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An Analysis of the Effects of Calcium Aluminate Cement Additive on Porcelain Forming and Final Product Properties*

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Abstract

A key step in artistic production surely involves the selection of materials. Each material has its own unique components and limitations. These limitations also determine basic production processes such as shaping and coloring. Today, these limitations are minimized thanks to optimization and R&D studies in the material industries. Studies on the optimization of materials offer a source for the development of different usage purposes as well as the main usage purposes of the materials and additional properties for the final product.
Concrete and cement-derived materials, which used to be associated with modernism and building in the past, have become alternative materials for artistic productions today. However, like every material, cement has some limitations that affect the design processes such as working range, coloring, shaping and physical and chemical resistance of the final product. In this study, the Calcium Aluminate cement produced under the name ISIDAÇ 40, one of the cements produced by ÇİMSA in accordance with the TS EN 14647 standard, and the granular porcelain casting mud produced by ECZACIBAŞI Esan will be mixed in different proportions, and its suitability for the shaping methods used in the field of ceramics and its effects on the products produced will be discussed.
*This study was produced from the thesis of proficiency in art.

1. INTRODUCTION

The first tools designed for use in daily life predate Homo sapiens. Some of the earliest known stone tools date back about two million years, while products made from less durable materials such as string, leather, and wood date back much earlier. The use of materials such as porcelain and concrete, on the other hand, is much more recent compared to raw materials in nature. Throughout the history, ceramics and its derivatives have emerged from needs of societies and have become widespread. The development of the resulting products has been shaped by the tastes and value judgments of the societies, with political and economic factors playing a role in this process. Although the use of cement-derived binder materials in building action dates back to the Neolithic ages, the discovery of Portland cement, which is in current use today, dates back to the 19th century.

Cement is a powder that forms a plastic mass when mixed with water, sets in time and hardens gradually with increasing strength. TDK defines cement as “ash-colored or white powder obtained by firing and crushing clayey limestones in special kilns, the mud quickly hardening and used as mortar material in buildings” URL-1. According to Yalçın and Gürü, substances with hydraulic binding properties are called cement [1].

The word “cement” comes from the Latin word “cementum” meaning rough, uncut stone pieces [2]. Cement manufacturers have a wide choice of raw materials. Although lime, silica and alumina are the most important components of cement production, all kinds of materials that provide these components are used in cement production.

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The properties of the materials to be added to the cement clinker determine the properties of the cement as well as the type of cement. Cements whose main component is aluminates are called aluminous cement, and cements in which fly ashes obtained by burning hard coal are used as additives are called fly ash cement. Hydraulic cements whose raw materials are white clay, limestone and marble are classified as white cement, while cements obtained by adding 1-5% oxide into white cement are classified as colored cement. Especially cements used in the construction sector are developed according to their intended application. To create a waterproof cement surface to be used in underwater structures, stearic acid is added to the clinker and these cements are classified as impermeable cement.

When mixed with water, binding agents in cement solidify and harden. This reaction of cement with water is called setting, and the time taken until the materials are mixed and completely hardened is called setting time. Additives are added at certain rates to shorten or prolong the setting time. The most commonly used additives are CaSO4 – 2H2O and CaCl2. The proportion of gypsum added to cement is reduced to delay setting and prolong the working time. To accelerate the setting, CaCl2 is used at the rate of 2% of the cement weight. Air temperature is another factor affecting the setting time. While high temperatures accelerate the setting time, lower temperatures extend it [3].

The most widely applied method for coloring cement is the pigment additive added during the mixing process. While the color chroma is higher in the case of white cement, the chroma value is lower in gray cements. The amount of pigment is usually 1-10% of the cement weight, but most common range in practice is 3-6%. The popularization of cement use outside of construction activities has been a strong driving force behind researching decor and shaping practice.

While the most common method used in cement shaping is the casting method, plastering, chipping and layered production technologies are used as well. Depending on the model to be made in the casting method, the mold material can be aluminum, Styrofoam, cardboard, plastic, wood and metal. The key point here is that the mold surface must have a surface and/or flexibility to allow easy removal of the cement, as the cement reaches a hardness close to stone when it sets.

Porcelain is a material that has been used for a much longer time in art practices than cement. The English Ceramics Dictionary defines porcelain as “a kind of glassy ceramic whiteware/ baked product” [4]. In TDK (URL-1) it is defined as “white, hard and translucent pottery made of kaolin”. Porcelain is a hard, non-porous material, impermeable even to glazing, white in firing color or artificially colored, and translucent when thin. The methods used in shaping porcelain are not different from the methods used in shaping other clay bodies and are directly related to the physical structure of the clay. While the most commonly used methods in artistic porcelain production are lathe shaping, hand shaping, and casting methods, computer-aided design and shaping and 3D printing methods are other methods that are expected to be widely used for artistic productions in the future. The most common method used to color plastic or cast porcelain is the addition of metal oxide or pigment. Since metal oxides are purer and stronger than pigments, better results can be obtained in lesser amounts. Depending on the color intensity and quality of the pigment, using them at 2% to 20% allows the mud to be colored in different chroma degrees, while the use of higher amounts spoils the chemical structure of the mud.

The current study analyzes the interactions of Calcium Aluminate cement produced under the name ISIDAÇ 40, and granular porcelain produced by ECZACIBAŞI Esan, using the dual system, and their effects on porcelain shaping and the final product.

During the research process, powder porcelain casting clay produced by ECZACIBAŞI Esan was used in the production of porcelain products and the preparation of cement-porcelain recipe compositions. The dry bond strength of ESC - SD granular porcelain is 20 kg/cm2, its firing shrinkage is 9% (at 1250 °C), and its firing color is cream. The chemical properties of porcelain casting clay produced by the company with the code ESC - SD are shown in Table 1.

Table 1. *Chemical properties of ISIDAÇ 40 cement (%)*

SiO_2	3,60
Al_2O_3	39,80
Fe_2O_3	17,05
CaO	36,20
MgO	0,65
SO_3	0,04
Ignition loss	0,30
Na_2E_q	0,16
Chloride	0,0090
Sulphur	0,01

Table 2. *Chemical analysis of ECZACIBAŞI ESÇ-SD granular porcelain clay (%)*

SiO_2	66,70
Al_2O_3	21,50
Fe_2O_3	0,50
TiO_2	0,60
CaO	0,30
MgO	0,30
Na_2O	3,60
K_2O	0,40
Ignition loss	6,10

The purpose of the thermal applications performed with cement and porcelain is to determine the interaction of the bodies obtained by mixing porcelain and cement in different proportions, and to explore their potential to be converted into products. As such, first, the suitability of cement and porcelain mixtures to porcelain shaping methods by using the dual system was investigated. Table 3 shows the rates of use and codes of porcelain-cement mixtures in the dual system.

Table 3. *Dual system values of ISIDAÇ 40 AC and granular porcelain clay (GP)*

Code		A1	A2	A3	A4	A5	A6	A7	A8	A9
Raw Material %	GP	10	20	30	40	50	60	70	80	90
	% 40 AC	90	80	70	60	50	40	30	20	10

2. EXPERIMENTAL STUDIES

Mixtures prepared through the dual system were first shaped in plaster molds by applying the casting method, but rapid drying and structural deterioration were observed on the surfaces in contact with plaster. Since these deteriorations show similar properties for all values between A1 and A9, these mixtures were determined not to be suitable for the casting method, unlike porcelain clay.

According to the working range calculations of the mixtures, it was observed that it sets and hardens within 1-2 hours, being inversely proportional to the amount of water it contains. Therefore, it was concluded that these mixtures are more similar to cement than porcelain and are not suitable for shaping by hand or shaping with a lathe due to the short working range. This necessitated the use of an alternative shaping method, and the silicone molding method was used to shape these cement-like mixtures. In Figure 1, on the left is the image of all mixtures between A1 and A9 after shaping in the silicone mold, and on the right after firing at 1200 °C.

Figure 1. *The image of all mixtures between A1 - A9 after shaping in a silicone mold (left), and after firing at 1200 °C (right) (Filiz, 2022)*

Physical deteriorations such as peeling and cracking were observed to occur after heat treatment in all mixtures from 1 to 6 in which more than 30% cement was used. Therefore, since the recipe mixtures containing more than 30% cement were observed not to yield positive results after firing, the groups numbered 7 (A7 - B7) with a ratio of 30%, which is the optimum value for which cement can be used for tests such as pressure, permeability and water absorption, were tested in the next stage of the research.

After the optimum value was determined, the suitability of the A7 - B7 mixtures for the pressing method was investigated and the water absorption, dry strength, firing strength, density, firing shrinkage and expansion tests of the samples were carried out in the Ceramic Research Center Laboratories. In the HAM and AC coded samples used in the tests, HAM (STD-P) refers to the sample produced with granular porcelain, and AC refers to the mixture of 70% granular porcelain - 30% alumina cement.

Granular and powder samples used in the tests were moistened at the rate of 6% and shaped in a laboratory type press with a press pressure of 200 kg/cm2, with 50x100 mm size. Figure 2 shows the images of the press forming process.

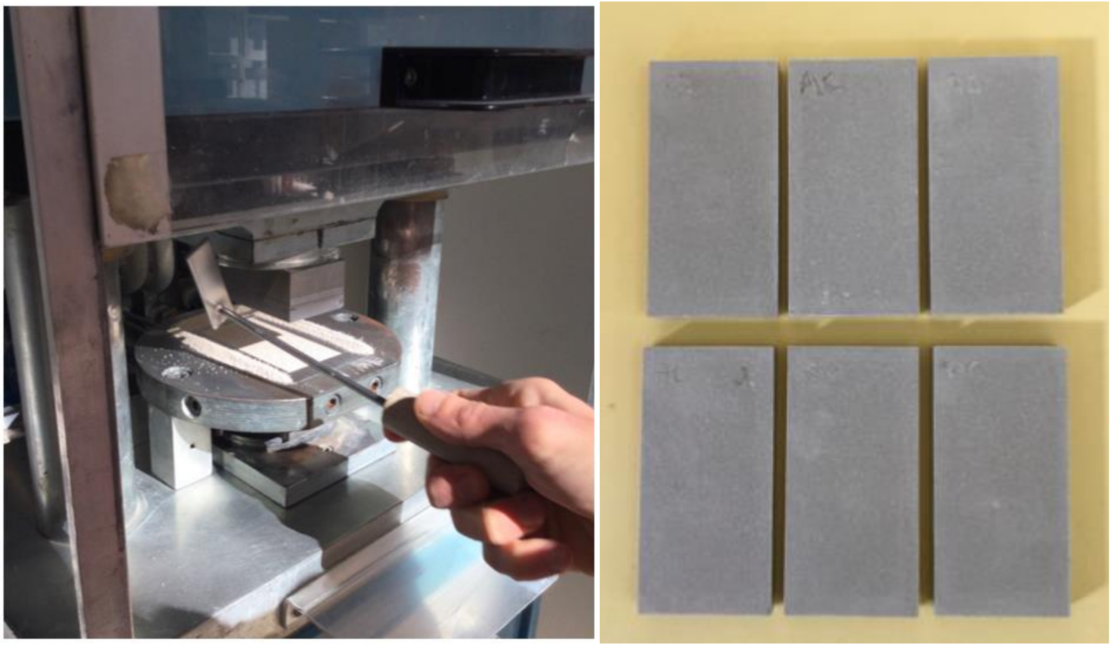


Figure 2. *Powder sample pressed with 200 kg/cm2 pressure (on the left), 50x100 mm shaped samples in the press (on the right) (Filiz, 2022)*

The pressed tablets were dried in an oven at 110°C until they reached a constant weight, and their dry strength was measured. The dried tablets were fired in the Nabertherm LS 12/13 rapid firing oven. Firing regime was applied at a peak temperature of 50 °C/min to 1200 °C, waiting for 6 minutes and cooling at 60 °C/min, for a total of 50 minutes firing regime. Dry strength, baked strength (TS EN 10545-4) and % water absorption (TS EN 10545-3) values of 3 baked and unbaked samples were measured in SAM Standard tests laboratory, and their averages were taken. The parameters for the samples are given in Table 4.

Table 4*. Dry strength, baked strength (TS EN 10545-4) and % water absorption (TS EN 10545-3) values of AC and HAM samples*

Sample code	Water absorption %	Baked strength kg/cm^2	Dry strength kg/cm^2	Density gr/cm^3	Firing shrinkage %	L	a	b
HAM	5,82	9,46	342,23	2,19	8,71	82,67	2,50	8,23
AC	14,99	28,46	154,87	1,94	1,84	61,77	6,59	15,57

"Water absorption can be defined as the water that the baked clay or ceramic mud can get into its open pores. Factors affecting water absorption are the consistency of the clay and the firing temperature. As the conciseness and firing temperature increase, the water absorption ability of the clay decreases. Ceramic muds with a water absorption value above 1% are classified as porous, and ceramic muds with a water absorption value below 1% are classified as non-porous ceramic muds" [5]. Thus, since the water absorption of HAM (STD-P) and AC samples is above 1% at 1200 °C, they are classified as porous muds. It is possible to reduce the water absorption rate through high temperature firing. Turkish Standards

Institute (TSE) groups tiles with a water absorption of more than 10% as wall tiles. A high water absorption rate indicates that the tile cannot be used as an outdoor ceramic. In addition, the increase in water absorption with cement additive is also an indicator of a decrease in the glassy structure (glass phase). Porcelain clay, which has a water absorption rate of 5.82% in its unbaked form, reaches 14.99% water absorption after with the addition of 30% alumina cement. As can be seen in the table, the cement additive increases water absorption. As such, it can be said that 30% cement additive to porcelain clay reduces the viscosity of the clay. The applications clearly reveal that the cement additive negatively affects the plasticity of the mud.

Porcelain clay, which had a dry resistance of 9.46 kg/cm2 without additives, reached a value of 28.46 kg/cm2 with 30% alumina cement. The cement additive added to the porcelain clay was observed to increase the dry strength and decrease the firing strength. The firing resistance of porcelain clay, which was 342.23 kg/cm2 without additives, reached 154.87 kg/cm2 with 30% alumina cement additive.

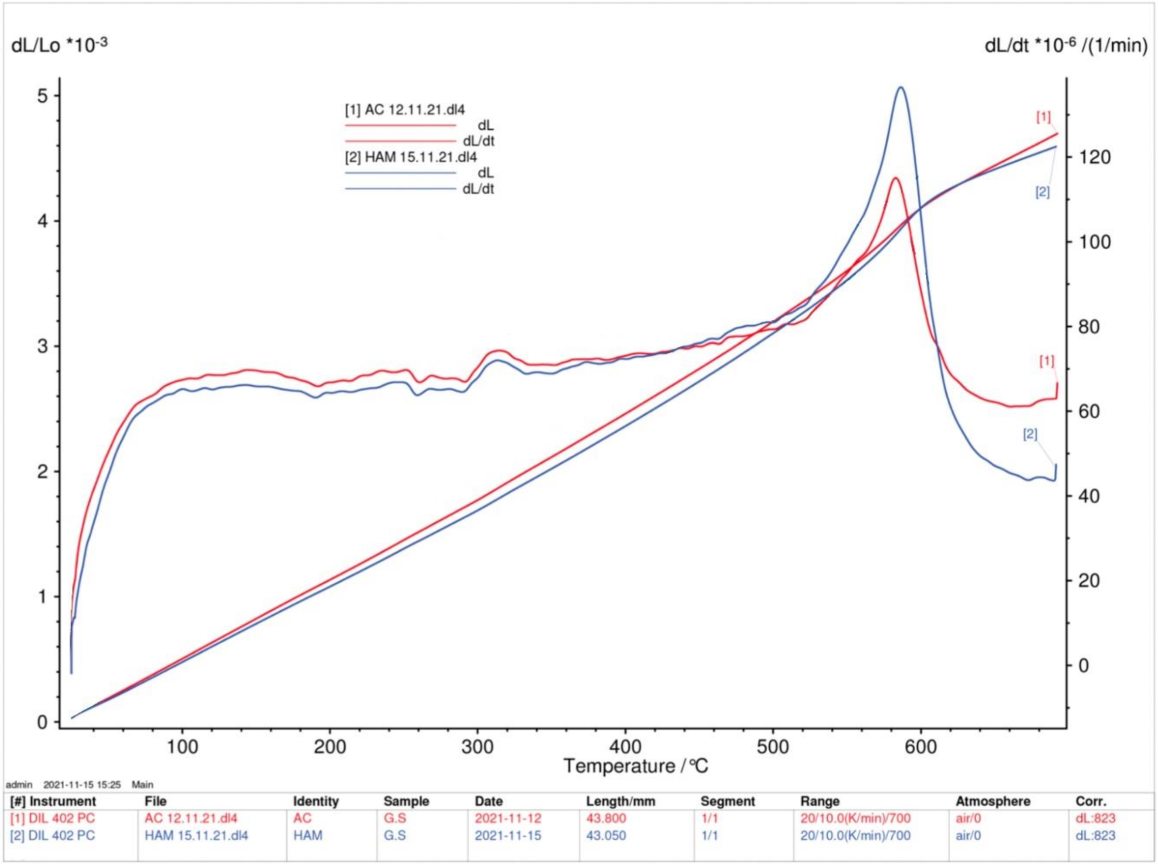
The amount of substance in a unit volume is called density (URL-1). While the density of porcelain mud without additives (STD-P) is 2.19 gr/cm3, with the addition of alumina cement it drops to 1.94 gr/cm3. Two of the most important properties of porcelain mud are low water absorption and high density. The data clearly show that, with the addition of cement to porcelain clay, its water absorption rate increases whereas its density decreases.

“A clay that is dried shrinks until it completely releases its shaping water. After this dry shrinkage, shrinkage continues when the clay is fired. The reason for this shrinkage is not the shaping water of the clay, but the burning of the organic materials in its structure, and the removal of gases and crystal water. As the firing temperature increases, the firing shrinkage and, accordingly, the collective shrinkage values increase” [5]. While the firing shrinkage of the pure porcelain clay sample is 8.71% at 1200 °C peak temperature, it decreases to 1.84% with the addition of 30% alumina cement. As shown by these data, the alumina cement additive reduces the firing shrinkage of porcelain by 79%. It can be concluded that deformations due to firing can be optimized in cement-containing samples when compared with standard samples.

When the color measurement (L-a-b) values are examined through spectrophotometer, the L value of pure porcelain clay was found to be 82.67, which decreased to 61.77 with 30% alumina cement additive. Therefore, it can be concluded that alumina cement additive reduces the whiteness of porcelain.

For the determination of the expansion coefficient of the samples, the size change of the materials against the heat was examined. Thermal expansion values are generally expressed by the linear expansion coefficient (α). In the dilatometer test, the baked sample is sized to measure ~25-50mm long, ~5mm wide, and ~5mm thick. Afterwards, the sample is kept in an oven at a temperature of ~105 °C±5 until it is completely dry. The sample is stabilized by keeping it at room temperature. A standard firing period with a heating rate of 10°C/min up to 700°C was applied for the samples. The dimensional change and expansion coefficients data at 50°C between ~50 °C and 650 °C are given in the table below.

Table 5. *Expansion coefficient graph and data table of HAM and AC coded samples*



Sample	α300x10^{-7}	α400x10^{-7}	α500x10^{-7}
AC	63,1	64,7	66,5
HAM	60,0	62,0	64,5

As part of the study, 3D form analyses were performed with the AC mixtures in the light of the above data. Small-sized forms were designed, and silicone molds of the prepared models were taken. Figure 3 shows the prepared model (model A) before the mold was taken.

Figure 3. *"Model A" form (Filiz, 2022)*

A silicone mold was taken over Model A, and AC (7) mixtures were poured into it, and filled forms were obtained. Forms whose casting process was completed gained their initial strength by setting within 1.5 to 2 hours in proportion to the amount of water in their content. Even if the mixture hardened enough, it was taken out of the mold 1 day after casting, to prevent potential deformations during the removal from the mold. The mold traces on the surface of the forms were retouched with the help of various tools and then fired in an electric ceramic furnace at 1200 ºC. In the form prepared with the AC mixture, no deformation was observed after the heat treatment despite the thickness reaching 10 cm in the inner structure. Figure 4 presents the "Model A" form formed with AC mixture after heat treatment at 1200 ºC.

Figure 4. *"Model A" form formed with AC mixture after heat treatment at 1200 oC (Filiz, 2022)*

It was revealed that the mass of the models prepared with AC mixtures decreased by about 30% compared to the initial mass after heat treatment. While the mass reduction increased in direct proportion to the amount of water, the setting time was inversely proportional to the amount of water. The mass variation of the minimum and maximum amounts of water that can be used for the mixture with 30%AC - 70% GP additive on the baked product is as indicated in Table 6.

Table 6. *The amount of water in the mixture with 30% AC - 70% GP and the mass variation on the baked product (%)*

The amount of watert (%)	Mass weight before firing (g)	Mass weight after firing (g)
65	118	87
75	116	85
90	112	75
100	106	73
110	104	71

Although the increase in water content makes the material lighter in weight, it prolongs the setting time of the material and reduces its strength after firing. Dry strength decreases in mixtures where the water ratio is above 110%, and when the water ratio is below 70%, the mixture solidifies at a rate that does not allow the use of casting method. Therefore, the optimum water ratio was determined as 75%.

One of the two same-volume molds were filled with white vacuum mud and the other with 30% AC - 70% GP additive containing 75% water, and their weights were measured one day later. Accordingly, the weight of the white vacuum mud was measured to be 180 gr, and its mixture weight ratio as 116 gr. The weight after shaping was 64% lighter compared to the white vacuum mud. This reduction is thought to be positive for large-scale sculpture production or for the production of tiles to be used indoors.

The analysis of the 3D form and the glazing potential of the surface continued by using a mixture with 30%AC - 70% GP additive. After the forms obtained from the mixtures were fired at 1200 oC, they were glazed with low-grade Raku glaze and fired at 900 oC. Although the weight of the form and its porous structure provide advantages for transportation and assembly, the application of the glaze did not yield positive results. Since the porous spongy structure absorbs most of the glaze during the firing process, the glaze did not form a glassy layer on the object surface, but created metallic effects in the glazed areas (Figure 5.)

Figure 5. *The image of the AC added form after glazing and firing at 900 oC, "Model A" form (Filiz, 2022)*

Since the glazing process could not develop due to the porous structure of the material, other methods were tried to stick the glaze to the surface. Among these methods, the most effective result was to fill the pores of the surface by applying a primer to the surface of the object after firing at 1200 oC. The results of the glaze tests performed after the primer application are shown in Figure 6.

Figure 6. *Samples glazed with Raku glaze (at 900 oC) after priming (Filiz, 2022)*

3. CONCLUSION

The tests performed by adding alumina cement (AC) components to a commercial porcelain clay and firing it revealed some significant findings regarding the potential of the resulting mixture to be converted into a product. Notably, the mass reduction in the mixture after heat treatment is a positive result that can be used in large-scale porcelain sculpture applications in public spaces. The AC additive mixture, which yields a lighter weight than a porcelain mass without cement additive, offers advantages such as moving the form more easily, portability, and mounting ease in its applications. In addition, the fact that AC additive reduces firing shrinkage by 79% shows that deformations caused by firing shrinkage can be prevented. Despite these advantages, the product is more concrete-like, which requires shaping with materials such as silicone and rubber, which are morecostly than other mold materials. In addition, the porous structure of the material, which is the source of its lightness, causes some application difficulties during the glazing process. However, the problems caused by glazing can be reduced by applying primer on the surface before the glazing process.

The test results show that AC additive mixtures are suitable for the press forming method, and they can be used as a novel alternative material in interior wall tiles. AC mixtures offer new surface effects not only in their structural properties, but also in the combination of the surface properties of concrete and porcelain. Furthermore, the mixture may be used as a source for developing new approaches or inspiring creative designs influenced by current architectural aesthetic trends, especially by the brutalist and antiquated.

REFERENCES

[1] Yalçın, H., Gürü, M. (2006). *Çimento ve Beton.* Ankara: Palme Yayınevi p.15

[2] Aragaw, T., A. (2020). Cement Types, Admixtures, and Technical Procedures of Cement

[3] Şimşek, O. (2004). *Beton ve Beton Teknolojisi.* Ankara: Seçkin Yayıncılık.

[4] Dodd, A. and Murfin, D. (1994). *Dictionary of Ceramics.* The Institute of Materials, London.

[5] Arcasoy, A., Başkırkan, H. (2020). *Seramik Teknolojisi.* İstanbul: Literatür Yayıncılık

[6] URL-1. https://sozluk.gov.tr/ Last Accessed: 24.10.2022