the halloysite mineral in the KUT-II sample indicates that it was fired at a temperature much below 900°C (Fig. 7a). This before mentioned mineral undergoes phase change above 900°C and turns into γ-alumina and mullite phase at higher temperatures (≅1200°C) [25]. The fact that this brick has higher pozzolanic properties might be related to this phase change.

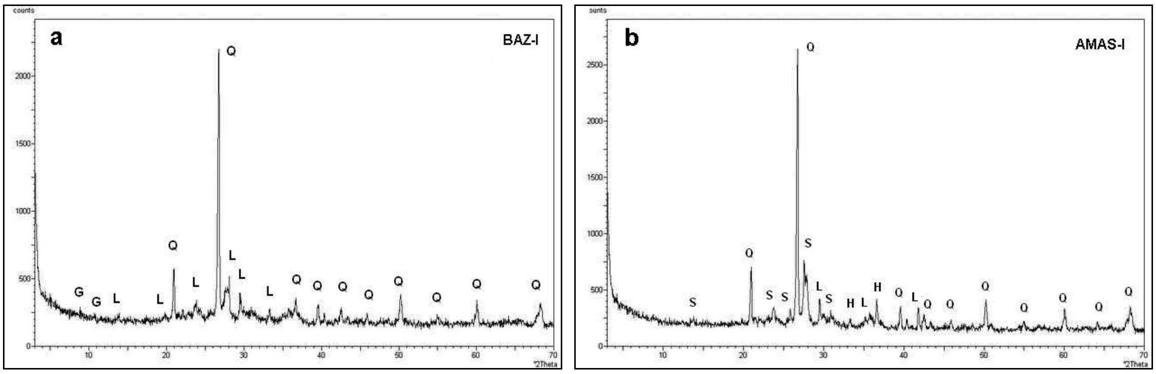

Figure 9. X-ray diffractions of (a) Roman Basilica brick and (b) Roman Amasra Castle brick (AMAS-I). *(Q: Quartz, L: labradorite, , H: hematite G: Glaucophane, S: Sanidine,*

The fact that such stable minerals as spinel, mullite and kristobalite were not found in any of the samples prove that all the bricks studied herein were fired at temperatures not exceeding 950°C and were fired at lower temperatures. One might deduce from this fact that this temperature range is suitable for pozzolanic activity. The fact that all the samples have pozzolanic properties in different ratios is an indicator of such a deduction. If the calcitanion temperature of clay is above 900 to 950°C, such stable minerals as mullite, kristobalite, etc. will be produced and therefore pozzolanic properties will decrease [38,39]. In the light of these data, it might be suggested that the calcinations temperatures of the bricks were relatively different from each other, but close to each other in general. In addition to calculation process, the different mineralogical structures of the raw materials used for producing the brick caused the bricks to develop pozzolanic properties in various ratios.

4. CONCLUSION

The data collected through this experimental study conducted on samples taken from various historic buildings located in Anatolia indicate that the bricks used for building structures in the past had pozzolanic properties in different ratios despite the fact that they were manufactured of different raw materials. This fact does not very much in terms of periods, regions and even buildings and appears as a result of the manufacturing technologies employed. This traditional application technique was employed in similar way in the Roman, Byzantine and Ottoman periods.

The mineralogical composition and calcination process of raw materials influence the pozzolanic properties developed by the bricks. Results of the mechanical analyses indicate that all the brick samples studied herein have pozzolanic properties in various ratios, and these results are supported by the results of the XRD analyses conducted.

The results indicate that all the bricks have pozzolanic properties whether or not the mortars used in the buildings contained brick powder because of the brick manufacturing technologies employed at the time. Because it was observed that all the samples taken from the structures built of mortar containing, or not containing crushed brick have pozzolanic properties. The most important role for the pozzolanic activities of the bricks depending on the firing temperature applied to them is played by the active SiO_2 and Al_2O_3 compounds in clay. Therefore, the higher the active mineral content of clay, the higher the pozzolanic activity of the material.

The relations observed between the ultrasound pulse velocity and modulus of elasticity and the pozzolanic properties indicate that the reactive compounds included in the brick powders reacted chemically with the calcium hydroxide content of the binder to produce calcium-aluminium silicate hydrate, C-S-H, and that this structure caused the mortar to develop a more rigid and more stable inner structure. This process increases the ultrasound pulse velocities and modules of elasticity of the mortar, makes the mortar to have better cohesion, and improves the mortar's mechanical properties.

In conclusion, it might be suggested that brick powder to be added as artificial pozzolan in repair mortars to be used for restoring historic buildings should be fired at low temperatures to ensure them to comply with the original materials, and that raw materials to be used for manufacturing such bricks should contain clay minerals at a sufficient level.

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