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A Study on the Use of "Sweet Plaster" in Traditional Anotolia Houses

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Abstract: Gypsum is predominately used as interior and exterior plaster material especially in the traditional houses of various Central Anatolian towns. Various plaster samples have been collected from traditional houses in the cities of Amasya, Tokat, Çorum and Sivas in Turkey and these samples have been subjected to physical, chemical, X-ray diffraction and thermogravimetric analyses to evaluate the general features and production techniques of the material. The purpose of these analyses is to use the plaster, locally known as "sweet plaster", "sweet lime" and "mortar of cas", depending on the region it is used, in the maintenance and reparation of traditional houses appropriate to their original characteristics, to cherish this tradition under modern conditions, to utilize local resources appropriately within the resource environment and to explain the production techniques of lime material in different cities. The findings of the experiment have revealed that the binding material of roughcast and finish plaster in Çorum and Sivas houses is gypsum and the binding material of plaster in Amasya and Tokat houses is lime.

Key words: Sweet plaster · Sweet lime · Gypsum · Traditional plaster · Characterization

INTRODUCTION

Plaster is one of the important building materials that give us an idea about the construction and material technologies of the period during which they were used because they were produced with traditional methods that differ from region to region with respect to their composition. In Anatolia, plasters used in traditional buildings were usually produced with binding materials such as clay, gypsum and lime. Though generically called clay, gypsum and lime plasters, especially gypsum plasters, these plasters are locally different in terms of their production methods and can be referred to as "sweet plaster," "mortar of caş," or "sweet lime." The word "sweet" refers to the addition of some type of material such as sugar to the mixture. This particular type of plaster is commonly known as "sweet plaster" because it does not hurt the skin upon contact.

Gypsum-based plasters and gypsum implementations are not unique to Anatolia. In the past, it was used in various parts of historical buildings in several parts of the world. In historical buildings, we encounter gypsum either kilned or in the form of natural anhydrite (dissoluble natural dry gypsum) as found in nature. Known as the "Ganges Plaster" in several Asian countries, such as Kazakhstan, Turkmenistan, Uzbekistan and Tajikistan, natural anhydrite plaster is still used today in relatively the same way as it was in the past. In these areas, plaster similar to natural anhydrite is manufactured artificially by firing gypsum stones to 800-850°C in a kiln. Because the material hardens slowly and difficultly, sodium and magnesium are also added to the mixture for solidification. In today's Anatolia, however, gypsum plaster is made of gypsum stones that are usually heated to 130-300°C. However, there is no serious study on natural anhydrite reserves in Turkey [1].

Amasya, Tokat, Çorum, Sivas, Siirt, Ankara-Beypazari, Kayseri, Van and Konya are among the Anatolian cities where gypsum is widely used as an exterior and interior plaster material. In Sivas, Tokat, Çorum, Amasya, Beypazarı, Kayseri and Van, gypsum plaster is called "sweet lime" or "sweet plaster". In some parts of Çorum and in Konya, it is known as "lime mortar with organic fiber" and as "mortar of cas" in Siirt and its surroundings. Known by different names, sweet plaster was traditionally taken from gypsum stone quarries and

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after being heated at the site of manufacture by different methods according to region, it was pulverized. Then, the material was mixed with water to obtain gypsum paste. Additionally, gypsum, as a binding material used in the preparation of roughcasts and finish plasters, was occasionally made by mixing and heating natural gypsum stones that differed by region. In some cities, to increase resistance, some animal and plant fibers, such as goat or horse hair, were added to the mixture.

Today, gypsum is soluble because it is produced by being heated to 120-130°C. For this reason, it is not used as plaster or on the exterior surfaces of buildings for various reasons. However, gypsum plaster has proven to be the most suitable choice of material in traditional buildings, which is evidenced by the fact that these buildings have survived to this day. Therefore, it is crucial to determine the production techniques and general features of this material.

Within the scope of this study, sweet plaster from the cities of Amasya, Tokat, Çorum, Sivas, Siirt, Ankara-Beypazari, Kayseri, Van and Konya was investigated. Among these cities, this particular plaster is more widely used in Sivas, Beypazari, Amasya, Tokat and Çorum with respect to other cities. Due to the similarities in climate and tradition, the study field was determined to include the cities of Sivas, Amasya, Tokat and Çorum.

With respect to the characteristic features of traditional houses in these cities, the method of construction is found to be similar, with wooden framing and mud-brick construction on stone foundation. Field studies have revealed that the mud bricks in some buildings were plastered with a layer of mud plaster measuring a few centimeters thick and containing straw and then roughcast and finish plaster in the form of sweet plaster were applied.

When it comes to the production of sweet plaster, two regionally distinct approaches exist. In Sivas, the binding material of sweet plaster was traditionally made from gypsum stones obtained from local quarries and heated in primitive ovens and boilers. Today, however, local craftsmen who try to maintain this production technique state that in the past, building craftsmen [1], some of whom were Armenians, used to heat the stones in large copper boilers (Figure 1a-b). First, stones from different quarries were broken into small pieces and heated in copper boilers. During this process, it was important to stir the stones in the boiler continuously so that they were heated homogenously. During these empirical and traditional processes, water vapor coming out of the boiler was evaluated as a measure of the heating temperature of the raw material. Throughout the entire heating process, the mixture was continuously stirred and the heating process continued until water vapor no longer appeared.

In Çorum, Amasya and Tokat, to make the gypsum plaster used in sweet plaster, gypsum stones were heated without being pulverized. They were arrayed side by side and on top of each other and heated with the help of wood that circumscribed the pile of stones. Today the same manufacturing technique is still used in these cities. However, because this technique does not allow all of the stones to be heated homogenously, the mixture contains both semi-hydrate and anhydrite gypsum. The findings of an on-site study revealed that gypsum stones were heated to approximately 130-220°C [1].

In Beypazari, which is not studied in this research but where sweet plaster was widely implemented in traditional buildings, the stones are fired in ovens with open tops, a base area of 270x300 cm and three walls that are 60 cm thick; the ovens stand 160 cm high and are circumscribed with hard and fast broken stones (Figure 1 c-d). Because a northerly wind sweeps through this area, the openings of the ovens face north. Before the heating process starts, hard and fast broken stones 25-30 cm high are placed at the center and by the walls of the oven and an iron grill is placed on top of the stones. The space between the iron

Fig. 1: [a] Boiling gypsum stones in boilers in Sivas; [b] taking the heated stones out of the boiler; [c, d] traditional gypsum oven of Beypazari

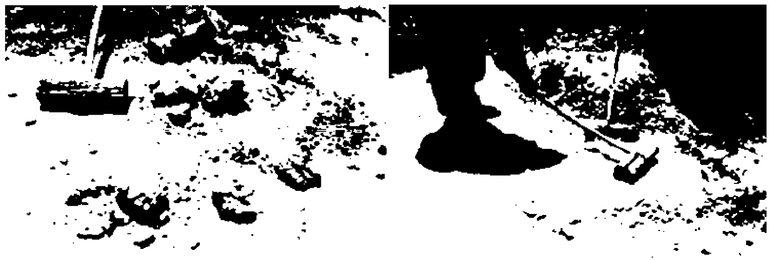

Fig. 2 [a-b]: Pulverizing the heated stones with wooden pestle [2]

grill and the soil base is filled deeply with wood cut from trees in the surrounding area. The stones are placed in the oven one by one from the largest to the smallest. After the heating process, which lasts approximately 10 hours, the oven is left to cool. Then, the stones are taken from the oven and laid on a flat surface. They are first broken into pieces with wooden paddles (Figure 2a-b) and then a tractor drives over the pieces to break them into grain-sized pieces [2].

In the Anatolian regions where gypsum is used in the way described above, the gypsum reserves are also found to be rich. Considering the advantages of gypsum, using this material has benefits both in modern buildings and in the restoration of traditional buildings. Moreover, gypsum is one of the most important materials for sustainable and ecological building projects today. For this reason, considering the climate conditions of the traditional houses studied herein, it is important to determine the techniques used to apply gypsum material, which is difficult to apply along the exterior of buildings and to preserve these traditional buildings today, remaining true to their original characteristics.

MATERIALS AND METHODS

Within the scope of the experimental study, finish plaster and roughcast samples were collected from the exterior surfaces of traditional houses in Çorum (38:27E, 39:14N), Amasya (35:51E, 40:39N), Tokat (36:43E, 40:19N) and Sivas (37:02E, 39:45N). Apart from these samples, gypsum material used in today's Sivas in the production of plaster was also taken as a sample. This material is made of gypsum stones obtained from different quarries. Based on the traditional techniques reported by the elderly masters in the region, gypsum stones from five different quarries are first collected, heated and ground and finally pulverized to produce this particular material. Physical, chemical, X-ray diffraction (XRD) and thermogravimetric (TGA) analyses were performed on the collected samples. Table 1 shows the cities from which the samples were collected and their code numbers.

Table 1: Cities where samples were collected and code numbers

Samples	Sample code
Amasya -1 finish plaster	A1-I
Amasya -2 finish plaster	A2-I
Çorum -1 roughcast	Ç1-K
Çorum -2 finish plaster	Ç1-I
Çorum -2 roughcast	Ç2-K
Tokat -1 finish plaster	T1-I
Tokat -1 roughcast	T1-K
Sivas -1 finish plaster	S1-I
Sivas -1 roughcast	S1-K
Sivas -2 finish plaster	S2-I
Sivas -2 roughcast	S2-K
Sivas gypsum powder mixture	ST

Chemical (ICP-ES) Analyses: To determine the chemical composition of the finish plaster and roughcast samples taken from the buildings in Amasya, Çorum, Tokat and Sivas and that of the gypsum powder mixture from Sivas, the samples were ground in a mortar to obtain 0.200-g samples sieved with a 125-micron fine sieve. Then, these samples were dissolved in a lithium metaborate-lithium tetraborate ($LiBO_2$-LiB_4O_7) fusion and subjected to inductively coupled plasma emission spectroscopy (ICP-ES) and ICP analyses (ACME Analytical Laboratories Ltd.). The overall chemical compositions of the samples determined by these analyses are represented as metal oxide (%) and other elements in trace amounts as trace elements (ppm).

XRD Analyses: In the assessment of the mineralogical composition of the liquids, ground samples sieved with a 125-micron fine sieve were used. XRD analyses were conducted with a Philips X-Pert Pro X-Ray Diffractometer (XRD) device (IYTE, MAM Lab.) (generator 45 kV, 40 mA, wave length (λ) 1.5443 Å (CuKα), 2 Theta Angles, 5-70).

TGA Analyses: All finish plaster and roughcasts were subjected to TGA analyses from 26°C to 1100°C at a heating rate of 10°C/minute. This analysis aimed to evaluate the phase transformations and mass losses that occur in the samples in each temperature range (switch the gas to nitrogen at 20.0 ml/min) (IYTE, MAM Lab.).

RESULTS AND DISCUSSION

The analysis results are evaluated separately in the following sections.

Chemical (ICP-ES) Analysis Results: Table 2 and Table 3 show the results of ICP analyses. For the overall composition of all samples, oxide is represented by (%) and trace element contents by (ppm).

The Amasya plaster samples (A1-I, A2-I), with respect to the total (TOT) minerals, showed high amounts of carbon (TOT/C) and low amounts of sulfur (TOT/S), which indicates that the binding material is lime. Additionally, the high amount of CaO reveals that there is calcium carbonate (calcite) in the composition of the plaster (Table 2). In addition, the high rate of loss of heating in these plaster samples is a sign of a high amount of calcite minerals. The SiO_2 content found in the samples (between 2.3-8.4%) indicates that silicate, lime or sand materials were used in Amasya plasters.

In Çorum plaster samples (C1-I, C2-I), the amount of carbon (TOT/C) is low and the amount of sulfur (TOT/S) is high, which indicates that the binding material is gypsum. The observed CaO content (between 30.8-31.8%) reveals that the samples are calcium sulfate-based. The slightly lower rate of heating loss in the Çorum plaster samples is another indication of the low calcium carbonate content of these plasters. As in the Amasya plasters, the Çorum plasters also contained SiO_2, which could be caused by silicate materials added to the plasters or by the raw material of the binding. Additionally, trace element analyses revealed that all samples similarly include high strontium (Sr) contents (Table 3). As is well known, gypsum stones are rich in Sr. Therefore, the high amount of strontium is another indication that these plasters feature high rates of calcium sulfate. Moreover, elements such as Sr, Ba, K, Na and Mg in the composition of gypsum play an important role in the dehydration process [3-5]. Very little strontium (Sr) is found in Amasya plasters.

Tokat plaster (T1-I, T2-K) samples were produced with lime as the binding material, as evidenced by the high content of calcium carbonate (calcite). However, when the carbon (TOT/C) and sulfur (TOT/S) rates are considered with respect to the total oxide compounds, it is evident that these plasters also contain sulfate-based materials. The amount of carbon (C) in these plasters is relatively low compared to that in the Amasya plasters. In contrast, finish plaster and roughcasts include high rates of SiO_2, Al_2O_3 and Fe_2O_3, which indicates that clayey silicate materials were used as aggregates in the preparation of these plasters. It is worth noting that in the T1-K sample, the rates of SiO_2, Al_2O_3 and Fe_2O_3 compounds are high. These findings indicate that with respect to finish plaster, roughcasts were prepared with higher amounts of silicate aggregates.

As shown in Table 2, Sivas plaster samples are also rich in calcium sulfate, which is evident in the TOT/S rates. In finish plaster, the rates of SiO_2, Al_2O_3 and Fe_2O_3 compounds are low, while in roughcast, they are high. The amount of "S" in finish plaster is 18% on average and 12% in roughcast. Accordingly, the majority of plasters feature high amounts of calcium sulfate and very low amounts of calcium carbonate, while roughcasts seem to have slightly higher amounts of calcium carbonate. The carbonate content in finish plasters is lower (av. 0.53%).

Trace element analyses show that all of the samples, including the ST sample, are similarly rich in strontium (Sr). According to these findings, the finish plaster sample is composed of high amounts of gypsum and low amounts of calcite, while the calcite content is slightly higher in the roughcast sample. The same is true for the oxide compounds mentioned above. With respect to finish plaster, the high rates of SiO_2, Al_2O_3 and Fe_2O_3 in roughcast indicate the presence of silicate materials in these plasters.

The ICP analysis of a raw sample (ST) partially used in the production of gypsum plaster today indicates that the compound contains a high amount of CaO due to the presence of calcium sulfate. Other oxide compounds determined to exist in relatively low amounts, however, are the result of minerals in gypsum stones that are sporadically clayey in character.

XRD Analysis Results: The mineral contents determined by XRD analysis of all of the plaster samples are shown in Table 4. High amounts of gypsum ($CaSO_4$ $2H_2O$), anhydrite ($CaSO_4$) and calcite ($CaCO_3$) were found in the plaster samples, with gypsum dominant in the Çorum and Sivas plaster samples and calcite ($CaCO_3$) dominant in the Amasya and Tokat samples (Table 4).

Silisium dioxide (SiO_2), a compound of quartz and silisium, was generally found in roughcasts. However, the same mineral was also detected in the A2-I finish plaster sample. The presence of this mineral indicates the existence of silicate material in plasters. These findings also overlap with the results of chemical ICP analyses conducted on the samples. The higher rates of basic oxide compounds (SiO_2, Al_2O_3, Fe_2O_3), with respect to those observed in finish plasters, detected in roughcasts by ICP analysis confirms the validity of these findings. Except for the Amasya A2-I finish plaster sample, all other

Table 2: The chemical composition of samples

Samples	SiO_2 %	Al_2O_3 %	Fe_2O_3 %	MgO %	CaO %	Na_2O %	K_2O %	TiO_2 %	P_2O_5 %	MnO %	Cr_2O_3 %	KK %	TOT %	TOT/C %	TOT/S %
A1-I	2,34	0,57	0,3	0,82	51,01	0,08	0,08	0,04	0,02	<0,01	<0,002	41,4	96,66	12,12	0.60
A2-I	8,38	1,74	0,97	1,09	50,66	0,4	0,26	0,12	0,03	0,02	0,011	36,3	99,98	9,97	0,29
Ç1-K	7,01	1,89	1,16	0,88	30,79	0,16	0,24	0,13	0,02	0,02	0,006	20,7	63,16	0,74	14,03
Ç1-I	4,43	1,32	0,68	0,32	31,75	0,05	0,19	0,07	<0,01	<0,01	0,002	21,0	59,98	0,56	15,04
Ç2-K	5,29	1,53	0,73	0,47	31,82	0,08	0,26	0,09	<0,01	0,01	0,003	20,7	61,33	0,92	15,03
T1-I	7,71	2,0	1,52	1,17	44,6	0,39	0,34	0,23	0,16	0,04	0,012	36,0	94,25	11,44	0,39
T1-K	22,77	6,86	4,31	2,85	30,48	0,78	0,99	0,62	0,24	0,08	0,025	22,2	92,31	7,58	0,13
S1-I	0,56	0,09	0,15	0,19	33,68	0,09	0,03	<0,01	<0,01	<0,01	<0,002	22,0	57,1	0,60	18,1
S2-I	1,79	0,41	0,27	0,16	33,08	0,02	0,09	0,02	<0,01	<0,01	<0,002	21,1	57,3	0,53	17,5
S1-K	12,76	2,89	1,63	1,28	29,25	0,72	0,63	0,17	0,22	0,03	0,028	24,0	73,9	2,87	10,7
S2-K	10,8	2,44	1,36	1,08	30,18	0,5	0,.48	0,14	0,20	0,03	0,02	24,4	72,0	2,51	11,8
ST	0,34	0,05	<0,04	0,06	39,6	<0,01	<0,01	<0,01	<0,01	<0,01	<0,002	2,5	42,83	0,33	21,79

Table 3: Trace element contents in samples

Samples	Cu ppm	Ba ppm	Zn ppm	Ni ppm	Co ppm	Sr ppm	Zr ppm	Ce ppm	Y ppm	Nb ppm	Sc ppm
A1-I	<5	25	10	<20	<20	110	12	<30	<3	14	1
A2-I	20	52	17	26	<20	184	17	<30	<3	6	3
Ç1-K	7	79	13	43	<20	843	17	<30	<3	13	3
Ç1-I	<5	57	13	<20	<20	956	13	<30	<3	7	2
Ç2-K	8	72	14	21	<20	2395	16	<30	<3	<5	2
T1-I	55	97	28	36	<20	181	35	<30	5	14	4
T1-K	80	176	53	104	<20	204	78	<30	11	21	11
S1-I	<5	10	16	<20	<20	2398	<5	<30	<3	<5	<1
S2-I	<5	32	9	<20	<20	2762	5	<30	<3	<5	<1
S1-K	25	104	43	76	<20	1978	36	<30	5	8	4
S2-K	22	89	29	70	<20	2117	33	<30	4	7	3
ST	<5	10	<5	<20	<20	2578	<5	<30	<3	8	<1

Table 4: The mineralogical composition of plaster samples

Minerals / Samples	Calcite ($CaCO_3$) (C)	Portlandite $Ca(OH)_2$ (P)	Gypsum ($CaSO_4$ $2H_2O$) (G)	Anhydride ($CaSO_4$) (An)	Gypsum (high deuterated) $Ca(SO_4)$ $(D2O)_2$	Kutnohorite, calcian $Ca(Mn,Ca)$ $(CO_3)_2$	Quartz (SiO_2) (Q)	Silisiumdioxide HP (SiO_2) (Co)	Calcium oxide (CaO) (CO)	Ferro-Axinite Ca_2 Fe Al_2 B Si_4 O_{15}
A1-I	++++	-	-	-	-	-	-	-	-	-
A2-I	+++	++	-	-	-	-	-	+	-	-
Ç1-K	-	-	+++	-	+++	-	-	-	-	-
Ç1-I	-	-	++++	-	-	-	-	-	-	-
Ç2-K	-	-	++++	-	-	-	-	-	-	-
T1-I	++++	-	-	-	-	+	-	-	+	-
T1-K	++++	-	-	-	-	-	-	++	-	-
S1-I	+	-	++++	+	-	-	-	-	-	-
S2-I	+	-	+++	+	-	+	-	-	-	-
S1-K	+	-	+++	++	-	-	+	-	-	-
S2-K	+	-	+++	+	-	-	+	-	-	-
ST	-	-	-	++++	-	-	-	-	-	++

++++= excessive, +++=great, ++=exist, += less, - = not exist-

finish plaster samples were produced without an aggregate; as a result, no quartz mineral was detected in the A2-I finish plaster sample. According to the X-ray diffraction results, the mineral contents pertaining to both finish plaster and roughcast samples from Amasya, Çorum, Tokat and Sivas all generally bear characteristics indicative of the traditional production techniques unique to each region.

The X-ray diffractogram pertaining to the Amasya finish plaster sample (A1-I) revealed a high rate of calcite mineral (almost 100%), which indicates that this plaster was produced with lime as the binding material. Similarly, in the X-ray diffractogram of the other plaster sample of Amasya (A2-I), a high amount of calcite mineral (90.5%), low amount of portlandite (calcium hydroxide, 5.1% ($Ca(OH)_2$) and silisium dioxide (4.4% SiO_2) were detected. The finding also indicates that this plaster was also produced with lime as a binder and the low amount of portlandite is an indication of some areas within the structure of the plaster that were not totally carbonized. The small amount of SiO_2 is due to the use of silicate aggregate in these plasters.

The X-ray diffractograms of the Çorum roughcast (C1-K, C2-K) and finish plaster (C1-I) samples reveal that these plasters were predominately, in fact totally, made of gypsum minerals (almost 100% $CaSO_4$•$2H_2O$). The ICP analyses showed that these plaster samples were rich in sulfur due to the presence of calcium sulfate. This finding shows that traditional Çorum plasters were produced with gypsum binding material. In building technologies, the use of gypsum binding material as plaster is a traditional and typical technique in the Çorum region that remains a part of the methods used today.

X-ray diffractograms of the Tokat finish plaster and roughcast samples (T1-I, T2-K) reveal that these plasters were predominately made of calcite minerals. In T1-I, calcite (almost 100%) and CaO were detected in trace amounts; in T2-K, in contrast, calcite (90.8% $CaCO_3$) and silisium dioxide (9.2% SiO_2) were detected. This finding shows that the Tokat plaster samples were produced with lime binding material. The low CaO content in the T1-I sample may suggest the presence of caustic lime mineral in the plaster and that the implementation was made quickly. Similarly, the SiO_2 detected in the T1-K roughcast sample is due to the presence of silicate aggregate.

It is known that in traditional Tokat houses, apart from lime-based plasters, gypsum plasters were also widely implemented. Thus, to gain more accurate information about plaster-implementation techniques in this region, we must perform more analyses on plaster samples taken from various other buildings.

The X-ray diffractograms of the Sivas finish plaster (S1-I, S2-I) and roughcast samples (S1-K, S2-K) reveal that these plasters predominately contained gypsum minerals ($CaSO_4$•$2H_2O$), while anhydrite ($CaSO_4$), calcite and the S2-K roughcast sample contained small amounts of quartz mineral (SiO_2).

The calcite ($CaCO_3$) in the finish plaster and roughcast samples suggests carbonization and therefore the existence of lime either added during the production process or already contained in the raw material. While small amounts of this mineral are contained in finish plasters, this mineral is found in slightly greater amounts in roughcasts. This finding indicates that lime was added to some extent, especially in the preparation of roughcasts. The low rate of calcite in finish plasters might be due to the raw material itself. As has been mentioned, the rate of lime is lower in finish plasters (4-5%). As mentioned above, the existence of quartz pigs only in roughcast samples is due to the addition of silicate aggregate to the mixture. These findings are also compatible with the results of the ICP analysis.

The coexistence of gypsum and anhydrite in the finish plaster and roughcast samples, as revealed by XRD, suggests that natural gypsum stones were not heated at equal and homogenous temperatures. Therefore, the material taken out of the oven at the end of the heating process was composed of a mixture of both hydrate and anhydrite and these plasters were produced from this mixture. In applying the plaster, the semi-hydrate material was retransformed into gypsum by a reversible reaction. The anhydrite ($CaSO_4$) also indicates that the raw material mixture was, from time to time, subjected to high temperature in an oven.

In XRD, pigs of gypsum powder compounds from Sivas composed of almost 90% anhydrate ($CaSO_4$) and 10% Ferro-axinite (Ca_2 Fe Al_2 B Si_4 O_{15}) were detected. (Figure 3). The high anhydrate content indicates that the gypsum stone was subjected to very high temperatures. Additionally, in the mixture, the presence of the compound Ferro-axinite, composed of iron, aluminum and silica minerals, is an indication of clay minerals found in the composition of gypsum stones. These findings show that the gypsum stones used in the production of gypsum plaster were of clay structure.

TGA Analysis Results: In a thermogravimetric analysis (TGA), a sample is heated according to a certain temperature program and the changes in sample weight are plotted as a function of temperature; thus, the weight lost by a sample material can be calculated in % according to the temperature range. This method is useful in determining the qualities and the thermal behavior of a material. It also gives us an idea about the behavior of other substances in the composition of a material. For example, TGA indicates the existence of calcite at 800-900°C, clay at 560-650°C and quartz at 573°C [6].

The graphs suggest three different physical processes related to the weight lost by the samples.

- Represents physical dehydration at approximately 100°C-164°C and the formation stage of Anhydrate III and semi-hydrate gypsum.
- Is related to chemical dehydration at approximately 164°C-720°C and the decomposition of CO_2, as well as the formation of Anhydrate II.
- Is related to CO_2 at approximately 720°C-1100°C. In the sample, this decomposition indicates the presence of $CaCO_3$ Above 1100°C, the transformation of Anhydrate I and the decomposition of CaO and SO_4 begin.

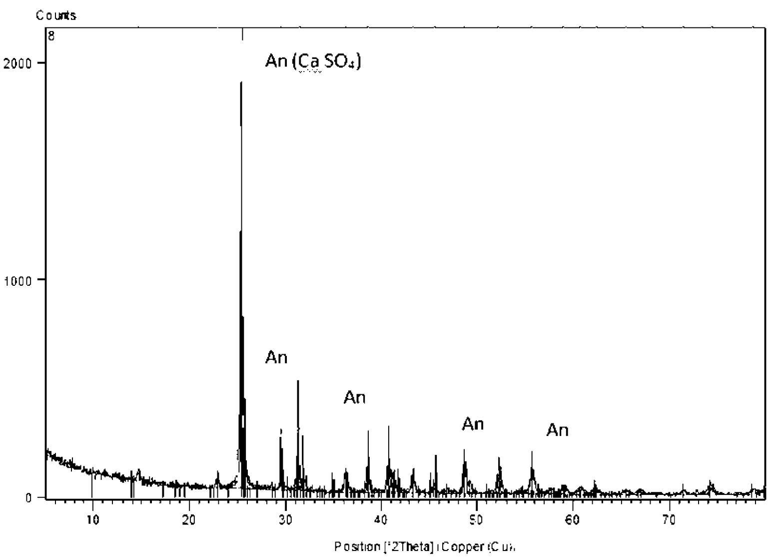

Fig. 3: X-ray diffraction of Sivas gypsum powder mixture (ST) sample (An:Anhydrate ($CaSO_4$), Ferro-axinite ($Ca_2\ Fe\ Al_2\ B\ Si_4\ O_{15}$)

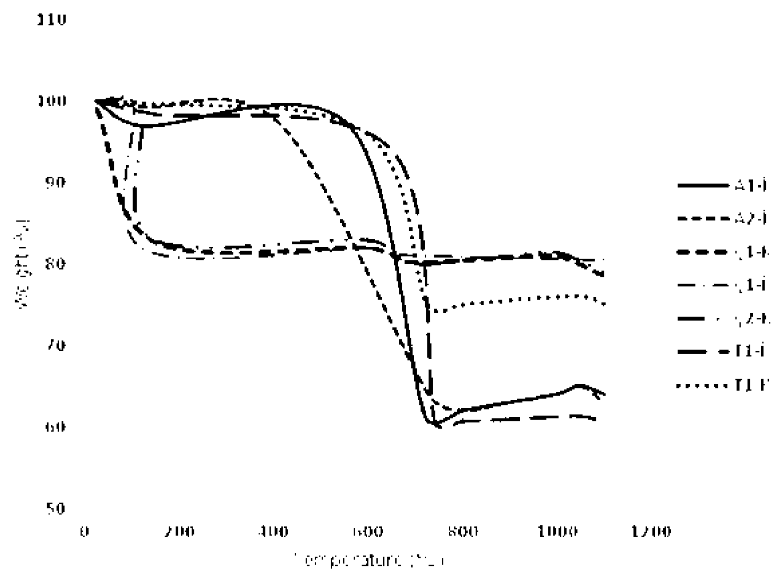

Fig. 4: TGA analyses of plaster samples taken from Amasya, Çorum and Tokat

Gypsum stone ($CaSO_4.2H_2O$), as it is known, loses all or part of its molecular liquid depending on the temperature range and goes through different phase transformations with distinct physical and chemical structures. Widely used in plaster work, gypsum is produced with gypsum stones heated to approximately 120-130°C and loses its physical water at 120°C, which marks the beginning of dehydration [7]. Anhydrate III is formed at approximately 120°C and after 180-190°C, the Anhydrate II phase begins to form [8, 9].

This formation can be chemically expressed as follows:

$$CaSO_4.\ 2H_2O \rightarrow CaSO_4.\ \frac{1}{2}\ H_2O + \frac{3}{2}\ H_2O \quad (1)$$

$$CaSO_4.\frac{1}{2}\ H_2O \rightarrow CaSO_4 + \frac{1}{2}\ H_2O \quad (2)$$

When the heating of calcium sulfate semi-hydrate c($CaSO_4.\frac{1}{2}H_2O$) is continued above 250°C, gypsum stone loses all of its crystal water and transforms into hexagonal Anhydrate II (calcium sulfate without water). The crystal structure of this material dissolved in water does not contain water and is porous. Once it enters into a reaction with water, it adsorbs 3/2 of the crystal water molecule into its body again and retransforms into gypsum stone [10, 11]. As this thermal process continues, beginning from 500-600°C, Anhydrate II that does not dissolve in water is obtained [6]. Figure 4 shows the results of the TGA analysis of plaster samples and Figure 6 shows the results of the TGA analysis of a gypsum powder mixture (ST) from Sivas.

The Amasya A1-I and A2-I plaster samples are similar (Figure 4). As the TGA lines representing mass loss indicate, the physical water within the body of the plasters was desorbed at approximately 120°C and at approximately 125-550°C, chemical water loss took place. Above this temperature range, CO_2 in the body began to decompose and at approximately 720°C, a mass loss as high as 38-36%. (due to CO_2 decomposition) was detected. This finding is another indication that these plasters were produced with lime as their binding material.

Similarly, the TGA graphs of the Çorum C1-K, C1-I and C2-K plaster samples are also similar in character (Figure 4). As indicated by the TGA lines, the slight weight loss in all of the samples at approximately 140-680°C is related to the decomposition of both chemical water and CO_2. For all plaster samples, the mass lost at approximately 680°C is approximately 29%. This finding explains the existence of calcite mineral in the body of the material. Therefore, it is understood that although small in amount, carbonated material was used to prepare the Çorum plasters. However, calcite mineral could be a result of carbonated aggregate or a small amount of lime added to gypsum. The similarity between the TGA thermograms of all three samples taken from Çorum plasters indicates that the material used was produced using the same technologies. It is noteworthy that these findings are also compatible with the results of the ICP analysis.

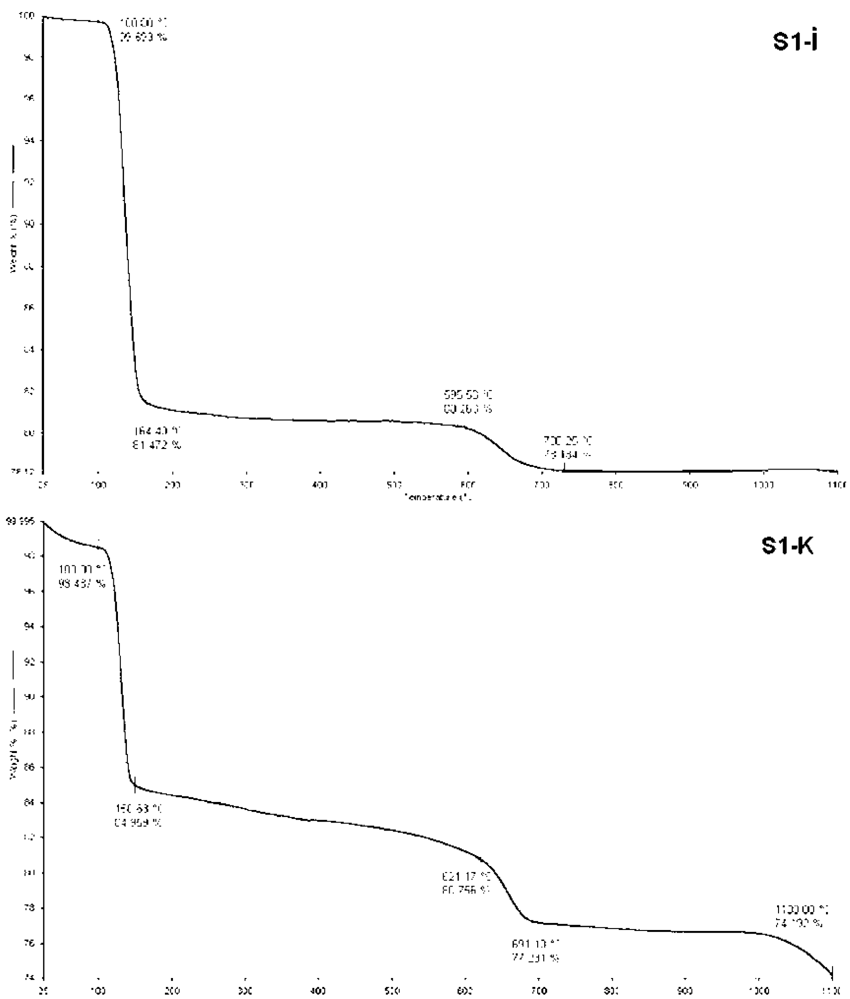

Fig. 5 [a-b]: TGA graphs of Sivas finish plaster (S1-I) and roughcast (S1-K) samples

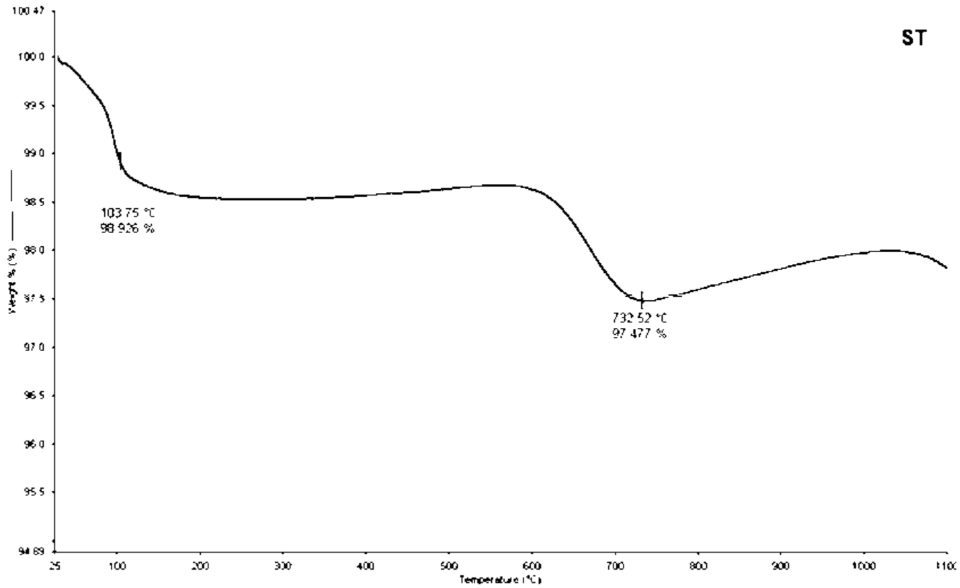

Fig. 6: TGA graph of Sivas gypsum powder mixture (ST)

As shown in Figure 4, the TGA thermograms of the Tokat T1-I and T1-K plaster samples are similar to one another and to the thermograms of the Amasya plaster samples. In finish plaster, the mass lost at approximately 740°C is 30% and in roughcast, the mass lost at 725°C is 25%. As the TGA lines representing mass losses and the chemical analyses clearly show, Amasya finish plaster and roughcast samples were produced with lime binding material.

TGA analyses of Sivas plasters were conducted on two samples (Figure 5 a-b). The TGA graphs representing these plasters look like those representing the Çorum plasters, indicating that these plasters were also produced with lime as the binding material. In the TGA analysis of finish plaster (S1-I), the weight loss rate at approximately 100°C is 0.3% and some water in the body is lost at this temperature. At 100-164°C, partial dehydration begins [7], with a weight loss of 18% (Figure 5a). This range also reveals some loss in the amount of crystal water, which is transformed, for instance, into semi-hydrate $CaSO_4$ + ½ H_2O. No significant change is detected between 164 and 600°C. After 600°C, more weight is lost, followed by a mass loss of 2.5% at 677.8°C. This range indicates that molecular water evaporates completely and Anhydrite II is formed [9]. It also indicates the existence of calcite mineral in the body and the beginning of CO_2 decomposition. The mass loss of the roughcast sample (S1-K) (Figure-5b) is 1.51% at 100°C; 13.53% at 150°C; 4.20% at 620°C; 3.53% at 691°C; and 3% at 1100°C. The total mass loss of roughcast between 150 and 700°C is 7.7%, which is higher than that of finish plaster. This finding indicates that there is more lime and carbonate in the roughcast. The XRD analysis results show that roughcast contains both gypsum and anhydrite together, which indicates that the raw material is made of a mixture of different materials heated to different temperatures. In summary, the general trend exhibited by the TGA thermogram lines representing the plaster samples does not change; only relative differences in mass loss are detected, depending on the temperature range.

The TGA graph of the (ST) sample represents a weight loss of 1.1% at approximately 100°C and the loss of some of the water in the body. However, the mass loss between 100 and 730°C is very small, 1.5%, which is related to the departure of molecular water from the body. The small weight losses indicate that this sample was composed of high amounts of gypsum minerals. When considered carefully, there is a remarkable similarity between the TGA curve of this raw material mixture and the curves of the plaster samples taken from the Sivas region (Figure 6).

CONCLUSION

"Sweet plaster" or "sweet lime" used in the traditional houses of Çorum, Amasya, Sivas and Tokat is a locally manufactured material that defines the architectural identity of these regions. Thus, to maintain the local identity of these regions with respect to their original production and implementation techniques, it is crucial that these manufacturing techniques are determined, this legacy is protected and passed on to new generations and that the surviving buildings are maintained in a manner appropriate to the structures' original characteristics.

According to the analytical results of this study, which were evaluated using samples from traditional houses, the binding material in Çorum and Sivas buildings is gypsum and in Tokat and Amasya, the building material is lime. In the Sivas region, gypsum and lime are found together. However, according to field studies, local craftsmen state that gypsum was widely used in all of the cities as an interior and exterior binding material as well as decoration.

Under atmospheric conditions, the use of gypsum as plaster on the exterior walls of buildings is related to the heating temperature of the material during production processing and the clay minerals in its inner structure. The heating temperature of gypsum used as a construction plaster in today's production industry is usually approximately 120-130°C. Thus, it characteristically dissolves in water. However, as the heating temperature increases, especially above 500-600°C, gypsum becomes insoluble in water because of the clay minerals in its inner structure; moreover, the insolubility depends on the amount of lime added to the mixture as a binding material. This explains why and how materials prepared in this way and used in gypsum plaster applied to 100-150-year-old traditional buildings have not been affected by atmospheric conditions. It is possible to obtain a material appropriate to atmospheric conditions with the gypsum prepared using this technique. The use of gypsum, which is an environmentally friendly and ecological material, is highly significant because it enables the conservation of rich local resources and provides sustainable ways of protecting the original characteristics of traditional buildings toward their conservation and restoration. Today, concrete/cement is the material that is most widely used as a plaster on the exterior surfaces of buildings. The production of this material not only requires more energy (1100°C), but also generates waste products harmful to the atmosphere and the environment. Therefore, this material is not good for use in the restoration of traditional buildings.

It is necessary to maintain "sweet plaster" used in the traditional houses of Anatolian cities such as Amasya, Tokat, Çorum, Sivas, Siirt, Ankara-Beypazari, Kayseri, Van and Konya to protect the local identity of these cities and to cherish the sustainability of this casting type, which is manufactured under primitive conditions today. Taking international conservation and sustainability principles into account, it is of great importance that materials similar to the original castings are applied in the restoration and conservation of buildings using traditional casting techniques that survive today. This will encourage the use of traditionally manufactured materials instead of cement, which allows for an approach that adheres to the principles of conservation. The parts of buildings that must be restored should be renewed with traditional castings, not with cement-based fixings. In addition to protecting the original architectural identity of building types, this approach is also necessary for cherishing the manufacturing techniques associated with traditional materials.

Turkey is rich with gypsum resources. However, considering the amount of resources, the use of gypsum is quite low. The use of available resources will be good in terms of the country's economy and environmentally friendly production processes.

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