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Development of a Low Density (Light) Colorful Gas Ceramic Floor Tile for Outdoor Floor Applications Using Recovered Ceramic Wastes Treatment

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Abstract: Nowadays, gas ceramics have become an important role part of making lighter and more durable tiles which are used for outdoor floor applications. In addition to this, its commercial potentials are quite high due to the long life of the gas ceramics. In line with this purpose, it is aimed to develop gas ceramic floor tiles for outdoor floor applications which have the advantages such as lightweight, low density, high strength and also being differently colorful. By adding 30-40% of production wastes into the recipes, it is supposed to get into market with new gas ceramic products which have both innovative properties and also to provide wastes recycling. Within the scope of this project, in order to have the desired structural and mechanical properties of the final products, the materials to be used in the recipes have been selected so that the furnace process be optimized. Raw materials such as clay, calcite, pegmatite and silicon carbide were obtained from different mines. Due to the fact that the tiles have been planned to be colorful, so that color pigments to be used were obtained from suppliers. In pretreatment stage the ceramic sludge was prepared then viscosity and density were controlled and prototype samples from furnace were tested and analyzed. In this context, engineering studies were made for pore size distributions /homogeneities, sieve analysis and firing process. This study is unique owing to the fact that new recipes will be tried in the factory. Moreover, this study is a research and development (R&D) project because with the addition of the production wastes in recipes not only will the production wastes be eliminated but also the consumption amount of supplied raw materials will be reduced. In the light of foregoing information about gas ceramic technology, final products will be more economical, have homogeneous structure and high compressive strength compared with other feasible alternatives. Furthermore, presented innovative final products have been planned to be colorful in accordance with raw materials and developed manufacturing methods. These products would be the first example in the ceramic/porcelain floor tiles industry which have been developed on a global scale with the use of wastes are raw materials.

Keywords: Waste management, gas ceramic, construction materials, filter press cake.

INTRODUCTION

Ceramic materials have some properties like fragile, low tensile stresses and impact loads, plastic deformation not like metals and low resistance to sudden mechanical and thermal changes and because of these properties the usage of monolithic ceramics in structural applications are prevented. The most important disadvantages of ceramics were low fracture toughness (1). Various methods have been developed to increase fracture toughness of ceramic materials. All these methods are based on the creation of mechanisms that allow the dissolution of energy during the fracture by uniformly distributing a second phase in the fragile ceramic matrix. The used secondary phases are as follows: Ductile materials, materials that provide phase transformation, the development of rhodonite grains in these structures by using in situ methods and to improve reinforcing materials in different forms (continuous fiber, etc.) was provided (2-3).

Silicon carbide (SiC) is a crystalline material that has a very high hardness, high chemical resistivity and thermal conductivity, also is an important semiconductor which has been widely used in extensive range of applications (4). Silicon carbide appears in two different crystalline forms, namely hexagonal α-silicon carbide, cubic β-silicon carbide and also occurs in several forms as non-fibrous and polycrystalline fibers (5).

There are several studies based on production of gas ceramics. Those studies focused mainly on the effects of compression strength and density of gas ceramic manufacturing. In the study of Suleyman Akpinar et al (6), cordierite-based silicon carbide doped ceramic foam materials production and characterization has been studied. In this study, the measured compression strength values vary in the range of 0,27 - 0,52 MPa. This compression strength values are well below the target value.

When the density values were compared, it was seen that data were obtained between 0.41 and 0.48 g/cm^3. It is seen that our product, which is planned to be low density, is higher than desired when compared with the values in the range of 0.21-0.41 g / cm^3. F.A. Costa Oliveira et al (7) calculated the bulk density of the materials obtained from similar studies in the related literature as 0.29 g / cm^3 and the compressive strength was 0.24 MPa. When these data are compared with the data obtained in the studies in the article, obtained values of compressive strength is 4.5 times and density values are 2 times lower than the literature.

In the literature, it is understood from the research that the amount of solid matter in ceramic slurry has great importance in the studies related to the production of ceramic foam filters. This causes an increase in the cost of the prescription and the energy consumption. Considering these disadvantages, we have worked on the development of a product which is homogenous with the use of 55-60% production waste and with a higher compressive strength and a more economical product compared to the existing alternatives. The colored gas ceramic technology developed in the project is the first example developed on a global scale for the use in outdoor floor applications with the advantage of its lightness and obtaining the desired colors. According to other commercial insulation materials, non-flammability property is one of the important parameters.

EXPERIMENTAL PROCEDURE

Materials and Method

This investigation was performed with an industrial spray-dried powder normally used for the production of gas ceramics. Within the scope of this project, the pore forming agent (SiC) was supplied from ESAN Magnesium Company in Turkey. The materials used in recipes albita, clay and calcite were obtained from quarries in Eskisehir. Pegmatite was purchased from Has Ozcelik Mining Company in Bilecik. All composition of raw materials are given in Table 1. Na-Silicate was used as a fluidizer. Since gas ceramic have been planned to be colorful, green, blue and pink pigments which have been selected from the suppliers, were purchased from Torrecid Company in Eskişehir.

Table 1: Raw Material Percentages in Colorful Gas Ceramic Recipes.

Component	Content (wt. %)
Production Waste	36
Clay Blend	32
Pegmatite Blend	18
Calcite	2
Albita	12
SiC(Foaming Agent)	0.3
Pigment	5

Filter Press Production

The total capacity of the wastewater treatment plant in our factory was 1350 m^3/day. 20 tons of filter press cake was obtained per day. Process waste water comes from the sludge preparation, glaze preparation, filter cake preparation, dimensioning and finishing, decor lines, decor cutting and glazing process were brought to the equalization tank where they were collected and mixed homogeneously. The collected wastewater was first passed through a coarse screen with a gap of 5 mm and then taken to the sand trap unit. With this grill and sand catcher, materials that are physically hold able in the wastewater and materials that may damage the equipment in the treatment plant were kept. From here, the wastewater would pass to the balancing pool.

Wastewater from this tank was sent to the coagulation pool which was the first unit of chemical treatment with waste water pumps at a constant flow rate. In this unit, PAC (Poly Aluminum Chloride) inorganic material derivatives were used as a coagulant. After that the waste water was sent to the flocculation tank. The chemical flocculants formed in this unit could easily be turned into large flocculants by using anionic polyelectrolyte as flocculant. Flocculants and coagulants were fed in dosages determined as a result of tests conducted according to the content of incoming waste water. After this stage, the waste water reached the precipitation tank and was separated by gravity precipitation process.

Wastewater in the balancing pool was taken to the coagulation pool by a pump. The coagulant was dosed to the appropriate coagulant (we used PACs). Wastewater passed into the flocculation pool after coagulation pool. The polyelectrolyte was dosed and mixed with the dosing pump in order to enlarge the resulting flocks. Wastewater passed to the sedimentation pool. In here, the flocks formed in the flocculation pool were allowed to settle. The wastewater was then taken to the neutralization pool. In this pool, acid was added to keep the pH neutral. Sludge particles from the sedimentation tank were collected in the sludge condensation tank. An industrial filter press was a tool used in separation processes, specifically to separate solids and liquids. The sludge at the bottom of the sedimentation pool is transferred to the sludge tank with the sludge pump. Filter presses were utilized in order to separate water from mud to reuse the water. In this unit, the sludge was reduced by compressing the water content and could be removed as solid waste or used as raw material in the plant. The filtrate from the filter press was given to the treatment plant entrance for purification.

The cakes began to form with high flow rate of the filtrate. Cakes were totally formed at the maximum pressure. After that, cakes discharged from filter press. As a result of the filter press system, humidity values of cakes were calculated between 28-32%. The sludge cake formed at the end of the filtration process was loaded from the system to the trailer and the dried sludge was conveyed to the storage area. The water treated in this system was recycled by re-using in the plant. In Figure.1, the waste water treatment is shown the process in our company.

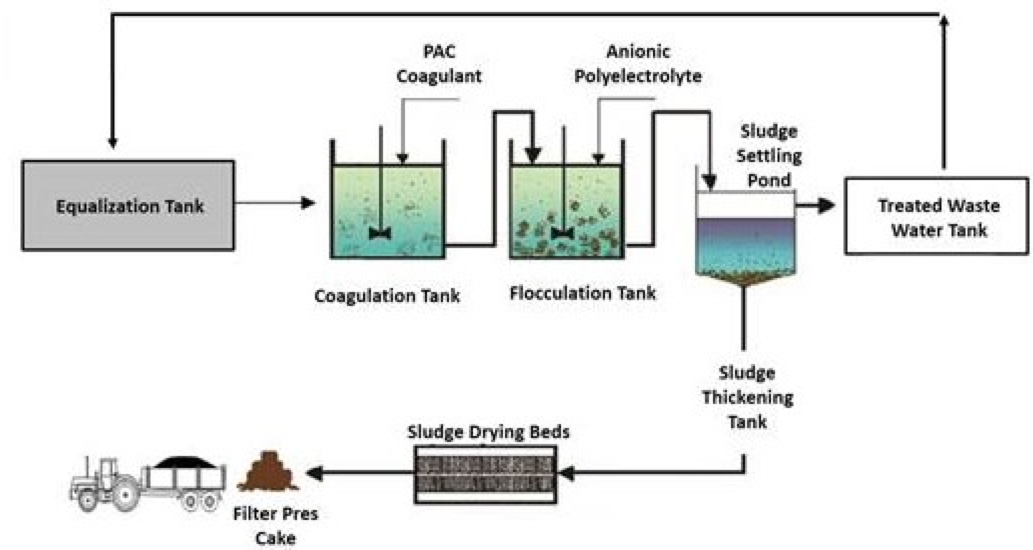

Figure 1: Waste Water Treatment Process Overview.

Gas Ceramic Preparation

In the present study, raw materials and pigments were weighed at 500 g and mixed with 45-46% water. Prepared recipes were milled using ball mills with a capacity of 800 mL. The slurry (ceramic powder and pore-forming agent) was mechanically mixed for 4 hours until uniform distribution was observed. The slurries normally contain 30 to 40 weight percent of production waste solids.

To optimize milling time, engineering studies were carried out to investigate the effect of grain sizes on pore distributions/homogeneity and density of the final products to find the optimal size with its corresponding milling time. The slurries characteristic parameters were summarized in Table.2. Also to evaluate milling efficiency, the slurry was passed through a 63- mesh sieve and its residue was weighted to see how much of the slurry was sufficiently milled. The slurries were dried on metal trays in the drying oven at 100 °C. Thus, the water in the slurries was evaporated.

Table 2: Slurry characteristic parameters.

Sieve Analysis	1.07±0.1
Viscosity (s)	45-50
Slurry Densities (g/L)	1650 ±30

After drying, dried sludge was reduced to fine particles with iron roll and the particles size distribution were determined by means of sieves. Granular particles ware simultaneously weighted at 700 g each of gypsum cassettes shown in Figure 2. Dimensions of gypsum cassettes were manufactured as 15 x 20 cm in our laboratory.

Figure 2: Gypsum Cassettes.

Gas Ceramic Firing Process

Granules particle in cassettes were baked at 1200 °C for 4 hours using an electric ceramic kiln. The initial furnace temperature was measured as 45 °C and then gradually increased to 1200 °C until the end of the furnace firing time reached. The required heat for the pre-drying was provided by the fan in the furnace at various points. Thus, the final moisture content of the formed products had been reduced to less than 1% at the end of the pre-drying process. Furthermore, in cases where the products were very humid and the drying temperature was not enough, the temperature was raised up to 160 °C. Subsequently at the end of firing, the furnace temperature was gradually reduced to 100 °C by means of the heat through the kiln shaft to the cooling zone. Afterward, the width, length and height of the gas ceramics were measured to calculate the density.

Material characterization

Semi quantitative analysis method is a unique and powerful method for elemental screening of materials. Besides, semi quantitative analysis in modern XRF method is performed without any reference materials used for the unknown sample analysis. In addition to this, optical analysis (Leica EZ4HD microscope) was applied used to investigate the porous morphology. Samples were cut from the final products using a cutting machine. At least three samples were prepared for each analysis. The images of samples were acquired with a digital camera combined with a microscope. The total and average pore area of samples were measured from images. The Archimedes' method (using ethylene glycol as immersion fluid) was employed to evaluate the open porosity, bulk density, and water absorption of the samples.

Determination of bending strength by the three point method was used for measuring the mechanical strength of samples. To measure the mechanical strength of the samples, bending strength was determined using three point method on five specimen while their porous layers were faced down.

RESULTS AND DISCUSSION

Microstructures of Gas Ceramics

Dry casting method is used for the production of gas ceramics. In this method, ceramic masse was obtained by pouring ceramic powder into a gypsum cordierite-based mold. No compression was applied. As a result of the optimizations for the standard foam recipe, the firing temperature was determined to be 1205 °C. Prepared foams were tested to determine the material properties. Density and viscosity values were measured. The obtained density, viscosity, and sieve residue values are given in Table 3.

Table 3: Density and sieve analysis values.

Test No	R-169	R-170	R-171	R-172	R-173
Density (g/cm^3)	0.209	0.269	0.177	0.172	0.143
Sieve Analysis	1.09	1.11	1.07	1.17	1.17
Viscosity (s)			45-50		
Density (g/L)			1650 ±30		

It was observed that the density value of the sample with the R-173 prescription code reached the desired low density. Experiments have been made on the temperature of the furnace for cost optimization via this recipe. It is foreseen that it will be sintered again by lowering the furnace regime. In the studies, the kiln regime temperature was decreased to 14 ºC and the sintering was determined as 1186 ºC for 4 hours. The sample code was recorded as R-174. The density value of the R-174 sample is calculated 0.204 g/cm^3 and the sieve balance is 1.1. The image of the gas ceramic tile with the final product is shown in Figure 3.

Figure 3: Standard (colorless) gas ceramic tile with foam structure.

The very fine structure of the powder dimensions increases the reaction surface and facilitates sintering. Therefore, it will be possible to carry out the reaction at shorter periods or at lower temperatures. Besides the differences in powder sizes, powder particle size distributions are also of great importance. Particular attention was paid to this parameter for masse density.

Experiments were made with appropriate molding parameters and kiln regime calculations in order to minimize the differences in color tones which may occur in the colors to be used in production. After the colorless optimization, the samples were sintered at 1186 ºC for 4 hours with the same procedures as various color alternatives. The visual comparison of the products obtained is given in Table 4.

Characterization of Gas Ceramic

In light of the past experience of our company and the information obtained from the literature, one of the biggest difficulties that we may encounter in our project will be the fact that the cake is not stable. The cake is not homogeneous because it is obtained from waste from all parts of the factory. In order to prevent this situation, the cake will be blended and dried in the summer months. The moisture content of the waste after drying is expected to be a maximum of 16%. Chemical analysis results are of great importance in terms of their use in prescription due to the lack of homogeneity of the cake samples obtained. Semi quantitative analyses demonstrates determination of the chemical composition in ceramic masse samples by using the semi-quantitative analysis method. Table 5 shows the results of the chemical analysis of production waste taken from our waste water treatment plant in the summer months.

Table 4: Gas Ceramic Surfaces with pigment Composition.

Pigment Composition (g)	Gas Ceramic Surface
100 g of Masse Composition	
100 g of Masse Composition +5 g of AL-3304	
100 g of Masse Composition +5 g of AL-73017	
100 g of Masse Composition +5 g of AL-1304	

Table 5: Semi-quantitative (SQX) Analysis Results for Production Waste.

No	Component	Result (Mass %)	Detn. limit	El. Line	Intensity	w/o normal
1	MgO	1.0542	0.0583	Mg-KA	0.5940	1.0489
2	Al_2O_3	14.1483	0.1104	Al-KA	25.4299	14.0772
3	SiO_2	63.8091	0.0653	Si-KA	107.3239	63.4887
4	P_2O_5	0.1244	0.0091	P-KA	0.6230	0.1238
5	K_2O	2.8160	0.0110	K-KA	28.6577	2.8018
6	CaO	6.5865	0.0138	Ca-KA	53.4828	6.5535
7	TiO_2	0.3575	0.0246	Ti-KA	1.4084	0.3557
8	Fe_2O_3	1.1323	0.0083	Fe-KA	32.1648	1.1266
9	ZnO	2.4076	0.0042	Zn-KA	255.0013	2.3955
10	ZrO_2	2.1202	0.0197	Zr-KB	167.5752	2.1095
11	A.Z	5.4440	-	-	-	5.4440

According to the results of the chemical analysis of cake waste during our pre-feasibility study, the fact that the fire loss is not very high, showing that there will be no loss of raw material and gas output will be minimum. There are criteria to be considered in determining the ratio of filter press waste during use in the recipe. These can be called storage problems and pollution. Due to the contamination of the cake, there is a high probability of surface defects such as perforation and dent on the glazed surface. In addition, the use of waste in the recipe can cause rheological problems.

The filter press cake obtained from the treatment plant was dried and blended and then added to the recipes. The results of the quantitative analysis to determine the content of the materials by semi - quantitative (SQX) analysis by X - ray spectroscopy are given in Figure 4.

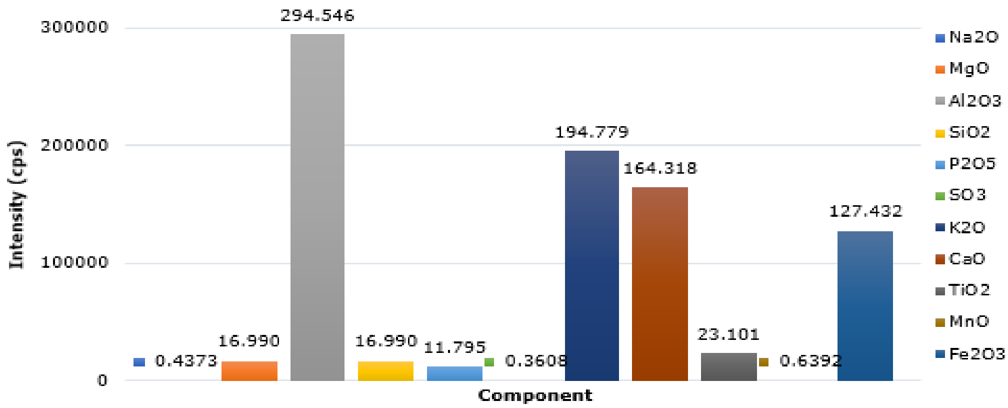

Figure 4: Semi-quantitative (SQX) Analysis Results for Gas Ceramic Masse.

At the end of the analysis, the components in the sample were determined. When the results were examined, it was found that the components complying with the operating standards did not contain any harmful components. It has been determined that fire loss is measured as 9,70% by mass and this value is suitable for working conditions. In addition, physical testing of the final products was performed.

Guidelines and Requirements of Gas Ceramics

Within the scope of the products obtained in our project, the original furnace process design, formulation and cassette designs have been done in order to create commercial potential in the properties such as color and pore homogeneity and strength. ISO creates documents that provide requirements, specifications, guidelines or characteristics that can be used consistently to ensure that materials, products, processes and services are fit for their purpose shown in Table 7.

For ceramic tiles, water absorption is used to classify products. This document outlines the procedures for the measurement of water absorption and related properties using classical Archimedean method. Impregnation of the open porosity is achieved by a vacuum method only. After the received samples had been tested according to standard ISO 10545-3, they measured is below the 0.05. In addition to this, frost resistance is a quality for tiles have when they are subjected to water at temperatures lower than 0 °C without being damaged by stress generated by their moisture content freezing. Ceramic tiles are defined as resistance or not. As the water absorption of ceramic tiles is very low most ceramic tiles are frost resistant as in Table 7.

This ISO 40545-9 standard defines a test method for determining the resistance to thermal shock of all ceramic tiles under normal conditions of use. The variation of the characteristics of the tested tiles was visually controlled. The results was determined as resistant. This crazing resistance test method is for the determination of the resistance to the formation of crazes by subjecting whole tiles to steam at high pressure in an autoclave, then examination of the tiles for crazes after applying a stain to the glazed surface. Resistance to chemicals is the capacity of the surface at room temperature to tolerate contact with chemicals (domestic products, staining chemicals, pool additives, acids and solvents) without alteration in its appearance. Unglazed tiles are divided into categories starting with U and for glazed tiles the category starts with G. Category A means they was no visible effect and for C there is a visible effect on the sides of the tile and the surface.

Light fastness and color fastness of ceramic tiles was determined by exposure to radiation of a mercury vapor lamp according to standard DIN 51094. This test enables the light fastness of ceramic tiles was evaluated with relation to changes in color under the action of artificial light, where the sample was tested and subjected for 28 days to the action of ultraviolet rays. The results showed that there were no visual differences between the tiles.

Table 6: Test Analysis Results for Gas Ceramic.

Tests	Standard Limits	Experimental Results
Water absorption, apparent porosity, apparent relative density and bulk density of ceramic tiles	ISO 10545-3	≤0.05
Resistance To Thermal Shock	ISO 40545-9	Resistant
Crazing resistance	ISO 40545-11	Resistant
Frost resistance	ISO 40545-12	Resistant
Resistance to high concentrations of acids and alkalis	ISO 40545-13	GA
Resistance to household chemicals and swimming pool salts	ISO 40545-13	A
Surface hardness Mohs	EN 101	7
Testing of the light fastness and color fastness of ceramic tiles	DIN 51094	Resistant

CONCLUSION

The effects of pore distributions / homogeneity and density on the properties of materials were investigated. It was observed that the size distribution of the colorful gas ceramic has a similar pore structure. It was determined that changes in the durability, density and heat permeability of the material to cause pore homogeneity and size distribution as well as open / closed pores. When the test results were examined, pore properties depend on the change of sieve residue and also pore sizes have been increase with the increase of sieve residue. As a result of this, volume of gas ceramic has increased and its density has decreased. Besides, the interaction of raw materials with between each other is also very important. Raw materials may increase the properties of each other positively or may reduce effect. Therefore, it seen that a difference in pore size distribution and density variation of the final products during the experiments. Most importantly, it is one of the innovative aspects of project that creates a healthy living space for the environment by holding the moisture owing to the high diffusion feature. The advantages of the final product and its superior properties from other alternative materials has high thermal insulation, high compression strength, flame retardant, low water absorption (~0) and low density. It was determined to use areas such as in heat insulation for ceramic floor tiles, in prefabricated buildings and also floor applications purpose for garden use decoratively considering that the properties of product. A competitive advantage is provided in virtue of the process design which can be changed according to the usage conditions and also the potential can be applied to the desired properties.

Within this scope, it is aimed to carry out alternative studies in line with the global demands. The final product, using by especially 30-40% of production waste, has become a new point of view for the market in gas ceramic applications. Seranit-Serra product range has been expanded and also has been entered into the new market considering the characteristics and structure of the products.

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