

# **Evaluation of Sivas Traditional "Sweet Plasters"**

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Received: 21/04/2010 Revised: 27/07/2010 Accepted: 06/11/2010

## ABSTRACT

Widely used in historical structures in various regions in Anatolia in the past, the material that is colloquially known as sweet plaster is analyzed in this study in terms of its chemical, physical and mineralogical characteristics and on the basis of its application in examples in Sivas. In this scope, thin and coarse plaster samples are taken from traditional houses and chemical analysis is performed by means of ICP-ES and mineralogical analysis through XRD. Loss of mass and phase transformations occurring in accordance with temperature values are examined by TGA analysis applied on coarse and thin plasters. As a result of all these analyses, it is identified that sweet plaster binder mainly consists of calcium sulfate and anhydrate. Additionally, it is confirmed that lime was also added during preparation of sweet plasters in respect of results of ICP, XRD and acid treatment analysis. Lime rate is obtained as 15-20% in coarse plasters and at about 5-10% within thin plasters. As an aggregate, the usage of clayed sand with tuffic characteristics in coarse plaster at the rate of 5-7% is also identified

Keywords: Sweet plaster, gypsum, physical characteristic, chemical characteristic, petrographical characteristic.

# **1. INTRODUCTION**

In recent years, there is a bigger emphasis on cultural values. Concepts such as the environment, ecology and protection are increasingly becoming more important. Trends highlighting material and technology based factors as significant inputs of architectural heritage have emerged much more strongly and a much more sensitive approach towards these issues is becoming more common.

During the development of society, it is the use of selected materials and the compliance to the associated technical rules of the relevant period that creates a structure with a purpose. The basic solution is to use the available regional materials and to shape them with minimum effort [1].

One of the most essential components during the formation of regional architectural identity is following the tradition of local material usage. The characteristics of material provide much information about material production and application technologies and should thus be identified in order to protect and sustain the specific identities of architectural heritage. These materials used in production of traditional residences were sourced mainly from the construction sites or their neighboring areas where they were easily available and in plentiful

and techniques.

identity, they are directed towards product variations presented by the rapid consumption economy. The orientation of this trend towards the natural environmental data is of vital importance in terms of both sustainability of local culture and maintenance of traditional material application techniques. Gypsum based applications that are colloquially known as sweet plaster constitutes one of regional and

amounts. Studies regarding the identification of material characteristics are also important in terms of

development of appropriate protection-repair methods

As today's people are not aware of ecology and

sustainability concepts within regions reflecting local

traditional material techniques in Turkey. In a study [2], it is indicated that sweet plaster has only been used in traditional houses of Ankara Beypazari; however, these applications are not specific to Beypazarı. In addition to internal and external plaster applications of many traditional Turkish houses in various cities of Anatolia (for example; Corum, Amasya, Tokat, Kayseri, Sivas, Siirt, Van, Konya etc.), sweet plasters have been used in many different forms for decoration of internal spaces. The same material is known as "Çaş Harcı" in South Eastern Anatolia Region [3].

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Plasters and mortars made of gypsum have not only been used in Anatolia during the Seljuk and Ottoman periods, but also this material is used in historical structures in many regions of the world. In particular, the usage of naturally available anhydrate gypsum as mortar and plaster in various Central-Asian countries such as Turkistan, Uzbekistan and Kazakhstan, goes back to the past and is still found today.

Despite the wide application area of gypsum binding plaster and mortars in the past, such application techniques have been significantly decreased due to emergence of cement usage in historical structures. When the wide consumption of cement in the construction sector is evaluated in terms of its high cost and adverse impacts on environment [4], a requirement to search for alternative and specific material binders emerges. On the other hand, except for a few studies, little research has been done regarding sweet plaster's resistance to water impact and atmospheric conditions. Sivas is one of the cities where it is possible to see sweet plaster application in traditional structures. Produced by gypsum binder in the past, sweet plaster is one of the significant materials in formation of architectural texture of neighboring areas such as Sivas and Divriği. In addition, the production and application of sweet plasters have decreased today due to increasing usage of cement binder.

Rich gypsum reserves are available in the geological formations of Sivas and its neighboring areas. Reserves cover an area having a length of 400 km and width between 50 km to 100 km, running from west side of Bünyan on the west and to Ecemiş Fault and continuing to north east of Munzur Mountains on the east. Gypsums are available in a zone with a thickness of 150 m and sub-leveled with marn and claystones. The range

of the formation age of gypsums is Upper Eocene-Miocene and their color changes between white, tattletale white, yellow white and grey. Presenting massive and grainy texture, Sivas also has celestine mines located in its southern side and developed syngenetically on jip [5]. When the above stated rich raw material source is taken into consideration, it is essential to use gypsum as a plaster and mortar construction material and to search for application possibilities in the restoration of historical structures in the region. In addition, its advantages such as heat retention, high fire resistance, humidity and acoustic effects, non-occurrence of wet shrinkage cracks during application, easy and cheap production process, as well as lower costs also present more reasons to choose this material.

Studies about the identification of material production and application technologies applied during construction period of traditional residences in Sivas are highly important in order to achieve the protection of this traditional residential architecture with its specific characteristics, to disseminate usage of this construction technique and to translate this technique to following generations. Determination of these technologies is also essential in terms of adhesion to specific structure and sustainability of this tradition.

# 2.TRADITIONAL RESIDENCE ARCHITECTURE OF SIVAS AND USAGE OF SWEET PLASTER

Traditional Sivas houses are mainly constructed with two or three floors using a wooden carcass system (Figure 1a, b, c). The filling material between the wooden carcass is adobe. Specific plasters consists of locally produced materials representing a local application technique named "Sweet Plaster" as stated above.



Figure 1. [a,b,c] Various structure samples in Sivas whose internal and external facades are plastered with sweet plaster.

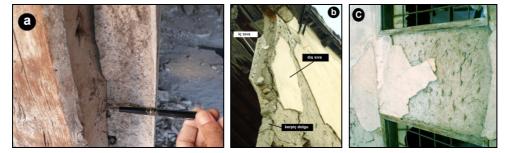


Figure 2. [a,b] Coarse and thin plaster layers, [c] chamfered surfaces on which plasters are applied.

The internal and external surfaces of all traditional houses built by carcass and adobe massive system are plastered with this material. Adobe fillings are generally plastered with fodder added clay and straw plaster with a thickness of a few centimeters on which coarse and thin plasters are applied. The thickness of thin plasters differs between 3 mm and 7 mm, whereas this figure increases up to 8 cm in coarse plasters (Figure 2a, b). In order to increase adherence between clay-straw plaster and gypsum coarse plaster, muddy surfaces are beveled (Figure 2c). Sweet plasters are applied all internal and external wall surfaces of traditional residences in Sivas. Plasters generally consist of 2 or 3 layers. Thin sweet plaster surfaces are covered with a dye layer in certain structures (Figure 3 a). In addition to such usage of sweet plasters, they are also utilized in overall embossing and ornament processes such as window construction, lamp stands, moldings, muqarnas (Figure 3 b, c) in inner spaces. Sweet plaster application in Sivas is mainly produced by material called sweet lime

or bitter lime. According to Kafesçioğlu, sweet plaster is obtained by mixing gypsum, lime and sand in certain rates and sweet lime is gypsum, whereas bitter lime is lime binder [6]. In the past, the binding of sweet plaster was obtained by heating gypsums supplied from local mines within primitive furnaces or boilers in Sivas. Local craftsmen still using this production method [7] stated that, in the past craftsmen, most of whom were Armenian, carried out the above heating process in large clay boilers. Stones obtained from various mines were broken down to smaller sizes by heating them in clay boilers. During this process, the stone mixture within the boiler was continuously stirred and heated homogenously. During the empirical and traditional process the material is mixed and heated until there is no longer any water vapor rising and this is due to the fact that water vapor is an indicator of the status of the material that is being processed.

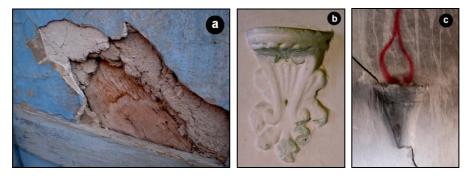


Figure 3. [a] Sweet plaster layers and dye applications on plaster, [b,c] gypsum lamp stands in interior spaces.

Sweet plaster applied in many cities had been fired in their original form as received from mines, in other words without milling, by arraying them side-by-side and one after the other and by placing burning wood around them especially in Çorum and other regions. The same technique was also used during the production of traditional sweet plasters in Beypazarı and the milling process of stones was done after they were fired. This firing method is applied today by following same primitive conditions. As this method cannot provide homogenous heating of stones, both semi-hydrate and anhydrate gypsum may be observed within the mixture. Today, the heating process of gypsums is generally performed under temperature values of 130-220°C [2]. The restoration works of these ruined traditional structures in Sivas, whether registered or not, have been put into agenda by decision of Board of Cultural and Natural Assets Protection. Restoration works of many structures have been completed and inner, as well as external surfaces of some buildings have been covered with cement binding plasters.

Surfaces have been covered with binding plasters and some of them have been dyed by plastic based dyes without application of any test or analysis on specific façade plasters. After a period of time, certain material related problems occurred in these plasters due to intense salt content, different physical and mechanical behavior (Figure-4).



Figure 4. Crackles, spillages and salt effects observed at cement binding plaster used on the restored façade of Abdi Ağa Residence.

Rich gypsum resources is valued by identifying compositions of plasters used at wooden carcass structures of Sivas and arranging new plasters to be produced during repairs and complying with specific plasters in all senses, as well as increasing usage area of this tradition in today's structures. Therefore, this study aims to identify mineralogical, chemical, physical and petrographical characteristics of plasters and production techniques of materials.

### **3. EXPERIMENTAL STUDY AND METHOD**

In this study, research is done on sweet plasters applied to traditional wooden carcass structures of Sivas. Samples have been taken from coarse and thin plasters of structures selected in the scope of research and their physical, chemical and mineralogical characteristics have been analyzed.

**3.1. Structures Where Plaster Samples Are Received** Structures where plaster samples have been received are three characteristic traditional structures located in Akdeğirmen Quarter (Bezirci) of Sivas province. Residences represent similar features in terms of their construction systems and techniques (Figure 5a, b, c). Being privately owned, all three structures have been registered in 1990.



Figure 5. [a,b,c] Historical wooden carcass structures from which plaster samples have been taken.

These residences belong to the late Ottoman period and were constructed at the end of 19<sup>th</sup> century. Residences have basements and two floors. The basement is made of stone and other floors have an adobe filling between wooden carcasses. All inner and external surfaces of structures are plastered with sweet plaster. In addition, internal decoration applications such as lamp stands,

moldings in rooms are made of the same materials (Figure 6a, b). Stone is used up to sub-basement level and other floors are constructed with an adobe filling between wooden carcasses (Figure 6c). The restoration of these ruined buildings has become part of the agenda today.



Figure 6. [a] Gypsum lamp stand, [b] Gypsum decoration on façade of structure B and its date of construction, [c] Plaster layers.

One sample for each thin (A-I, B-I, C-I) and coarse (A-K, B-K, C-K) plaster samples have been taken from three structures in the scope of the study and raw material (T) sample has been taken from a gypsum mine being currently used in order to make a comparison during TGA analysis and all of above stated samples have been subjected to the following analysis to identify basic characteristics of plasters.

### **3.2.** Physical Experiments

During the determination of basic physical characteristics of plaster samples, TS EN 13755 [8] and EN 1936 [9] standard have been considered, whereas basic physical features, such as water absorption and porosity rates have been identified in accordance with the Archimedes method. With the purpose of identification of carbonated material rate that can be dissolved in acid, samples have been treated with HCI

acid diluted at the rate of 10% at  $60^{\circ}C$  (±3) as a result of which their binding rate was determined.

# 3.3. Chemical (ICP-ES) and XRD Analysis

For the purpose of determination of chemical composition of the thin and coarse plasters received from the above stated structure samples, ICP analysis dissolved with lithium metaborate- lithium tetraborate (LiBO<sub>2</sub>-LiB<sub>4</sub>O<sub>7</sub>) fusion is applied to milled, 0,200 gr weighted and 125 micron undersized samples Inductively Coupled Plasma Emission Spectroscopy, ICP-ES (ACME Analytical Laboratories Ltd.). The general chemical composition of samples identified with this analysis is indicated as metal oxide (%) and other substances existing in their scope in trace amounts are indicated as trade element (ppm). Mineralogical composition of samples is identified by XRD analysis and through usage of Philips X-Pert Pro X-Ray Diffractometer (XRD) equipment (IYTE, MAM Lab.).

# 3.4. TGA Analysis

TGA analysis of all thin plaster samples and one coarse plaster sample is applied by increasing temperature by 10°C per minute from 26°C to 1100°C and phase transformations, as well as loss of mass are evaluated in sample and relevant results are compared with plasters.3.5. Petrographical and Microscopic Analysis

Samples embedded to epoxy under vacuum are thinned to 1 mm and their sections have been arranged (RAKU tool EL-2200 and EH-2900) after which these thin pieces have been thinned to  $30\mu$  by adhering sheet bar and by means of STRURES Dicoplan –TS model thin section equipment. Stereo microscope (single nicol) is used during analysis and examinations applied to identify general and microscopic textures of samples and soif polaris (double nicol) microscope is used for thin section samples of mortars.

accordance with temperature ranges (İYTE, MAM

Lab.). The same analysis is also applied to a gypsum

# 4. EVALUATION OF EXPERIMENTAL RESULTS

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

### 4.1. Physical analysis

Basic physical characteristics detected during analysis of thin and coarse plaster samples are submitted in Table 1.

Samples	Unit weight	Open porosity	Water absorption	Density
	$(g/cm^3)$	(%)	by mass	$(g/cm^3)$
A-I	1,32	33,9	25,8	1,99
B-I	1,30	30,1	23,1	1,86
C-I	1,30	33,5	25,8	1,95
A-K	1,21	42,9	35,4	2,12
B-K	1,25	39,7	31,7	2,07
C-K	1,21	43,5	36,0	2,14

Table 1. Physical characteristics of plasters.

Basic physical characteristics of thin and coarse plasters having three different structures are similar to each other and all plasters have low unit volume weights. Porosity rate of thin plasters is 32%, whereas this value is approximately 42% for coarse plasters. Thin plaster samples have lower water absorption and porosity rates when compared to that of coarse plasters. The similar characteristic of three different structures of thin and coarse plasters is an indication of their same or similar production technology.

# 4.2. Analysis with Acid Treatment

Samples are treated with HCL acid diluted at a rate of 10% and it is identified that thin plasters include carbonated material dissolving in acid at a rate of 10%, whereas this figure is identified as 25% for coarse plasters (Calcite minerals are determined in overall samples during XRD analysis). According to analysis results, amount of substance within coarse plaster and dissolving in water is 24 % in A-K sample, 22% in B-K sample and 26% in C-K sample. When it is considered that carbonated materials exist within plasters at a rate of 5-10% according to stereo microscopic examinations,

it may be added that the rate of lime is 15-20% within coarse plasters. As it is obvious, amount of lime within coarse plasters of each structure has similar figures. As for thin plasters treated with acid, rates of dissoluble substances are 10%, 13% and 9% for A-I, AB-I and C-I samples respectively. Again, the amount of lime in thin plasters has similar values representing their arrangement by means of same or similar technology. Coarse plaster has been re-treated with HCL acid diluted at the rate of 10% at 60°C ( $\pm$ 3) and its overall binding zone has been dissolved at the end of which it has been identified that rate of silicate aggregate not dissolved was 5-7%, consisting of material having clayed and tuffic characteristics. In conclusion, the binder of coarse plasters consists of lime at a rate of 15-20%, gypsum rating to 70-80% and resting part is formed by aggregate components having tuffic clayed sand+soil mixture, whereas 5-10% of thin plasters consist of lime and resting amount is formed by gypsum. The amount of substances not dissolving in water within these plasters is fairly low. This data represent that thin plasters include less lime when compared to coarse plasters. The existence of a small

amount of this lime identified in plasters may be due to raw material and a higher amount may occur due to lime added to mortar during production.

# 4.3. Chemical Analysis (ICP-ES analysis)

The general chemical structure of all samples was identified as oxide (%) and other trace amounts of substances included within them is defined as trace

element (ppm) during ICP analysis and associated results are represented in Table 2 and Table 3. When the rate of carbon (C) and sulfur (S) within them is considered, thin and coarse plasters consist of a higher amount of gypsum and lesser amount of lime mixtures. Loss of ignition rate is relatively higher in coarse plaster which indicates that coarse plasters include more carbonated material.

Samples	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	$P_2O_5$	MnO	Cr <sub>2</sub> O <sub>3</sub>	KK	Σ	Σ/C	Σ/S
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
A-İ	0,56	0,09	0,15	0,19	33,68	0,09	0,03	<0,01	<0,01	<0,01	<0,002	22	57,1	0,60	18,1
B-İ	2,86	0,61	0,4	0,31	32,93	0,23	0,15	0,03	<0,01	0,01	0,006	21,6	59,4	0,77	16,9
C-İ	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
A-K	12,76	2,89	1,63	1,28	29,25	0,72	0,63	0,17	0,22	0,03	0,028	24	73,9	2,87	10,7
В-К	9,93	2,29	1,31	1,01	30,2	0,55	0,44	0,13	0,07	0,02	0,025	22,6	68,9	1,71	14,0
С-К	10,8	2,44	1,36	1,08	30,18	0,5	0,.48	0,14	0,2	0,03	0,02	24,4	72,0	2,51	11,8

Table 2. Chemical composition of samples.

Table 3. Trace element content of samples.

Samples	Cu	Ba	Zn	Ni	Со	Sr	Zr	Ce	Y	Nb	Sc
	ppm	ppm	ppm	Ppm	ppm	ppm	Ppm	ppm	ppm	ppm	ppm
A-İ	<5	10	16	<20	<20	2398	<5	<30	<3	<5	<1
B-İ	<5	34	20	25	<20	2716	8	<30	<3	8	<1
C-İ	<5	32	9	<20	<20	2762	5	<30	<3	<5	<1
A-K	25	104	43	76	<20	1978	36	<30	5	8	4
A-K	11	77	22	58	<20	2183	27	<30	5	<5	3
С-К	22	89	29	70	<20	2117	33	<30	4	7	3

As it can be seen from Table 2, thin plaster samples include a high rate of CaO (app. 33%). This higher rate of CaO in thin plasters is due to excess of calcic sulfate within their content. Rates of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> components are fairly lower in these samples, whereas associated rates are higher within coarse plasters. Total " $\Sigma$ /S" amount is approximately 18 % in thin plasters and 12 % in coarse plasters. Accordingly, plasters include a higher rate of calcium sulfate, a lower amount of calcium carbonate; however, calcium carbonate rate of coarse plasters is higher. The amount of carbonate is less in thin plasters (app. 0,53 %). During trace element analysis, it is identified that all samples include high rate of Strontium (Sr) similarly (Table 3). In addition, elements such as Sr, Ba, K, Na and Mg included within composition of gypsum play significant role during dehydration process [10,11,12].

When compared to thin plasters, carbonated oxide rates are higher in coarse plasters in accordance with  $\Sigma/C$  and  $\Sigma$ /S rates. According to these evaluations, thin plaster samples consist of a high amount of gypsum and a fairly small amount of calcite, whereas the calcite rate is higher in coarse plasters due to lime added to the mortar

during the production of plasters. The same is also valid for the other oxide components discussed. In comparison with thin plasters, higher rates of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in coarse plasters represent the existence of silica materials within these plasters.

#### 4.4. XRD Analysis

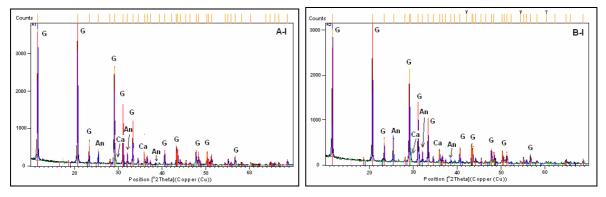
Mineral contents of thin and coarse plaster samples identified by XRD analysis are represented in Table 4 and their diffractograms are presented in Figure 7 and Figure 8. All plaster samples include gypsum (CaSO<sub>4</sub>  $2H_2O$ , Anhydrate (CaSO<sub>4</sub>) and calcite (CaCO<sub>3</sub>) minerals. While there is an adequate rate of Anhydrate in all samples t is clear that Gypsum is the dominant material. (Table 4). While calcite is in lesser amounts within thin plaster samples, its amount is higher in coarse plaster samples. Quartz mineral is only identified in coarse plasters indicating existence of silica material within coarse plasters. Additionally, when ICP analysis of thin and coarse plaster samples are compared, the higher rate of basic oxide component (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>) within coarse plasters also supports this claim. As thin plasters are produced without aggregate, no quarts mineral was identified (Figure 7).

Minerals	Gypsum	Anhydrate	Calcite	Quartz	Carbon			
Samples	(CaSO <sub>4</sub> 2H <sub>2</sub> O) (G)	(CaSO <sub>4</sub> ) (An)	(CaCO <sub>3</sub> ) (Ca)	(SiO <sub>2</sub> ) (Q)	(C)			
A-I	++++	++	+	-	-			
B-I	++++	++	+	-	-			
C-I	++++	+++/++	+	-	-			
A-K	++++	++	++	+	-			
B-K	++++	+++/++	++	+	+			
C-K	++++	++	++	+	-			
++++= exc	++++= excessive , +++=great, ++= exist, += less, - = not exist-							

Table 4. Mineralogical composition of plaster samples.

Mineral contents of both thin and coarse plasters defined by means of X-ray diffraction are similar to each other. Carbon mineral was detected in one coarse

plaster sample (B-K) (Figure 8). This finding supports the theory that gypsums were fired in a open furnace where burnt wood mixed with the raw material.



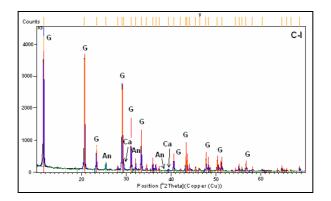


Figure 7. X ray diffraction of thin plaster samples.

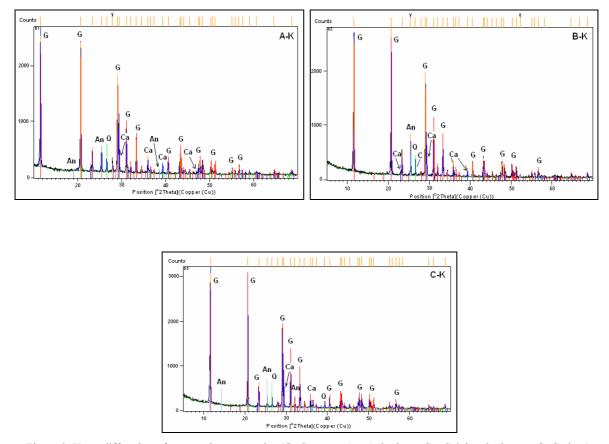


Figure 8. X ray diffraction of coarse plaster samples (G: Gypsum, An: Anhydrate, Ca: Calcite, Q: Quartz, C: Carbon).

Calcite (CaCO<sub>3</sub>) peaks of thin and coarse plaster samples represent carbonation and accordingly, the existence of lime added to gypsum during production phase or included within raw material is represented. While the amount of this mineral is less within thin plasters, the amount increases in coarse plasters (Figure 8). This situation is another indicator of the addition of certain amounts of lime during preparation of coarse plasters. A smaller amount of calcite within thin plasters (5-10%) may be due to the raw material. Occurrence of quartz peaks only within coarse plaster samples is due to silica aggregates added to the mixture as stated above. This data also complies with results of ICP analysis.

The existence of gypsum and Anhydrate together at XRD peaks of samples means that overall natural gypsums are not heated under equal and homogenous temperatures. Therefore, material taken from the furnace at the end of heating process consists of both semi-hydrate and anhydrate mixtures and plasters have been produced with this mixture. Semi hydrate material has been transformed to gypsum by reversible reaction during plaster application. The existence of anhydrate represents that mixture has been subjected to high temperatures during Anhydrate II phase.

### 4.5. TGA Analysis

With Thermogravimetric (TGA) Analysis, sample is heated at specific temperature, changes in its weight are indicated as a function of temperature and loss of weight of material sample is calculated in terms of % in accordance with temperature ranges. This type of analysis is appropriate in terms of the detection of material characteristics and identification of basic behavior. Progression of gypsum dehydration can be easily followed through this method. In addition, information may be supplied regarding the behavior of foreign materials included in its scope. To illustrate, indications were found regarding existence of calcite between 800-900°C, clay between 560-650°C and quartz at 573°C [13].

TGA analysis results of samples are explained in Figure 9 and Figure 10. TGA graphics of "A-I, B-I and C-I" thin plasters represent typical gypsum curve. In order to make a comparison, TGA analysis of a gypsum sample (T) used during production of sweet plaster and received from a gypsum mine in the region has also been performed. As it can be seen from the figures below, thermogram lines of gypsum (T) and thin plaster samples represent similar behavior and almost overlap (Figure 9).

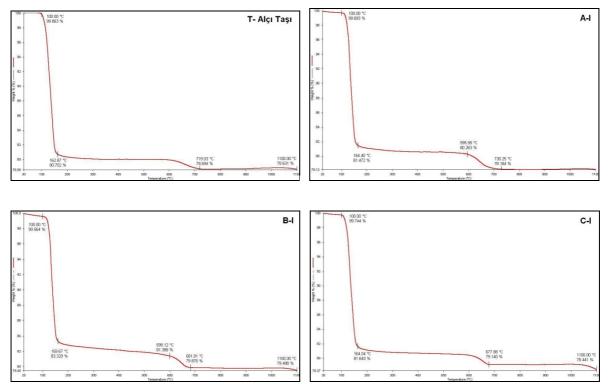


Figure 9. TGA graphics of gypsum (T) and thin plaster samples (A-I, B-I, C-I).

Three different physical processes can be observed regarding loss of weight during TGA analysis of samples. The first defines physical water loss approximately between  $100^{\circ}$ C -  $164^{\circ}$ C and formation phase of Anhydride II and semi hydrate plaster. The second defines chemical water loss approximately between  $164^{\circ}$ C -  $720^{\circ}$ C and decomposition of CO<sub>2</sub>, formation of Anhydrate II. The third is regarding CO<sub>2</sub> between  $720^{\circ}$ C -  $1100^{\circ}$ C. These decompositions indicate existence of CaCO<sub>3</sub> in the sample. After  $1100^{\circ}$ C, transformation of Anhydrate I and decomposition of CaO and SO<sub>4</sub> initiate.

As it is already known, gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) undergoes different phase transformations, with different physical and chemical structures, by losing its overall or partial molecule water in various temperature ranges. In general, plaster used in plastering works is obtained by heating gypsum to 120-130°C and its dehydration is initiated by losing physical water at120°C [13]. Anhydrate III forms approximately at 120°C and Anhydrate II phase occurs after 180-190°C [14,15].

Chemical definition of this process is as follows:

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

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

When the heating process of semi-hydrate of calcium sulfate (CaSO<sub>4</sub>. $\frac{1}{2}$ H<sub>2</sub>O) continues, gypsum losses it overall crystal water and turns to hexagonal Anhydrate II (waterless calcium sulfate). The crystal structure of

this product dissolving in water is waterless and porous and turns to its plaster structure by taking in 3/2molecule crystal water by reacting with water [16, 17]. If the thermal process is continued above and over 500-600°C insoluble orthorhombic Anhydrate II remains [13].

To illustrate, a weight loss rating to 0.3% is observed within C-I thin plaster at about 100°C and some part of water in its scope comes out. Partial dehydration initiates between 100-164°C and loss of weight rating to 18% is observed. This temperature range also represents loss of certain part of crystal water and passage to semihydrate  $CaSO_4 + \frac{1}{2} H_2O$  form. No significant change is observed between 164 °C and approximately 600 °C, whereas weight loss again initiates after 600 °C and loss in mass rating to 2,5% is observed at 677,8 °C. Loss of weight of overall thin plasters changes between  $1.5\frac{1}{2}$ and 2.5% between 600-700 °C. This rate is 3,53% for coarse plaster samples between the same temperature range. Associated temperature range indicates vaporization of entire molecule water, as well as existence of calcite mineral in the scope and start of CO<sub>2</sub> decomposition. The rate of weight loss is more in thin plasters when compared to that of coarse plasters.

Similar behavior is also valid for gypsum [T] sample. After 1100 °C, phase change and mass loss of stone and plaster samples occurs after which Anhydrate I arises. The same behavior is also observed overall thin plaster samples. This rate is 0,7% for C-I sample and 1,72% for gypsum (T) sample. Anhydrate II exposes to partial decomposition at 1180°C and turns to sulfur trioxide  $(SO_3)$  and calcium oxide (CaO) as a result of which free lime diffuses within the mass [13]. This material known as Anhydrate-I which is not a complete

plaster, freezes late, but then after freezing creates a harder and more durable mass known as "flooring plaster".

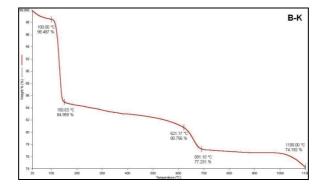


Figure 10. TGA thermogram curve of K-2 Coarse plaster sample.

The same TGA analysis has been applied to one coarse plaster sample (B-K) (Figure 10). The following loss of mass occurs at following temperatures; 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 loss of mass of coarse plaster is 7,7% between 150 and 700°C which represents higher value than overall thin plasters. This case indicates that existence of carbonated material is higher within coarse plasters. In summary, the general trend in TGA thermogram lines of samples does not change, but relative differences arise in loss of weight in accordance with temperature ranges. These rates are higher in coarse plasters.

Anhydrite II occurs in various forms which are classified according to reactivity. Sparingly soluble anhydrite is produced when gypsum is burnt at temperatures between 200 and 400° C, and insoluble anhydrite is formed in the temperature range from 400

to 700°C. At temperatures above 700°C so-called flooring plaster is produced. Under these conditions anhydrite dissociates partially into CaO and SO<sub>3</sub>, and the quicklime formed activates the hydration of the anhydrite [18].

### 4.6. Microscopic and Petrographical Analysis

Textures and mineral contents of thin sections of coarse and thin samples arranged by embedding them into epoxy, as well as associated rates are analyzed by soif stereo microscope (single nicol) and soif polaris microscope (double nicol). In accordance with soif stereo microscopic observation results, white masses (plaster + lime) rating to 20-25% exists in coarse plasters having binding area of 60-70%. Tuffic particles rating to 10-15% and nodule shaped aggregates within clay character may be observed (Figure 11a, b). Their pores are generally small, springy and homogenous. Their layers have fairly regular structure.

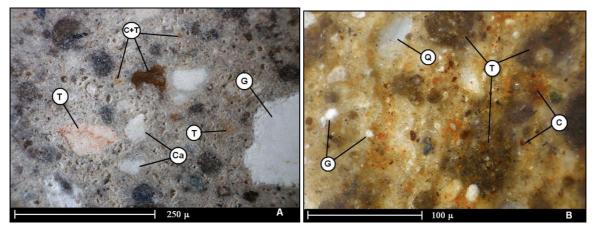


Figure 11. (a, b) Stereo microscopic appearances of coarse plasters (single nicol).

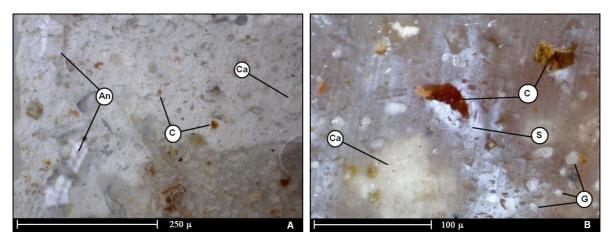


Figure 12. (a,b) Stereo microscopic appearances of thin plasters (single nicol) (G: Plaster, An; Anhydrate, C: clay, Ca: calcite, T; tuffic particles, Q quartz, S; NaCl.

As for thin plasters, smaller dimensioned particles of same material can be observed in certain areas. Having plaster particles rate of 15-20% and including a smaller amount of clay/tuff dusts, these plasters have micro pores (Figure 12a). Their surfaces have regular structures. In their inner structure, salt (NaCl) formations may be seen in some places. These plasters have micro pores and include plaster particles in a rate of 15-20% and small amount of clay/tuff dusts (Figure 12a). Their layers have fairly regular structure. In their inner structure, salt (NaCl) formations may be seen in some places (Figure 12a).

Under a polaris microscope, small-sized crystals are observed within certain areas of thin and coarse plaster samples, having a transparent bluish, cordal and cleavaged character of a anhydrate mineral [19] (Figure 13a). According to XRD analysis results, anhydrate also exists within plastering together with plaster. In addition, opaque minerals having amorphous structure also exist in their scope. Existence of quartz minerals within coarse plaster sample is due to aggregates having clayed and tuffic characteristics (Figure 13b).

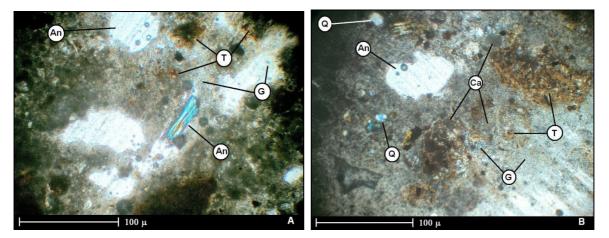


Figure 13. (a,b) Polaris microscope (double nicol) appearances and mineral contents of coarse plasters.

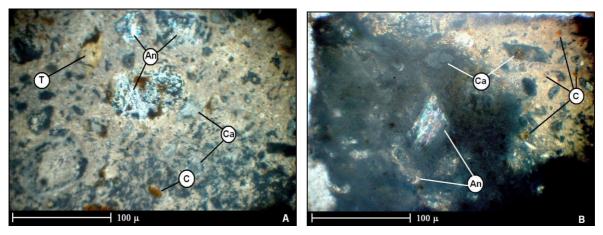


Figure 14. (a,b) Polaris microscope (double nicol) appearances and mineral contents of thin plasters.

Anhydrate also exists in thin plasters where aggregates having amorphous, clayed and tuffic characters can be observed. Their rate is less when compared to coarse plasters (Figure 14a, b). According to this data, coarse plasters are made of land-originated sand aggregate with clayed and tuffic natures. Same aggregates are also observed within thin plasters. General evaluation of petrographical analysis results is summarized in Table 5.

Table 5. Petrographical analysis results of plaster samples.

Sample	Macroscopic observation	Microscopic observation	Mineral composition (%)	Evaluation
Coarse plaster	Carbonated material consisting of different sized, less angled mineral in dirty brown color, foaming in acid rapidly	Widely opaque (irony) matrix with calcite. Includes porous, angled different sized rock/mineral.	Jibs: 40-50 Quartz +Feldspars: 5- 10 Opaque mineral: 20 Calcite: 15-20	Plastering material consisting of calcite jibs mixture, opaque mineral and porous structure, carbonate matrix and gypsum additive.
Thin plaster	Having mixture of white beige colors, porous, light structure leaving dust by hand and reacting with acid.	Matrix structure including opaque, porous, different sized, angled-semi angled calcite crystals.	Jibs: 85-90 Opaque: 5-8 Calcite: 5-10	Gypsum plastering material consisting of calcite jibs, porous structure and less amount of opaque mineral mixture.

Result:

Coarse plaster: Having jibs and sand mixture (quartz+feldspar+mica) and possibly received from decomposition zone of material consisting of mica schist or granite.

Thin plaster: Consists of mainly jibs weighted calcite + clay + opaque (iron) components. Decomposition product of iron, calcite, clay (irony), clayed limestone.

### 5. CONCLUSION AND GENERAL EVALUATION

As a result of experiments performed in the scope of this research, it is identified that binder used in inner and outer sweet plasters of Sivas houses is composed of high amount of plaster and lesser amount of clay mixtures. While thin plasters are produced without aggregate, clay-sized river sand was used as aggregate in coarse plasters. The identification of anhydrate during XRD analysis of plasters represents that certain parts of raw material gypsums have been subjected to lower temperatures due to the existence of a higher rate of plaster. Binding material of sweet plasters is obtained by such a heterogeneous heating process. This situation also indicates a shorter duration of the heating process. Material subjected to low temperatures and having semi-hydrate characteristics became solid by gaining physical water loss when mixed with water during application and turned to plaster. Therefore, XRD analysis shows that some parts of the plaster is identified. The existence of anhydrate indicates a rise

of heating temperature to 500-600°C in some regions. As this material is insoluble, it has not entered into an intense reaction with water and as a result sustained its characteristics. Again calcite mineral determined during XRD analysis and mass losses occurring at about 700°C represent the usage of lime in production of plasters due to decomposition of CO2. Calcite identified during polaris microscopic analysis arises due to carbonation of lime. While mixture rates of lime is less in thin plasters (app. 5-10%), this rate is higher within coarse plasters (app. 15-20%). Claved sand having coarse particles in certain zones and tuffic characteristics has been used in coarse plasters with a rate of 5-8%. In conclusion, similar characteristics of thin and coarse plaster samples of structures, both in the physical and chemical sense, indicate that the technology used in the preparation of sweet plasters and the processes followed while heating gypsum are not so different from each other.

It should be a requirement to produce materials considering international protection and sustainability principles and by complying with specific plasters used in restoration and protection works of the decreasing number of structures representing "Sweet Plaster" applications in Sivas. Instead of cement based materials, the usage and application of widely available traditional sweet plasters presents a more appropriate approach towards the principles of protection. The restoration of structures should be done with "Sweet Plaster" and the usage of cement binding plasters should be prevented. This approach is essential not only in terms of protection of specific structure identity, but also to sustain the production technology of traditional material. The mixture rates of "Sweet Plasters" should be determined in accordance with these principles. Achievingg a continuity of traditional sweet plaster production and its application techniques as well as sustaining utilization techniques for traditional materials are essential in this era where ecological applications are playing an increasingly vital role.

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