Overcoming the Free Calcite Problem in Pottery in the Light of Chemical and Thermal Analysis Results of Avanos, Malatya Clays

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Abstract

The Avanos district of Nevsehir is a major handicraft center of both the Cappadocia region and of Turkey. The craft sector has become increasingly important for commercial purposes, with pottery being considered to be the most important area of the sector. The clay used in Avanos pottery is taken from clay deposits in the region or is brought in from other provinces. Unfortunately, chemical analyses of the clay mixes are never performed and excess calcite creates various problems. In this research, the chemical and thermal properties of the clays (Avanos clay and Malatya clay) used in Avanos pottery were analysed to improve the quality of pottery production by detecting the amount of calcium oxide and the removal temperature of carbon dioxide from the clays. The clay used in the production of pottery affects the shaping of the final product, the firing process and the physical and mechanical properties. XRF (X-ray fluorescence) was used to determine chemical composition and XRD (X-ray diffraction) was used to determine the phases of Avanos and Malatya clays used in pottery making. A TG-DTA device was used to examine the mass losses and reaction temperatures of the clays. As a result, the calcite phase was observed in both clays, but the amounts differed. Avanos clay contains more than twice the amount of calcium oxide and the temperature of carbon dioxide removal is higher compared to Malatya clay.

Key Words: Pottery, Clay, Chemical Analyses, Thermal Analyses

INTRODUCTION

In Central Anatolia, Avanos is located at the mid-section of the Kızılırmak River. The Kızılırmak River divides Avanos into two parts. Since the start of settlements in the region from the Neolithic period, the growth of cultural diversity with its various forms of art and crafts has seen the Cappadocia region become an important handicraft center. Avanos pottery is a traditional handicraft which encourages art tourism and contributes to the economic growth of the area. It is thought that the Kızılırmak River represents abundance, because the river separates its clay into different grain sizes, and fine grain sized clay for pottery production, in a natural way.

The final properties of ceramics are the sum of many production steps, such as shaping, drying, glazing and firing. Shaping is very often the basis of the whole process and has a substantial influence on the quality of the product and the efficiency of a production line [1].

Clay is one of the few materials which has no value its own right, but which can be formed into valuable objects. The value is created by the potter. Clay itself is relatively formless, and the forms the potter shapes are entirely his own, drawing little from the inherent form of clay [2].

Avanos Potters, prepare pottery recipes with clays from clay deposits in the region or from other provinces. These recipes do not prepared with scientific methods. For this reason, the amount of calcium oxide in the body can never be understood.

For pottery production, clays are taken from clay deposits in the region or are brought in from other provinces. The clays are mixed with water and rested in a pool. After a kneading process, mud is sent to a cylinder and vacuum press. The mud is shaped and the products are allowed to dry. Outdoor firing, the simplest firing method used in potteries, is still being used in many districts of Anatolia today [3]. In Avanos there is a traditional pottery kiln named Black Kiln. Firing is performed generally at 700°C with wood firing fuel, such as sawdust and straw in

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the Black Kiln, which symbolizes Avanos. In addition to the Black Kiln, electric furnace firing is also used in the region.

Even though the shaping process of the products is performed well, the final properties of the products appear as a result of firing. Calcite in low-fired pottery can be the cause of lime-spall and throwing. Avanos pottery is generally sintered at 700°C (wood firing at Black Kiln) with lime-spall and throwing being a problem for Avanos pottery (Fig. 1). In this research, the chemical properties of clays (Avanos clay and Malatya clay) used in Avanos pottery were analysed to determine the amount of CaO by XRF (X-ray fluorescence). Phase analyses were then performed to detect the origin of CaO by XRD (X-ray diffraction).

Figure 1. Lime-spall and throwing due to calcite.

Thermal analysis methods are used with ceramics for many purposes. Binal investigated ceramic raw materials and body properties using this method [5]. Tunali used thermal analysis techniques to solve the surface problem under industrial conditions[6]. Fabbri et al. observed the de-carbonation process of calcite during reheating of archaeological ceramics by the thermal analysis method [7].

During sintering of products, $CaCO_3$ decomposes to CaO and CO_2. If CaO can not form new phases, it reacts with water over time and $Ca(OH)_2$ phase occurs. Therefore, throwing on the product is also formed [7]. This reduces the quality of production and causes problems in use.

In this study, thermal analysis was used to determine the carbon dioxide removal temperature from clays used for Avanos pottery production. The thermal analysis technique includes thermogravimetric (TG) and differential thermal analysis (DTA).

EXPERIMENTAL PROCEDURE

Chemical analysis of clays was performed by XRF-Rigaku ZSX Primus. X-ray diffraction (XRD) was used for the qualitative determination of crystalline phases present in the formulations. This was performed using a Rigaku Rint 2200 diffractometer (with Cu_K radiation) at 40 kV and 30 mA. Samples were scanned from 2 , 5 to 70°, at a scanning speed of 2°/min. Netzsch STA 409 PC/PG was used for the thermal analyses. Analyses were performed under controlled heating (20°C/min) at air atmosphere and 1100°C. Weight loss, due to reactions occurring during heating, was determined by thermogravimetric analysis (TG), and exothermic-endothermic peaks, due to the effects of thermal reactions, were detected by differential thermal analysis (DTA). Analyses were performed at Anadolu University, Materials Science Engineering and Ceramic Research Center.

RESULTS AND DISCUSSION

The chemical analyses of clays are given in Table 1. The amount of calcium oxide in Avanos clay is 11.25 (wt. %) and the amount of calcium oxide in Malatya clay is 4.83 (wt. %). Avanos clay contains more than twice the calcium oxide of Malatya clay. The origin of calcium oxide in the calcite phase is shown in Figures 2 and 3. The calcite peak’s intensity is higher for Avanos Clay than Malatya clay due to the greater amount of calcite. Muscovite and quartz are other phases present in Avanos clay (Figure 2). Kaolinite, illite, zeolite, albite and quartz are present in addition to calcite in the Malatya clay, as seen in Figure 3.

Table 1. Chemical analysis of clays determined by XRF (wt. %).

Clays	L.I.*	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	BaO	P_2O_5	MnO	SO_3
Avanos	13.83	48.63	14.72	5.15	0.56	11.25	1.49	0.72	3.04	0.26	0.10	0.12	0.14
Malatya	8.28	52.47	15.30	8.12	1.07	4.83	5.75	1.71	1.97	-	0.14	-	0.35

L.I.*: Loss on Ignition

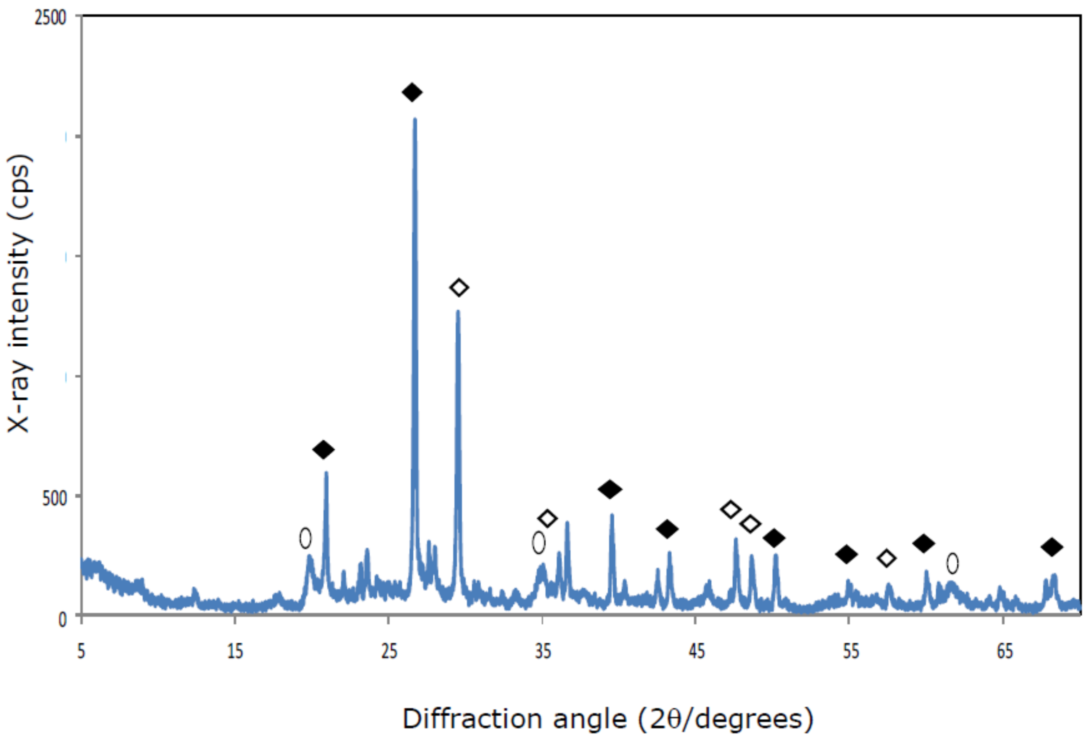

Figure 2. Representative XRD spectra of Avanos clay.
(◇ :Calcite, ◆ : Quartz, O:Muscovite)

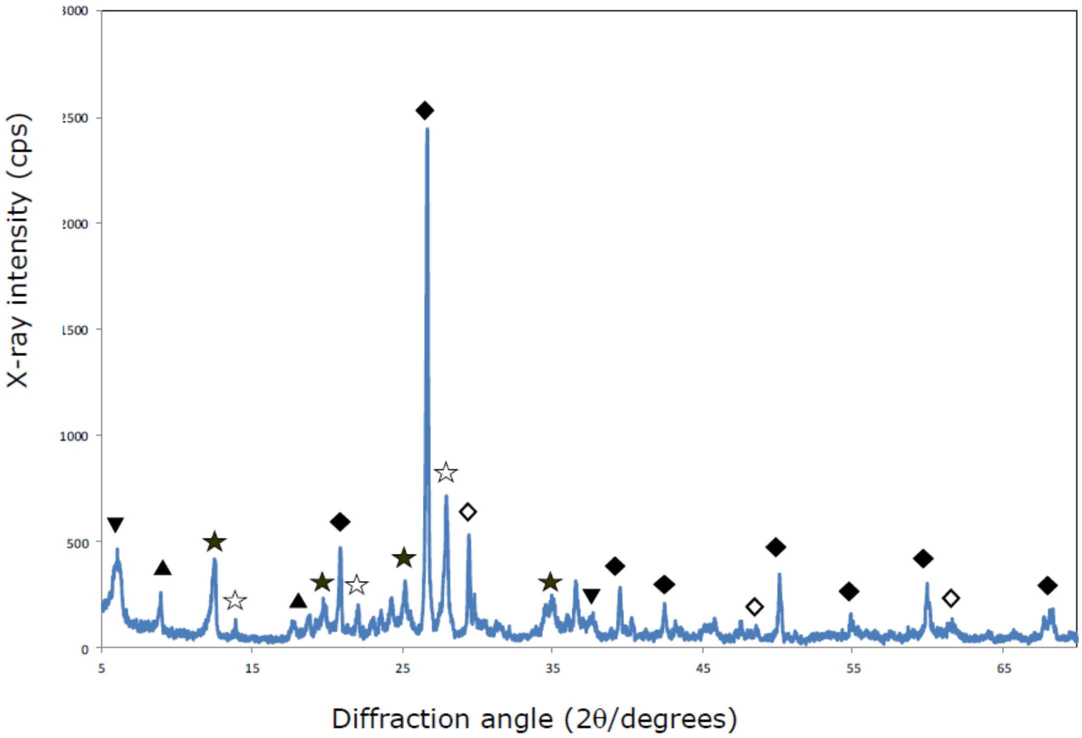

Figure 3. Representative XRD spectra of Malatya clay.
(★:Kaolinite, ◇ : Calcite, ◆ : Quartz, ☆: Albite, ▼ :Zeolite, ▲:Illite)

While calcite decomposes at 784.2°C (mass loss 8.93 wt. %) for Avanos clay (Figure 4), it decomposes at 763.5°C (mass loss 3.34 wt. %) for Malatya clay (Figure 5). Increasing the amount of calcite increases the carbon dioxide removal temperature and mass loss.

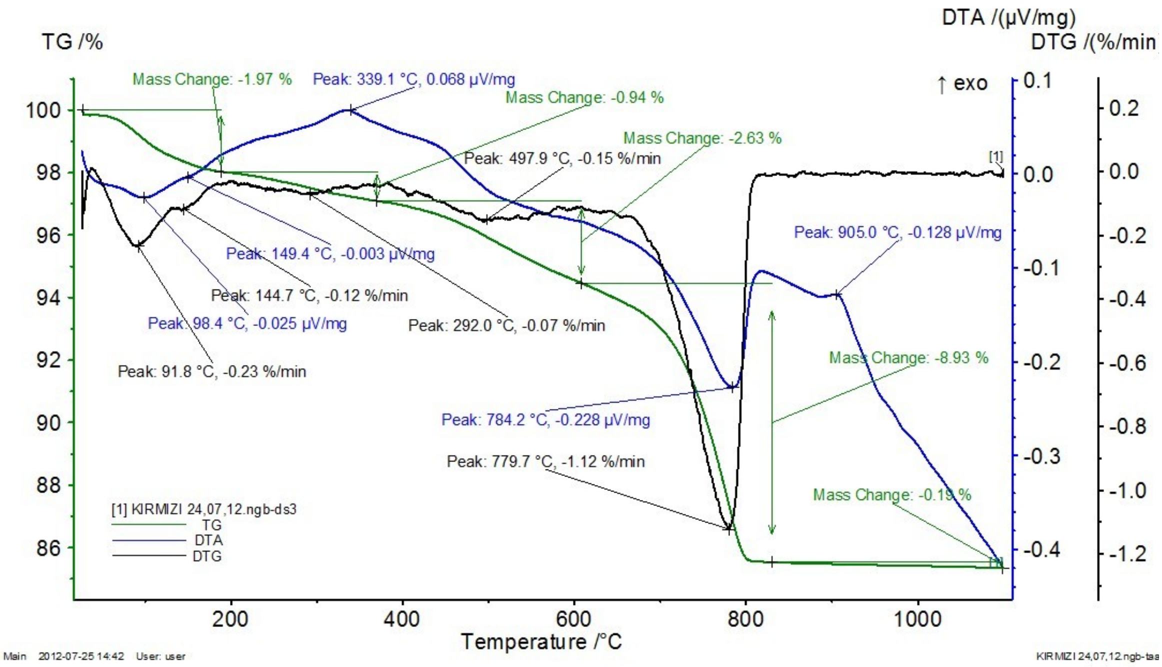

Figure 4. TG/DTA curve of Avanos clay.

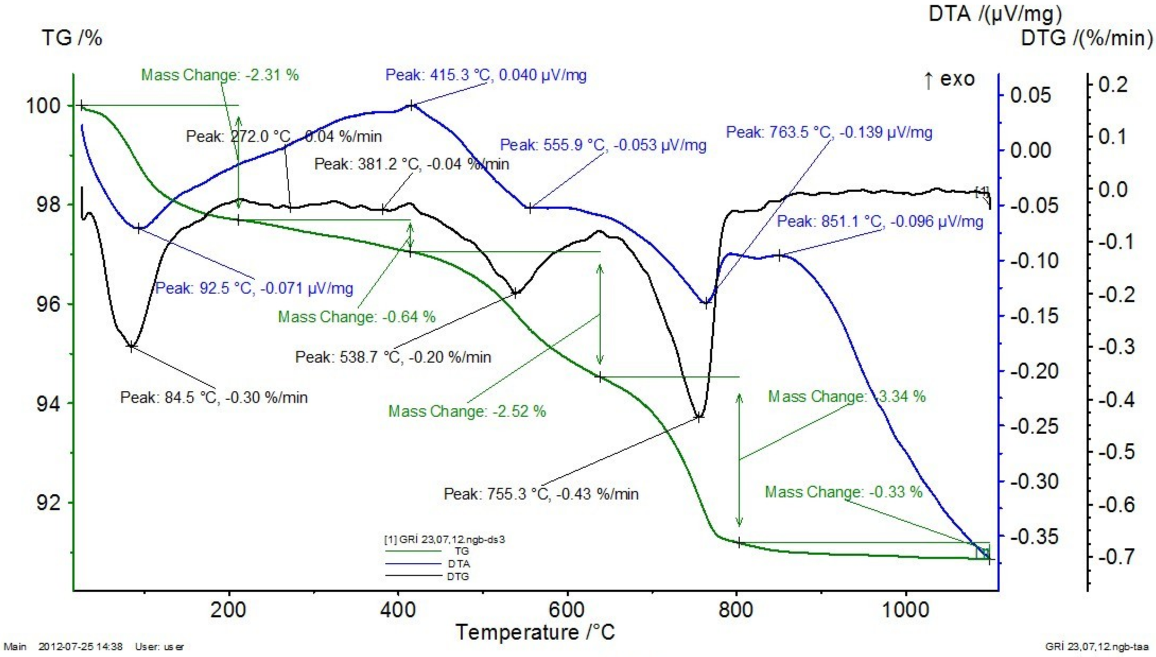

Figure 5. TG/DTA curve of Malatya clay.

CONCLUSIONS AND SUGGESTIONS

In this study, two different clays (Avanos and Malatya clays) used for Avanos pottery production were investigated. The calcium oxide present in the clays was determined by X-ray fluorescence, the origin phase of the calcium oxide was detected using X-ray diffraction and the removal temperature of carbon dioxide from pottery was determined by thermal analysis. The amount of calcite present and the decomposition temperature of the calcite are higher for Avanos clay than for Malatya clay. The calcite decomposition temperature of both clays is higher than the sintering temperature of Avanos pottery, with calcite remaining in the pottery. Due to this residual calcite, lime-spall and throwing are problems.

The most appropriate method of cleaning coarse calcite grains from the clay is dissolving the clay in the pool, sieving for remove coarse calcite grains, and then shaping consistency with inflicted water. In order to prevent lime-spall and throwing of sintered pottery products, after kiln coming to a certain temperature without thermal shock, products dipped to water for remove calcium.

The present study suggests that the lime-spall and throwing problems of Avanos pottery, due to the presence of calcite, could be solved by increasing the sintering temperature of kilns, after decreasing grain size in the preparation stage of clays.

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