DEVELOPMENT OF POROUS CERAMICS FOR AIR DIFFUSER APPLICATIONS

A Thesis Submitted to the
Graduate School of Engineering and Sciences of
İzmir Institute of Technology
In Partial Fullfilment of the Requirements for the Degree of

MASTER OF SCIENCE

in Materials Science and Engineering

by
Aslı KÜÇÜK

June 2009
İZMİR

We approve the thesis of **Aslı KÜÇÜK**

Assoc. Prof. Dr. Sedat AKKURT
Supervisor

Assoc. Prof. Dr. Selahattin YILMAZ
Co-Supervisor

Prof. Dr. Muhsin ÇİFTÇİOĞLU
Committee Member

Asst. Prof. Dr. Şebnem ELÇİ
Committee Member

30 June 2009

Prof. Dr. Mustafa GÜDEN
Head of Material Science and
Engineering Department

Prof. Dr. Hasan BÖKE
Dean of the Graduate School of
Engineering and Science

ACKNOWLEDGEMENT

I would like to thank the Materials Science and Engineering Department at Izmir Institute of Technology for accepting me into their program and giving me the opportunity to attain an M.S degree in this field. I am greatly thankful to my advisor, Assoc. Prof. Dr. Sedat Akkurt for his patience, encouragement, and guidance during this study. I would like to thank all of my friends who help me all of the steps in this work and Center for Materials Research staff for their help.

Finally, I would like to thank especially to my family for their support, patience, understanding, encouragement and help.

ABSTRACT

DEVELOPMENT OF POROUS CERAMICS FOR AIR DIFFUSER APPLICATIONS

Porous ceramic for bubbling air into water at 1 bar of pressure was successfully developed. Different compositions were tested. The use of superground alumina was not successful because the particle size was too small and the pores were closed thereby forbidding any air transport through the ceramic. Additions of corn starch to this material did not help much because any contribution of porosity was closed porosity and that was useless in air transport. Limited success was accomplished when clay, quartz and corn starch were used but this time the pressure needed to produce a reasonable amount of bubble in water was higher than 1 bar which was the initially set goal for this project. Bayer alumina was used as a replacement for superground Alcoa alumina to help with porosity because these powders are well known to be agglomerated and to offer high amount of porosity. Smaller fraction of quartz was added to help with strength and clay to assist in forming and very good results were obtained. Ceramics made from 50% Bayer alumina and 50% clay provided very good oxygenation of water. However, their strength was not as good as samples made from 50% Bayer alumina, 20% quartz and 30% clay. These latter samples had higher strength and slightly lower oxygenation. The use of these ceramics as air diffusers can help oxygenate water which is needed in a lot of different applications.

Key words: Porous ceramic, air diffuser, alumina

ÖZET

HAVA DİFÜZÖRÜ UYGULAMALARI İÇİN GÖZENEKLİ SERAMİK GELİŞTİRİLMESİ

Bu tezde 1 bar basınç altında hava kabarcığı oluşturabilen gözenekli seramiklerin geliştirilmesi amaçlanmıştır. Bu amaç doğrultusunda değişik kompozisyonlara sahip örnekler test edilmiştir. Çalışılmış olunan ince taneli alumina (superground alumina) başarılı olmamıştır. Bunun nedeni parçaçık büyüklüğünün ufak olması ve gözeneklerin kapalı olmasından dolayı seramikten hava geçişinin engellenmesidir. Mısır nişastasının organik gözenek oluşturucu olarak ince taneli aluminaya eklenmesi sisteme ciddi bir katkı sağlamamıştır. Bunun nedeni oluşan gözeneklerin kapalı olması ve hava transferini sağlamamasıdır. Kil, quartz ve mısır nişastası sisteminde küçük bir başarı elde edilmiştir ancak başta amaçlanan 1 bar da geçirgenlik sağlanamamış daha yüksek basınçlarda geçirgenlik sağlanabilmiştir. Bayer alumina aglomere olan yapısından dolayı gözenek miktarını arttırmaktadır. Bu nedenle ince taneli alumina Bayer alumina ile değiştirilmiştir. Mukavemeti arttırmak amacıyla sisteme kuvarz eklendi ve seramiğin kolay şekillenmesini sağlamak için sisteme kil eklendi. Bunlar sonucunda başarılı örneklere ulaşıldı. %50 Bayer alumina ve %50 kil içeren örnek, suyun oksijenlendirilmesinde çok başarılı oldu. Ancak mukavemeti %50 Bayer alumina, %20 kuvarz ve %30 kil içeren örneklerden daha az olarak ölçüldü. Bu son örnekler (Bayer alumina, kuvarz ve kil içeren) daha yüksek mukavemet değerine ve az miktarda düşük oksijenlendirme oranına sahiptir. Birçok farklı uygulamada suyun oksijenlendirilmesinde seramiklerin hava difüzörlerinin kullanımı yarar sağlayabilecektir.

Anahtar kelime: Gözenekli seramik, hava difüzörü, alumina

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Porous ceramics are attracting attention because of their specific structural properties such as low bulk density, low specific heat, low thermal conductivity, high surface area and high permeability. Characteristic properties of porous ceramics make them suitable for different applications like: filters for molten metals and hot gases, refractory linings for furnaces, and porous implants in the area of biomaterials (Sepulveda and Binner 1999), thermal coatings, human bone substrates. (Sadowski and Samborski 2007). And also porous ceramics are widely used as catalyst carriers, separation membranes and diffusers (Isobe and Tomital 2006).

Generally, closed pore ceramics are preferred as thermal insulator, open pore ceramics are prefered for fluid transport, such as filters and diffusers, micropores are selected for sewage purification, macropores are used for bone implantation and combination of different morphologic pores are designed as monolithic matrix (Mao and Wanga 2008). An excellent literature review of porous ceramics was recently done by Studart et.al. (Studart and Gozenbach 2006).

The use of porous ceramics in air diffuser applications is commercially achieved. There are products in the market that are competing with polymeric and metallic porous materials in producing air bubbles underwater. There are lots of advantages for ceramic air diffusers like high oxygen transfer efficiency, high resistance to clogging, high resistance to corrosion, wide air flow range, low pressure loss, water-stirring effect and intermittent operation capability (Pondexpo 2009).

Air diffusers are used for aquariums, fish farm and fish pond aeration, pond filter system aeration, lake and stream aeration, municipal and industrial wastewater treatment, septic system aeration, clean water treatment and sludge stabilization.

Air diffuser is very important for marine life. Because oxygenation occurs by air diffuser. When air is pressured through these materials, tortuous pores allow air to make its way to the other end of the ceramic material and then into the water. When the

bubbles are created at the point of contact between ceramic and water, the bubbles quickly rise to the top surface of the water. During this travel of the bubble, oxygen is transferred from the bubble to the water. Water can be oxygenated up to the saturation point (Parkhill and Gulliver 1997). Increase in dissolved oxygen amount in water means that increasing fish stocks for fish ponds (TC. Başbakanlık GAP projesi 2004)

In this thesis, porous diffuser ceramics are made by aluminosilicate compositions. A cost effective solution to the manufacture of porous aluminosilicate ceramic is proposed. Bayer alumina which is a semi-product of aluminum metal production was investigated to understand if it could be suitable for use as a ceramic powder. Because of their large concentrations of sodium and large amounts of porosity in the as-calcined state they are so far not used in ceramics industry to a significant degree. This failure is turned into an advantage in this study by utilizing the porous character of these powders in making a porous ceramic.

CHAPTER 2

LITERATURE SURVEY

In this chapter, information provided about properties of porous ceramics, permeability of the porous ceramics, air diffusers, oxygenation of water, Bayer process for producing alumina, forming methods of the ceramics and phase equilibria in aluminosilicate systems are introduced.

2.1. Porous Ceramics

Porous ceramics are used for many special engineering applications. Their specific structural properties make them perfect materials for some applications. Especially thier high separation efficiency, non-corrosive structures and thermal resistance as well as mechanical strength and structural stability makes them very efficient materials for engineering applications (Dong and Diwu 2007). Moreover porous ceramics have low mass density, high chemical saturation and resistance to abrasion. The other causes of preference for porous ceramics for engineering ceramics are the abundance of low-cost source of raw materials. (Erol 2008)

Characteristic properties of porous ceramics make them suitable for different applications like: filters for molten metals and hot gases, refractory linings for furnaces, and porous implants in the area of biomaterials (Sepulveda and Binner 1999), thermal coatings, human bone substrates. (Sadowski and Samborski 2007). And also porous ceramics are widely used as catalyst carriers, separation membranes and diffusers (Isobe and Tomita1 2006).

The critical properties of porous ceramics for this thesis are high permeability and mechanical strength. The pore size and homogeneous distribution of pores are

important for permeability. Conventional partial sintering methods generally form pores of about $1\mu m^3$ (Isobe and Kameshima 2007). Mechanical strength is also important for diffusers. Crack free samples are important for this property. However, it is not possible to obtain a material with high permeability and strength. These two factors are inversely proportional to each other. Permeability generally increases with increasing porosity, regardless of the mechanical strength (Acchara and Souzaa 2009).

2.2. Permeability of Porous Ceramics

For this thesis permeability of porous ceramics is very important parameter for air diffusers. According to fluid dynamic model, permeability of a given material is presented by constants fitted. (Innocentini and Pandolfelli 2001).

Relationship well accepted in the literature that expresses the parabolic relationship between the pressure drop (ΔP) through the medium and the resulting superficial velocity (v_s) is expressed in Forchheimer's equation ; (Innocentinia and Rodriguesa 2009);

$$\frac{\Delta P}{L} = (\frac{\mu}{k_1})v_s + (\frac{\rho}{k_2})v_s^2 \tag{2.1}$$

For incompressible flow (liquids):

$$\Delta P = P_i - P_o \tag{2.2}$$

and for compressible flow (gases and vapours):

$$\Delta P = \frac{P_i^2 - P_0^2}{2P} \tag{2.3}$$

Where Pi and Po are, respectively, the absolute pressures at the sample's inlet and outlet surfaces exposed to airflow; v_s is the superficial air velocity; L is the sample thickness; μ is the air viscosity and ρ is the air density calculated for P_o at the testing temperature. The terms k_1 and k_2, are known as Darcian and non-Darcian permeability constants (Innocentini and Pandolfelli 2004). Forchheimer's equation is particularly

reliable for ceramic materials and can be expressed for airflow (Canon and Sandler 1997)

According to fluid dynamics and hydrology, an equation that described the flow of a fluid through a porous medium is formulated by Henry Darcy as Darcy's law. This law is formulated by using the results of experiments about the flow of water through beds of sand so it can be used for airflow in the permeable porous ceramics. Darcy's law is obtained by making some simplifications in Forchheimer's equation (Dryden Aqua 2009).

Darcy's law is not valid for all flows. It is only valid for slow, viscous flow or laminar flow. According to Reynolds number, flow regime of the system can be found. Reynolds number is a unitless parameter and when it becomes less than one the flow becomes laminar. Therefore, Darcy's law can be used for this system. Formulation of Reynolds number is shown in equation 2.4. (Edinburg University 2002).

$$Re = \frac{\rho v d}{\mu} \tag{2.4}$$

Where ρ is the density of the fluid (units of mass per volume), v is the specific discharge (with units of length per time), d is a representative grain diameter for the porous medium and μ is the dynamic viscosity of the fluid. If the Reynolds number shows that the flow is laminar Darcy's law can be used. Figure 2.1 shows simple Darcy flow through a medium (Dryden Aqua 2009).

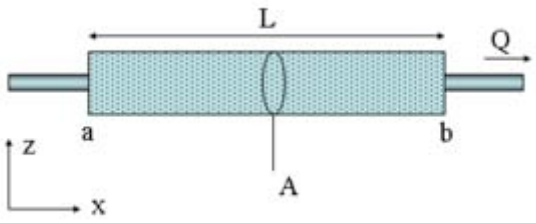


Figure 2.1. Schematic of simple Darcy flow
(Source: Edinburg University 2002)

The equation of Darcy Flow is given in equation 2.5;

$$Q = \frac{-\kappa A}{\mu} \frac{(P_b - P_a)}{L} \tag{2.5}$$

Where Q is total discharge, κ is Darcy permeability, A is the the cross-sectional area $P_b - P_a$ the pressure drop, μ is dynamic viscosity and L length of the flow (Edinburg University 2002).

Permeable ceramics contain open pores with high tortuosity and a proper pore size distribution. Increasing sintering temperature cause decrease in Darcian (viscous) permeability (Shuqiang and Yu-Ping 2007).

2.3. Air Diffusers

Air diffusers are porous permeable systems that can be made by all materials. Ceramics are useful for air diffusers because of structural properties.

Advantages of ceramic air diffusers are high oxygen transfer efficiency, high resistance to clogging, high resistance to corrosion, wide air flow range, low pressure loss, water-stirring effect and intermittent operation capability. Because of all these advantages air diffusers are used for fish farm and fish pond aeration, pond filter system aeration, lake and stream aeration, municipal and industrial wastewater treatment, septic system aeration, clean water treatment and sludge stabilization (pondexpo 2009).

For many years diffuser systems are used for hydropower reservoirs to increase the oxygen concentration in the hypolimnion, where water is frequently withdrawn through the hydropower intakes and released downstream. Example of this usage is reservoirs that employ aeration systems include Richard B. Russell in South Carolina and Georgia, Douglas in Tennessee, Watts Bar in Tennessee, Spring Hollow in Virginia and the Upper San Leandro in California.

Construction of large wastewater reservoirs is also motivating for environmental aspect. Providing storage for combined sewage and stormwater during big storms that would otherwise be discharged untreated into area waterways like in Chicago, Illinois. (Schierholza and Gulliverb 2006)

Air diffusers also used for fish ponds in order to increase oxygen amount in another word increase in quality of water. Figure 2.2 shows the phograph of an air diffuser.

Figure 2.2. Photograph of air diffuser
(Source: Dryden Aqua 2009)

Air diffuser is used in fish pond by pumping compressed air out to the bottom of a pond or lake with the use of a diffuser, the rising air bubbles and the friction caused in the water will bring bottom water to the surface where it is exposed to the atmosphere. (Living Water Airation 2009).

2.4. Oxygenation of Water

Oxygen is the most significant atmospheric gas. It can be dissolved in water. Dissolved oxygen has also vital importance for marine life. Like fish and other aquatic animals, oxygen breathing aerobic bacteria also need oxygen to live. If oxygen concentration in water decreases, anoxic conditions may develop which can decrease the ponds ability to support life. (Wikipedia 2009)

For example, in fish pond for trouts, in their breeding time dissolved oxygen in water should be at least 7 mg/l. Dissolved oxygen amount determines the amount of larva for production. By using air diffuser, dissolved oxygen amount can be increased so the production of fish is increased (TC. Başbakanlık GAP projesi 2004).

Many physical, chemical, and biological factors effect the dissolved oxygen amount in water. The saturation concentration, or solubility of oxygen must be defined

to determine dissolved oxygen amount of water (Parkhill and Gulliver 1997). The variation of oxygen solubility according to some important environmental factors like temperature and salinity is well described (APHA 1992). However saturation limit of the water also change with salinity of water and the type of waters. Figure 2.3 shows the effect of salinity of water and Figure 2.4 shows the effects of water types on dissolved oxygen.

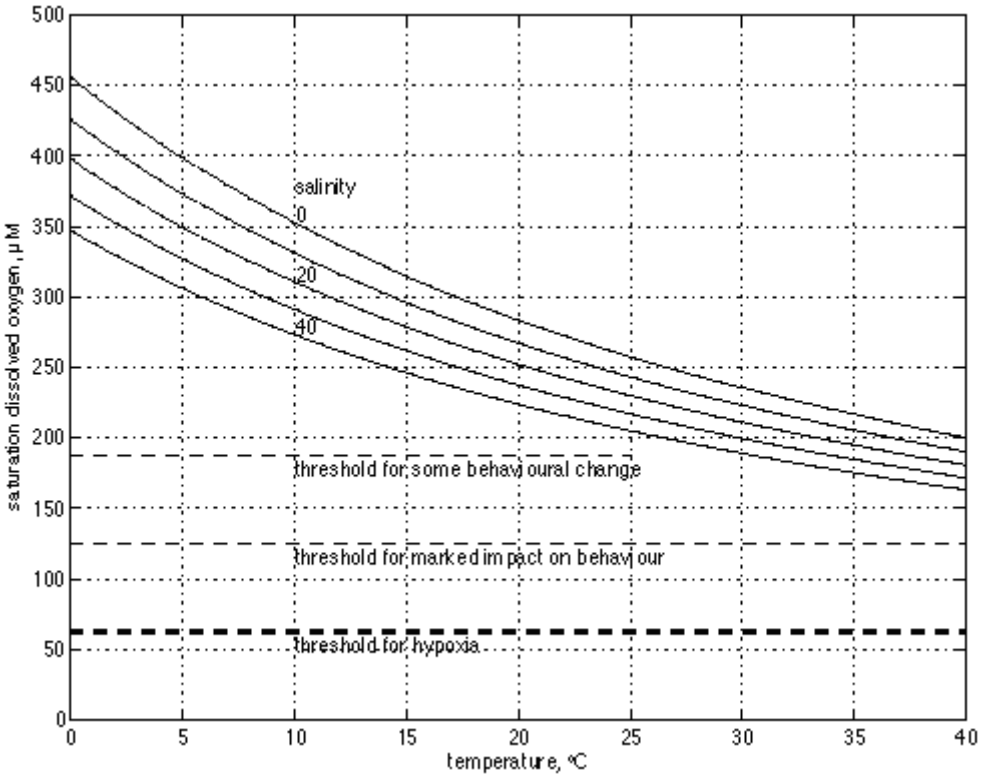


Figure 2.3 Effect of salinity on dissolved oxygen amount in water
(Source: Life Science 2006)

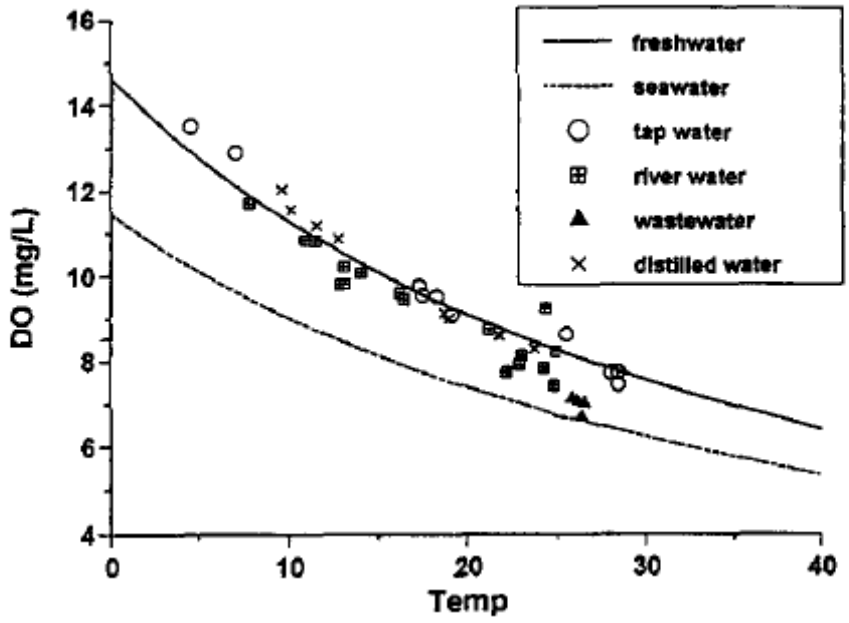


Figure 2.4. Effects of water types and temperature on dissolved oxygen (DO) amount in water (Source: Parkhill and Gulliver 1997)

2.5 Bayer Process for Alumina Powder Production

Industrial meaning of Bayer process is refining bauxite to produce alumina. Bauxite, the most important ore of aluminium, contains only 30-54% alumina, Al_2O_3 the rest being a mixture of silica, various iron oxides, and titanium dioxide.

Bayer process consists of five steps; first step is grinding of bauxite, second is digestion, third is clarification, fourth is precipitation of $Al(OH)_3$ from the solution by the use of nucleating agents, fifth step is calcination. The schematic illustration of Bayer process is shown in Figure 2.5

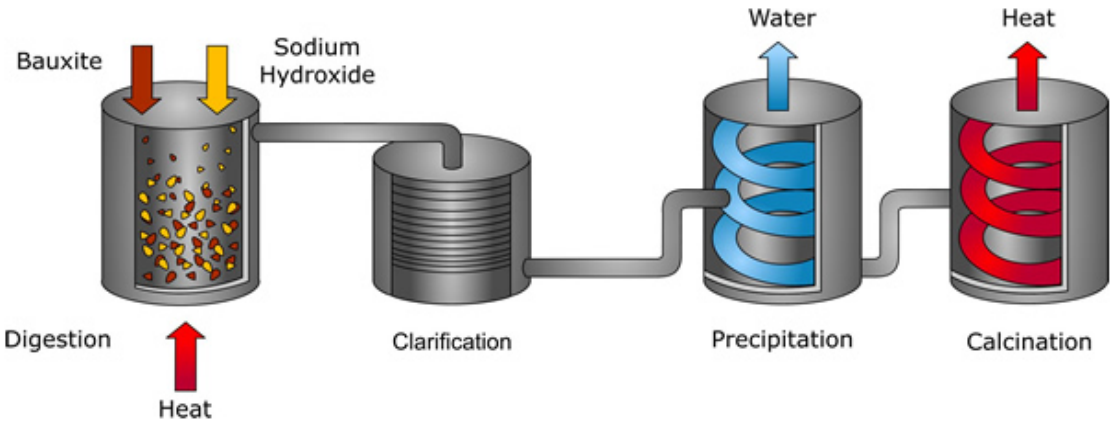


Figure 2.5. Schematic flow diagram of the Bayer process for alumina powder production (Source: Aluminiumville 2007)

The first step of Bayer process is digestion, in this step most of the hydrated alumina goes into solution as sodium aluminate in sodium hydroxide (caustic soda) solution under a pressure of about 25-35 atmosphere and at a temperature of about 250°C. Insoluble part of the solution is called red mud which has iron, silicon and titanium. This is disposal of Bayer process (Şahin 2000). The sodium aluminate solution is seeded with very fine gibbsite ($Al(OH)_3$) and at lower temperature the aluminum hydroxide forms as the stable phase. The agitation time and temperature are carefully controlled to obtain a consistent gibbsite precipitate. The gibbsite is filtered and washed to reduce its sodium content and is calcined at 1100-1200˚C to obtain α-Al_2O_3. High-purity (up to 99.5%) alumina with a particle size ranging from several microns to submicron can be produced by this process (Gitzen 1970) . Structural properties of Bayer alumina are given with details in Chapter 4.

2.6. Ceramic Forming Techniques

Ceramic materials are shaped in forming step before densification. Lots of different forming techniques are used for ceramics shaping. The manufacturing processes include uniaxial pressing or dry pressing, cold isostatic pressing, slip casting,

tape casting, roll compaction and extrusion (Reed 1995). In this thesis two of them are used: slip casting and dry pressing.

2.6.1. Slip Casting of Ceramics

Slip casting is a very traditional technique for forming ceramics. Figure 2.6 shows the schematic representation of slip casting technique.

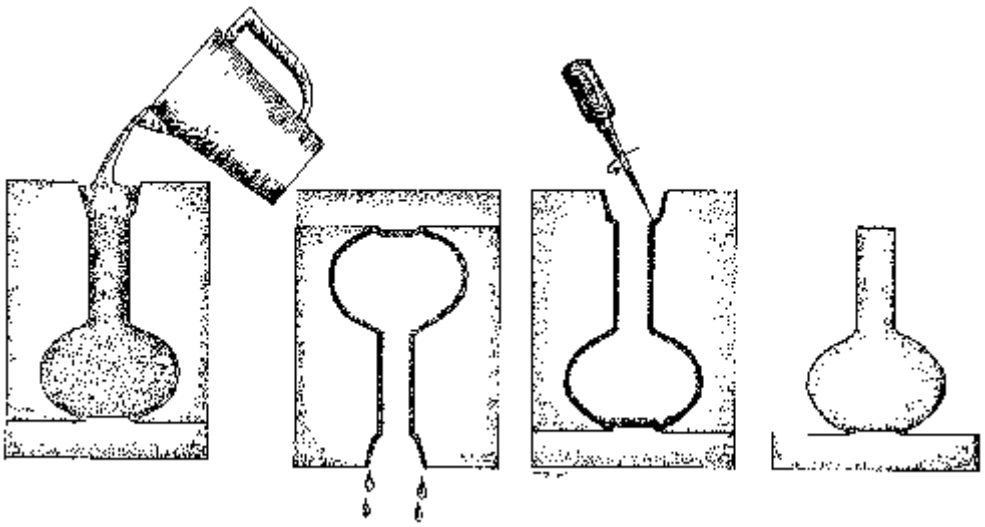


Figure 2.6. Schematic representation of slip casting method
(Source: Norsker and Danisch 1991)

First step of slip casting technique is pouring the ceramic suspension into a porous mold. Water in the ceramic suspension is withdrawn into the porous mold through a fine network of pores in the plaster structure. Because of the capillary action, a ceramic cake forms on the walls along the boundaries with the mold. The thickness of the walls increases with time. If the final shape should be a hollow shape, after the walls are dried, wet suspension is poured (drained) from the mold. When the ceramic body has dried long enough to support itself, it is removed from the mold. (Reed 1995). The technique is also known as drain casting.

2.6.2. Dry Pressing of Powders

The simplest and most popular method is dry pressing. Figure 2.7 shows the schematic representation of dry pressing technique.

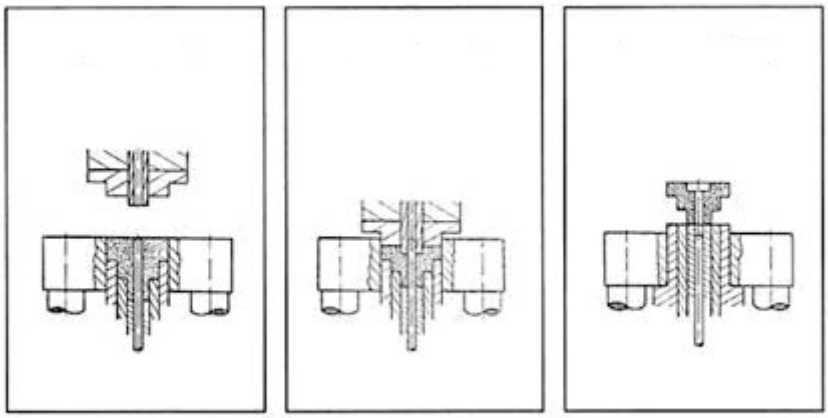


Figure 2.7. Schematic representation of dry pressing method
(Source: Sembach 2007)

In dry pressing process ceramic powder is pressed, the powders compact to each other. Dry pressing has many advantages. First of all it is a low-cost method, form shapes to close tolerances and it can be easily automated. For this reason dry pressing is widely used in the ceramic industry to manufacture such components as ceramic tiles, spark-plug insulators, chip carriers, seal rings, valve components, refractories and other products of simple morphology (Kingery 1976).

2.7. Sintering of Ceramics

Once a powder compact is formed to the desired shape, it is fired at elevated temperatures to impart the ware sufficient mechanical strength. Strength is derived largely from bonds between powder particles developed during the high temperature treatment which allows significant diffusion. Material transport occurs from the bulk of

the powder particles to the neck area via lattice diffusion, vapor transport, surface diffusion (Figure 2.8). Some shrinkage of roughly 10-20% occurs when atoms migrate from the body of the particles to the neck area. Sometimes a second liquid phase is used to help increase densification (Liquid Phase Sintering-LPS). Traditional ceramics are generally formulated to produce a vitrified bond phase (flesh) between larger filler grains (skeleton). A low-melting material is usually added to help reduce the sintering temperature. In high purity electronic ceramics solid state sintering is more common during which particles bond to each other by diffusion rather than by a liquid phase that wets other particles together. The driving force for sintering is reduction in total surface area. So a powder raw material with small particle size and large surface area is desirable. Surface area per cm^3 of material of 1-10m^2 are common.

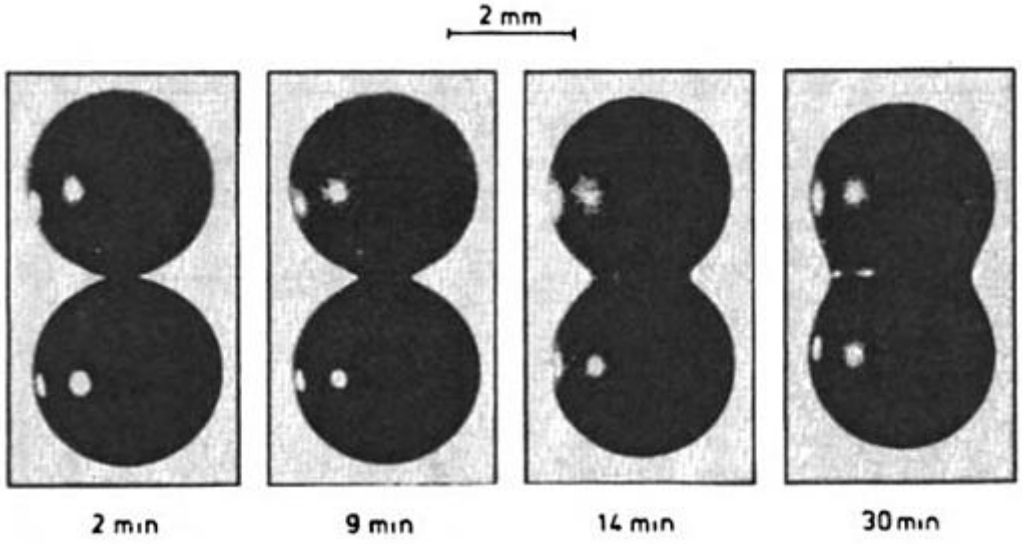


Figure 2.8. Schematic representation of sintering
(Source: Rahaman 2003)

2.8 Phase Diagram

During sintering of the ceramic, phase changes occur due to high temperature treatment. Clay loses chemically bound water around 500^oC to form metakaolin which on further heating dissociates into mullite and glass. The thermodynamic equilibrium between Al_2O_3 and SiO_2 is expressed by the phase diagram given in Figure 2.9. This diagram is valid only if complete thermodynamic equilibrium is achieved. When

alumina and clay particles are heated together thermodynamic equilibrium is not completely attained but the phase equilibrium diagram still provides useful information about the expected phases. For example, if a 50% alumina and 50% clay mixture is heated to 1300^{o}C and cooled it is expected to have roughly 60% Al_2O_3 composition. The resulting phases are mullite and silica which forms as a glass to produce the vitrified ceramic. Bayer alumina is expected to completely transform into alpha alumina phase upon heating at 1300^{o}C and to stay as such on cooling. Therefore, a mixture of Bayer alumina and clay will produce alpha alumina particles bonded by a glassy phase.

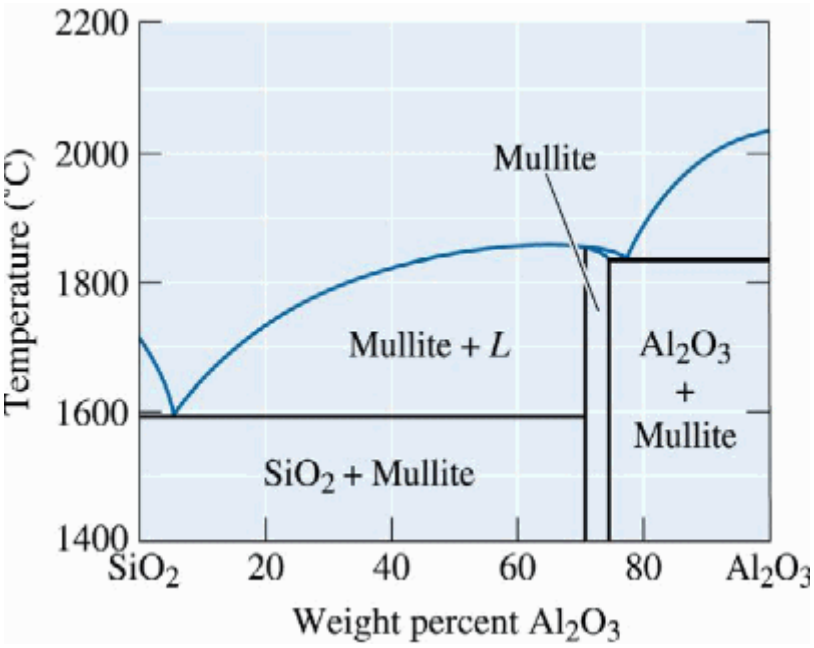


Figure 2.9. Alumina- silica phase diagram
(Source: Aksay and Pask 1975)

CHAPTER 3

EXPERIMENTAL

In this chapter, the materials used in the thesis, the experimental setup and the procedure are explained.

3.1. Materials

In order to develop porous ceramics for air diffuser applications two types of alumina were used, one of them was superground Alumina CT-3000 SG (Alcoa Industrial Chemicals Europe, Frankfurt, Germany) and the second was coarse metallurgical grade Bayer alumina that was obtained from Seydişehir Aluminum Plant in Turkey.

Quartz was also used in the experiments. Like alumina, two types of quartz were used. First quartz type was obtained from Kaltun Mining Company, Aydın, Turkey while the second type of quartz was from Kalemaden Mining Company, Çanakkale, Turkey.

In addition to these materials, a commercial clay with a designation of 244 was obtained from Kalemaden Mining Company. This clay, which was available in tonnage quantities, was industrialy used by traditional ceramic manufacturers in wall tile and floor tile production. Finally, corn starch was used as organic pore former that was produced by Piyale Company, Istanbul, Turkey

3.1.1. Characterization of Raw Materials

Raw materials were characterized by XRD (X-Ray Diffraction, Philips X-Pert, Netherlands), SEM-EDS(Scanning Electron Microscope, Philips XL30 SFEG, EDAX, Netherlands), XRF (X-Ray Fluorescence, Spectro IQ2, Switzerland), Optical Microscope, Nikon L-150, Japan).

3.2. Experimental Method

3.2.1. Production of Porous Ceramics

Two different methods were used for the production of porous ceramics: slip casting and dry-pressing. Slip casting was initially the preferred technique with superground Alcoa alumina and corn starch containing samples. Dry pressing was adopted later in second half of the study. Chronologically the progress of the work in this thesis was as follows:

(1) Slip casting of 70 weight % Alcoa alumina suspension and 5-30% corn starch and pouring into plaster molds.

(2) Dry pressing of small sized pellets from Bayer alumina and clay mixtures with or without quartz. The size of the pellets, which were pressed in steel dies, were 30mm in diameter and roughly 10mm in height. These pellets were dried in an oven at 60^{o}C before firing at 1300^{o}C for one hour. Fired pellets were tested for density, porosity, mineral composition, compressive strength, microstructure, air permeability into water.

(3) Dry pressing of large ceramic plates of 135x58x8mm dimensions were done using mixtures of Bayer alumina, clay and quartz with some PVA (Poly Vynil Alcohol) as binder (5wt%). Blending of the powders was done in a laboratory scale tumbling ball mill for 10 minutes without the use of a grinding media. Well-mixed powders were further mixed with 5% aqueous solution of PVA to assist in bonding. The powders were dried in oven, moistened by 10% water and pressed in rectangular steel dies. In order to

achieve crack free samples with good green strength drying was done in the kiln where firing took place. Dwell times at the predetermined soak temperature were 1 hour. Crack-free, sound and dimensionally stable porous ceramics could be repeatedly and successfully produced.

Small sized pellets were studied before large sized plates in order to understand the compositions, forming and firing conditions for larger samples. Successfully produced small samples paved the way to the development of larger plates with correct compositions and pore structures.

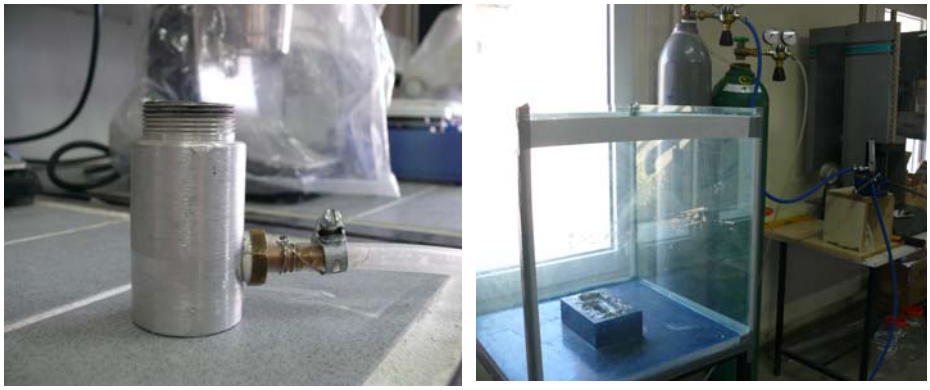
3.2.2. Characterization of Ceramic Samples

Porous ceramics were characterized by XRD (X-Ray Diffraction, Philips X-Pert, Netherlands), SEM-EDS(Scanning Electron Microscope, Philips XL30 SFEG, EDAX, Netherlands) and Optical Microscope, Nikon L-150, Japan). Mechanical test was done on a Shimadzu universal mechanical testing machine (Shimadzu 250kN, Japan). Samples for SEM were prepared either by fracturing the ceramics or by polishing sections to observe the porous internal structures. Rectangular samples with 10x10x10mm were cut with a diamond saw from the large plate type ceramic diffuser samples for uniaxial compressive strength tests.

Archimedes test was used to measure density and porosity of the samples. Samples were soaked in boiling water for 5 hours after they were dry-weighed. Procedure used was similar to ASTM C 20-87

3.2.3. Permeability Testing of Porous Ceramic Diffusers

In order to test for the permeability characteristics of the porous ceramic samples two different apparatuses were custom made in the university machine shop. Drawing of both apparatuses are given in Figures 3.1 a) and b).



a) b)

Figure 3.1. Drawing of the permeability apparatuses used in this study a) Small sample permeability test apparatus b) Large sample permeability test apparatus.

Porous ceramic diffuser samples were mounted and affixed in the custom made cavity at the end of the apparatus by water resistant silicone sealant. Pressurized air was fed from the other end of the apparatus. It was possible to obtain an air tight connection and to test the ceramic samples for the degree of their permeability for air in water. The apparatus shown above was capable of accommodating continuous permeability tests which were run about 8cm underwater. When small cylindrical pellet ceramic samples were tested a visual grading system was used to judge their degree of permeability. This grading system ranged from high to very low. High means highly permeable while medium is moderately permeable and low is even less permeable. A grade of very low is almost impermeable. A fixed air pressure of 1 bar was used in all tests. This was the same pressure adapted in commercial air diffusers. For large plate type ceramic samples, the degree of bubble production was measured indirectly from oxygen concentration measurements. A flowmeter was also used to check the amount of air flow through the ceramic (Argoshield, SG-1201-F).

3.2.4. Oxygen Concentration Measurements

An experimental setup was constructed to measure the amount of increase in oxygen concentration of water after exposure of bubble through the porous ceramic diffusers after some time. The photograph of the apparatus is shown in Figure 3.2. Pressurized air is fed to the apparatus and many bubbles are produced as the air exits the pores in the ceramic. The bubbles quickly rose in the water and disappeared on the top. The transfer of oxygen from the bubble to the water took place during the ascent of the bubble. The oxygen concentration of water was measured before air bubbling and after air bubbling using a water quality measurement device (DKK-TOA, WQC-24, Japan). Large plate type ceramic samples were used in these tests. Surfaces of these samples were vitrified so a SiC grinding paper was used to remove about half a millimeter of surface layer to expose porous interior of the samples.

Figure 3.2. Oxygen concentration measurement system used in this study.

3.3. Experimental Plan

In this study, evolution of the development of porous ceramics for air diffuser applications progressed in the following order.

3.3.1. Dry Pressing of Alcoa Alumina

Superground alumina (CT 3000 SG) was uniaxially dry-pressed and fired in different operation conditions (Table 3.1).

Table 3.1. Experimental conditions for superground Alcoa alumina pellet samples.

	Test Conditions		
Code	Compaction Pressure (MPa)	Firing Temperature ^{o}C	Firing Time (min)
A1	250	1400	120
A2	100	1400	120
A3	250	1400	15
A4	100	1400	15
A5	250	1200	120
A6	100	1200	120
A7	250	1200	15
A8	100	1200	15

3.3.2. Slip Casting of Alcoa Alumina and Corn Starch Mixtures

Additions of corn starch were made to superground alumina to act as space holder. These samples were formed by slip casting into plaster mold. 20%,30% and 40% corn starch concentrations had worked.

3.3.3. Slip Casting of Clay, Quartz and Corn Starch Mixtures

Clay (Code 244 Kaltun Mining Company), quartz and corn starch mixtures were used instead of superground alumina in different concentrations and firing temperatures (Table 3.2). A stable slurry was prepared by using 1wt% Darvan-C as deflocculant. Formed and dried samples were fired at the targeted temperature for 1 hour.

Table 3.2. Mixture compositions and firing temperatures for slip cast samples that contain clay quartz and corn starch

Quartz (Kaltun: D_{50}=11µm)	**Clay (244)**	**Corn Starch (%)**	**T (^{o}C)**
50	50	20	1050
50	50	30	1050
50	50	20	1100
50	50	30	1100
50	50	35	1100
50	50	30	1150

3.3.4. Dry Pressing of Clay, Quartz and Bayer Alumina Mixtures: Small Pellets

Clay (Code 244 of Kalemaden), Bayer alumina and quartz (761-Kalemaden Mining Company) mixtures were prepared in mortar and pestle in different proportions (Table 3.3 and Figure 3.3). These samples were named as S1, S2 and so on to designate small sized pellet samples. An aqueous solution of 5% PVA was added to the blended powders before drying in oven at 60oC overnight. Agglomerates were broken in mortar and pestle and powder mixtures were uniaxially pressed at 100MPa in a cylindrical steel die. The pellets so obtained had satisfactorily good green strength and were fired at the designated temperatures for 1 hour to obtain sound porous ceramic pellets of 30mm diameter and 10mm height.

Table 3.3. Small sample pellet mixture compositions and their firing temperatures.

Exp. No	Bayer Alumina	Clay	Quartz	T (C)
S1	70	30	0	1300
S2	60	40	0	1300
S3	50	50	0	1300
S4	40	60	0	1300
S5	30	70	0	1300
S6	60	20	20	1300
S7	70	20	10	1300
S8	60	30	10	1300
S9	70	10	20	1300
S10	50	30	20	1300
S11	60	10	30	1300
S12	50	20	30	1300

For clay(244), Bayer alumina and quartz (Code 761 Kalemaden) mixtures experiments were designed on a triangle (Figure 3.3). Initial tests quickly indicated success on the left corner of the triangle. Bayer alumina and quartz were used as the skeleton of the samples and clay was used as a forming aid. In addition, polyvinyl alcohol (PVA) and water mixture was used to provide homogenity and to help improved bond during forming.

Uniaxial pressing was used in two different sample sizes and geometries to better understand the effect of increased scale of samples to their permeability performances.

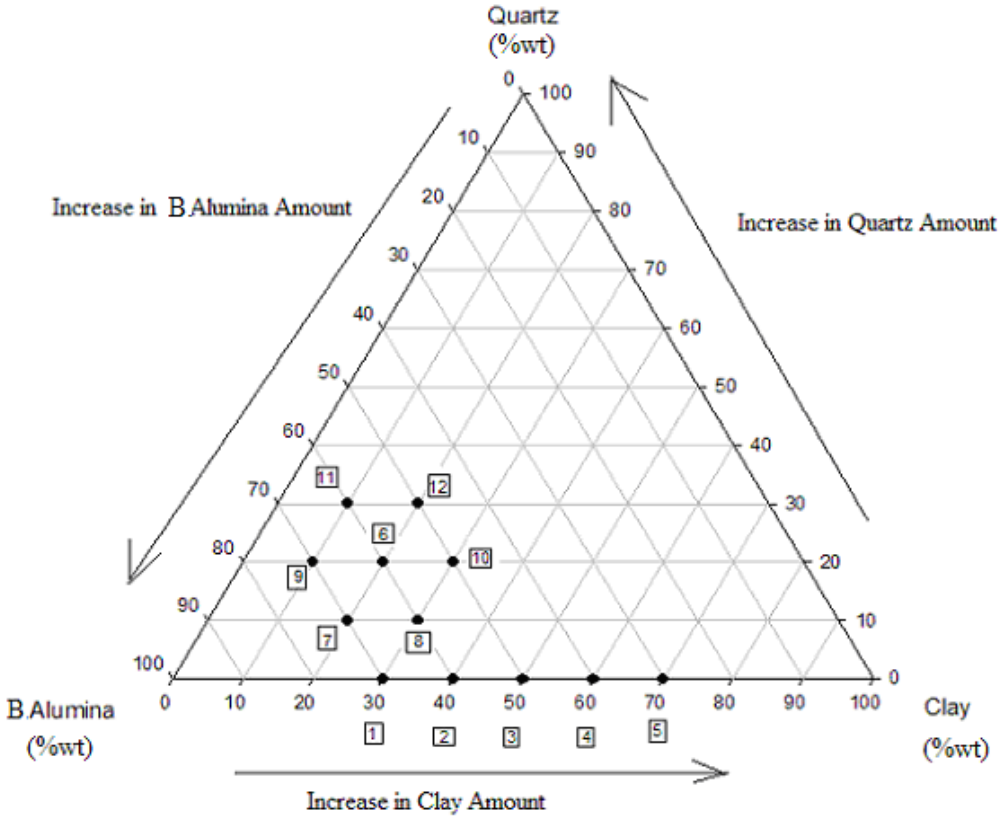


Figure 3.3 Mixture compositions for pellet shaped small samples

3.3.5. Dry Pressing of Clay, Quartz and Bayer Alumina Mixtures: Large Plates

Larger samples with rectangular geometry were produced by first blending clay, quartz and Bayer alumina in a ball mill. After addition of PVA to the mixture and a drying step the blended mixtures were ready for uniaxial pressing in a hydraulic press (Yildiz Press). Large samples are pressed at 120 MPa. Compositions of mixtures are given in Table 3.4 and Figure 3.4. Large plate samples were named L1, L2, etc to designate large sample size. Triangular plot in Figure 3.4 shows the mixtures that were fired at 1300°C. Some of the selected mixtures were also fired at 1260 and 1340°C to observe the effect of temperature on porosity and permeability. Experiments in Figure 3.4 were composed of selections of successful compositions based on experiments in Figure 3.3 in addition to a few more tests under different conditions. Some points were added and some others were ignored. For example, L3, L4, L7 and L9 were not studied although their small sample counterparts S3, S4, S7 and S9 were tested. This was because these samples showed no permeability to air in the small sample permeability test.

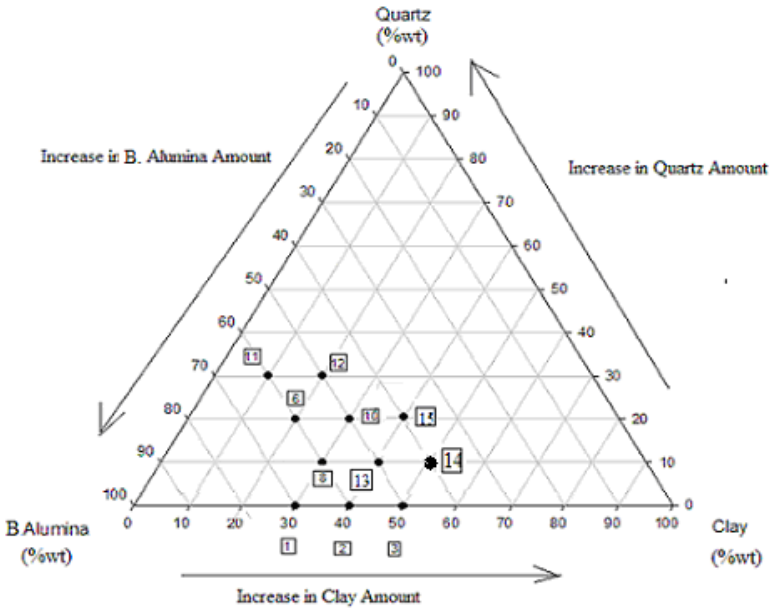


Figure 3.4. Triangular plot for large plate sample compositions.

Table 3.4. Compositions and firing conditions for large sized plate samples.

Exp. No	Bayer Alumina	Clay	Quartz	T (C)
L1	70	30	0	1300
L2	60	40	0	1300
L5	30	70	0	1300
L6	60	20	20	1300
L8	60	30	10	1300
L10	50	30	20	1300
L12	50	20	30	1300
L13-1	50	40	10	1260
L13-2	50	40	10	1300
L13-3	50	40	10	1340
L14	40	50	10	1300
L15	40	40	20	1300

3.3.6. Firing Plan of the Samples

In this study three different firing schedules were used. First firing schedule took into account the weight loss between 273 ^{o}C and 325 ^{o}C due to the burning of corn starch. So these samples were fired between these temperatures very slowly.

The pellet samples that had no corn starch were fired with a ramp up rate of 10^{o}C/min before being held at the soak temperature for 1 hour.

For the large plate samples that contained Bayer alumina, quartz and clay, a specific program was used. These samples were pressed in a moistured state so they were dried in the kiln, not in a drying oven and were placed perpendicularly during firing. Hold time for drying at 60^{o}C was 9 hours to ensure complete drying. Figure 3.5 shows the orientation of the large plate samples in the oven. After drying is finished, temperature of the kiln was increased up to the desired temperature in 5 hours (about

5^{o}C/min). Heating process was very slow for these samples to obtain crack free undistorted samples.

Figure 3.5. Placement of the large plate samples in the oven

CHAPTER 4

RESULTS AND DISCUSSION

In this chapter, results of characterization of original raw materials used for porous ceramic production are given. Hence, characterization and classification of raw materials are completed before any porous ceramic production. Secondly, the same characterization techniques like microscopic, X-ray diffraction and SEM (scanning electron microscopy) are utilized for analysis of the produced ceramics. Results of air bubble diffusing tests into water are also given.

4.1. Characterization of Raw Materials

Materials used in porous ceramic production were clay, quartz, Bayer alumina, superground alumina and corn starch. Results of characterization of these materials are given below.

4.1.1. Superground Alumina CT-3000 SG (Alcoa Industrial Chemicals Europe, Frankfurt, Germany)

Table 4.1 shows the published properties of superground alumina which is very fine with a lot of surface area and a homogeneous size distribution. Large surface area of this powder makes it a good material for sintering around 1540^{o}C to achieve full density. Particle size distribution of superground alumina is shown in Figure 4.1.

Table 4.1. Chemical analysis and physical properties of Alcoa CT3000SG Alumina

Oxide	Weight %
Al_2O_3 (%)	99.76
Na_2O (%)	0.08
Fe_2O_3 (%)	0.02
SiO_2 (%)	0.03
CaO (%)	0.02
MgO (%)	0.09
Specific Surface Area / BET (m^2/g)	7.0
Average Particle size, (μm)	0.7
Press Density / 90 Mpa (g/cm^3)	2.25
Fired Density / [1540°C/1h] (g/cm^3)	3.90
Shrinkage / [1540°C/1h] (%)	16.8

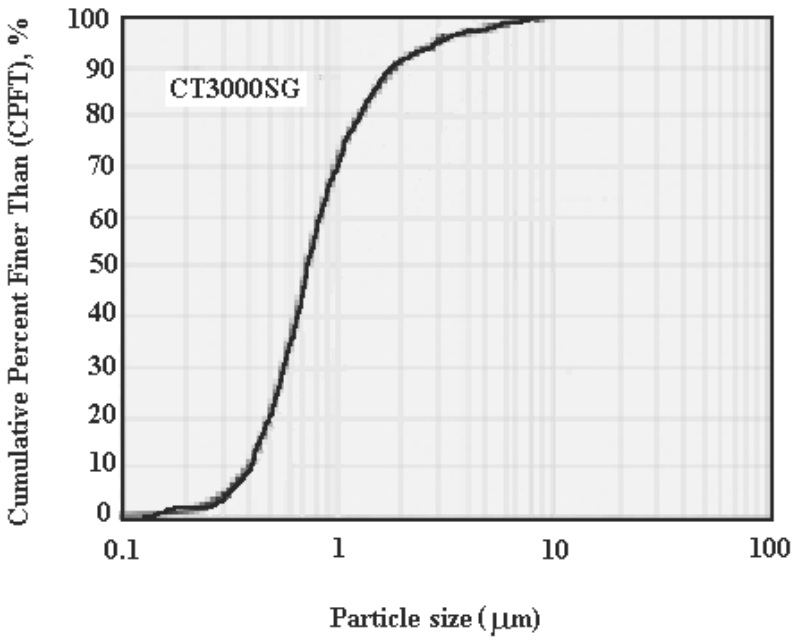


Figure 4.1. Typical particle size distribution of Alcoa CT3000SG alumina powder

Figure 4.1 shows that average particle size of the supergrounded alumina is 0.7μm. Therefore during the refining process of superground alumina very fine and relatively highly pure alumina is obtained.

4.1.2. Bayer Alumina (Seydişehir Aluminum Factory, Turkey)

Bayer alumina used in this study was a metallurgical grade alumina powder with mainly Al_2O_3 (97.5%) and some impurities. There were two different precipitated Bayer aluminas available in Seydişehir aluminum works plant. First one was white colored and was locally known as coarse alumina (Seydişehir Kaba Alümina) while the second one was smaller with a gray color and was collected from underneath the electrofilters. The first coarser powder was used in this thesis and was named Bayer alumina. Table 4.2 shows the chemical analysis of Bayer alumina that was obtained by using XRF. The amount of Na is not indicated here but it was found in another study to be about 0.5% which was very high for alumina to be used in ceramics manufacture.

Table 4.2. XRF analysis results of the Bayer Alumina

Symbol	Weight (%)
Al_2O_3	97.5
MgO	1.7
SO_3	0.34

Figure 4.2 shows the XRD analysis of the Bayer alumina used in this thesis to indicate that the powder was largely γ-alumina with some remaining α-alumina. The latter γ-alumina was observed because it was incompletely transformed into the alpha phase because of low calcination temperatures of less than 1200^{o}C. Table 4.3 shows the physical properties and sieve analysis of Bayer alumina.

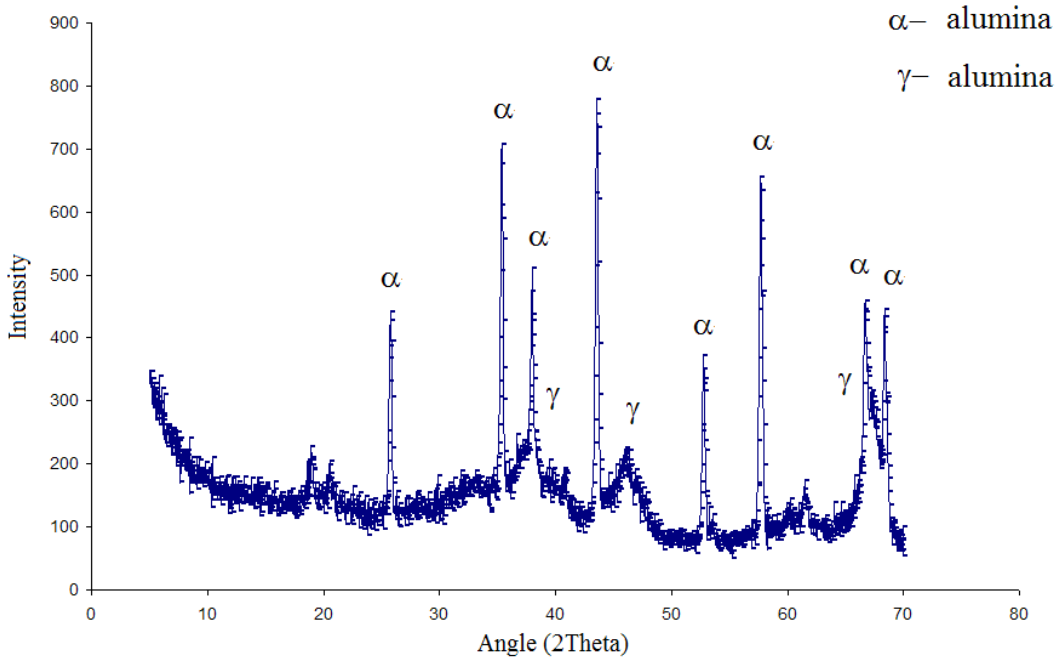


Figure 4.2 XRD analysis of Bayer alumina (CuKα radiation)

In addition to these data by sieve analysis, another test was performed by using sedigraph technique and the average particle size of Bayer alumina was determined as 38 μm. Figure 4.3 shows graph of particle size distribution of Bayer alumina.

Table 4.3 Physical properties and sieve analysis of original Bayer Alumina powders.

Physical Properties	
Absolute density, (g/cm^3)	3.3-3.6
Loss of Firing (1100°C) (%)	1 max.
α-Al_2O_3 content	15 % min.
Sieve Analysis (Tyler)	
+100 Mesh	3-10 %
-100 Mesh +200 Mesh	25-40 %
-200 Mesh +325 Mesh	30-50 %
-325 Mesh	15-30 %

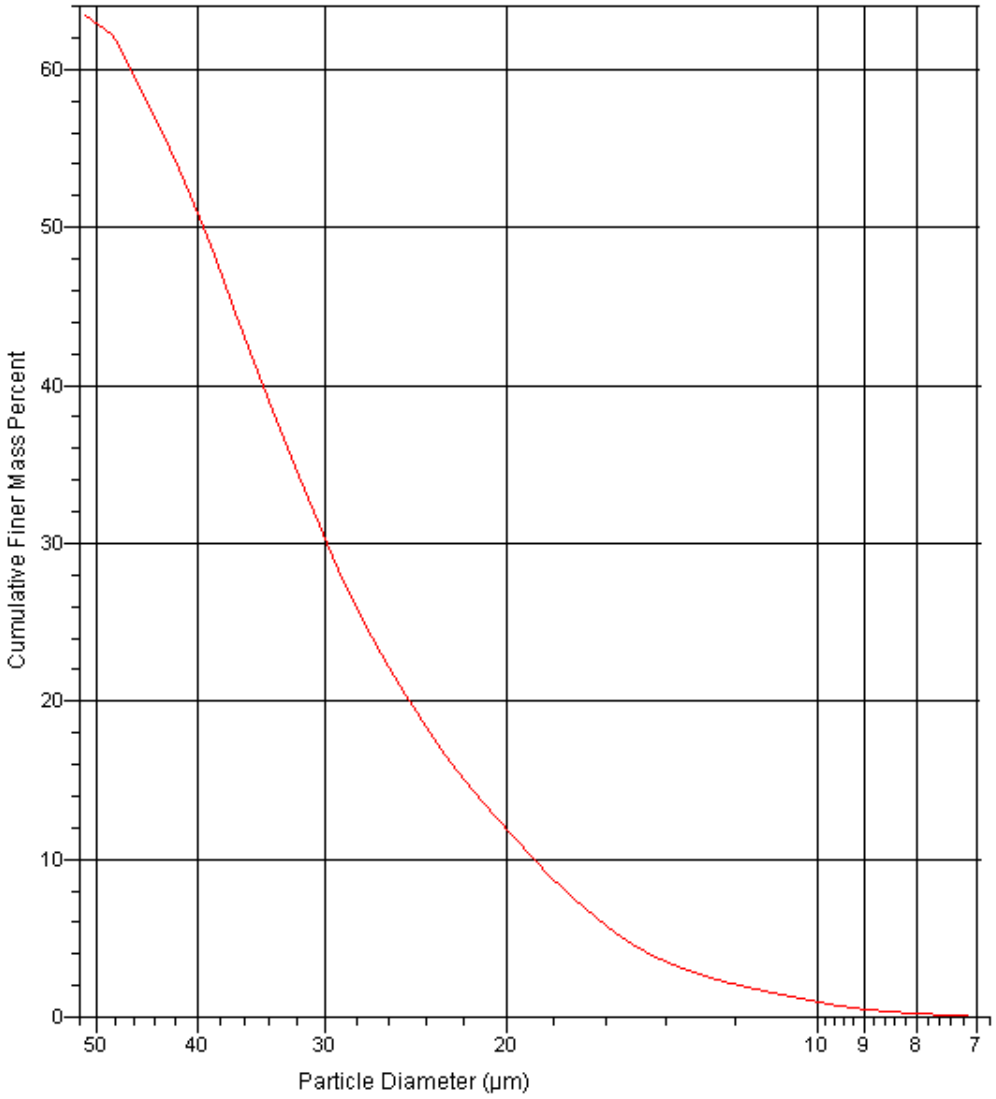
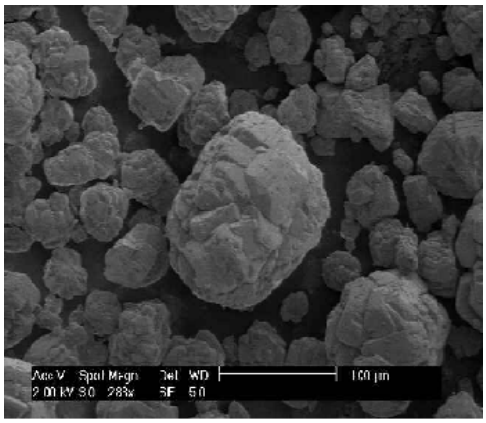
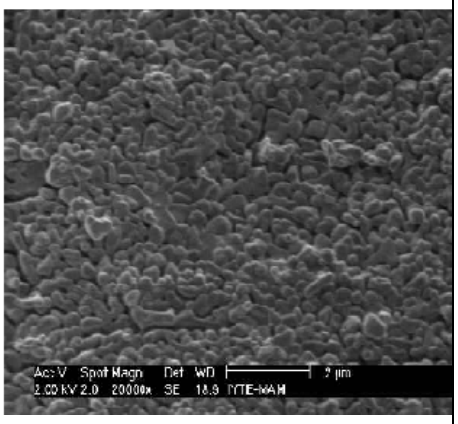


Figure 4.3. Particle size distribution of Bayer alumina

BET surface area of alumina was measured to be 43 m^2/g with Micromeritics Gemini machine. Because of the relation between BET surface area and the average particle size, structure of Bayer alumina consists of agglomerates of small sized alumina particles bonded together like a grape. Figure 4.4 shows the structure of Bayer alumina in SEM (Scanning Electron Microscope, Philips XL-30 SFEG) at different magnifications.



a)



b)

Figure 4.4. SEM image of Bayer alumina in different magnification. a) SEM image of bayer alumina at 288x magnification b) SEM image of bayer alumina at 20000x magnification

Figure 4.4 shows the structure of bayer alumina to consist of very small fundamental particles of alumina bonded together during the calcination process with a high surface area. Under normal circumstances a 1 μm cubic particle is supposed to have $1m^2$ of surface area per cm^3 of sample volume. Because of this structural property, Bayer alumina could not used to produce a dense ceramic. Several different researchers attempted to produce a ceramic grade alumina powder from Seydişehir Bayer alumina by multiple number of washing steps to reduce Na and a vigorous milling step to reduce particle size (Tambas and Ozgen 2007). These studies were only partially successful if not gross failures. Because these powders are not originally produced to aim for a ceramic product, but only a semi finished product to be used for aluminum electrolysis their ceramic properties are not entirely satisfactory. This failure was actually used as the inspiration in this study which aimed to produce a porous ceramic, not a dense one like its predecessors. The porous nature of Bayer alumina was used as an advantage in this case. The pore channels between alumina particles were roughly 100-200nm and were perfect for air transport. If these large (40μm) particles with many air channels could be bonded by a proper ceramic binder like clay and silicates then a successful air diffuser could be developed. This was the key to the success of these samples as air diffusers. Quartz was supposed to act mainly as a filler and also as vitrification aid. Clay

was supposed to help in green forming to provide green strength and once fired to act as bond between alumina particles by producing vitrified areas in the microstructure (Kingery 1976) .

4.1.3. Quartz (Kalemaden Mining Factory, Çanakkale, Turkey)

Quartz is the second most abundant mineral in the Earth's crust. Quartz that was used in this project was characterized with several techniques. Table 4.4 shows the result of XRF analyses of quartz that was obtained from Kalemaden Mining Company. Figure 4.5 shows the XRD data of the quartz.

Table 4.4. XRF analysis results of the Quartz

Symbol	Weight (%)
SiO2	97.83
Al_2O_3	1.57
Cl	0.3

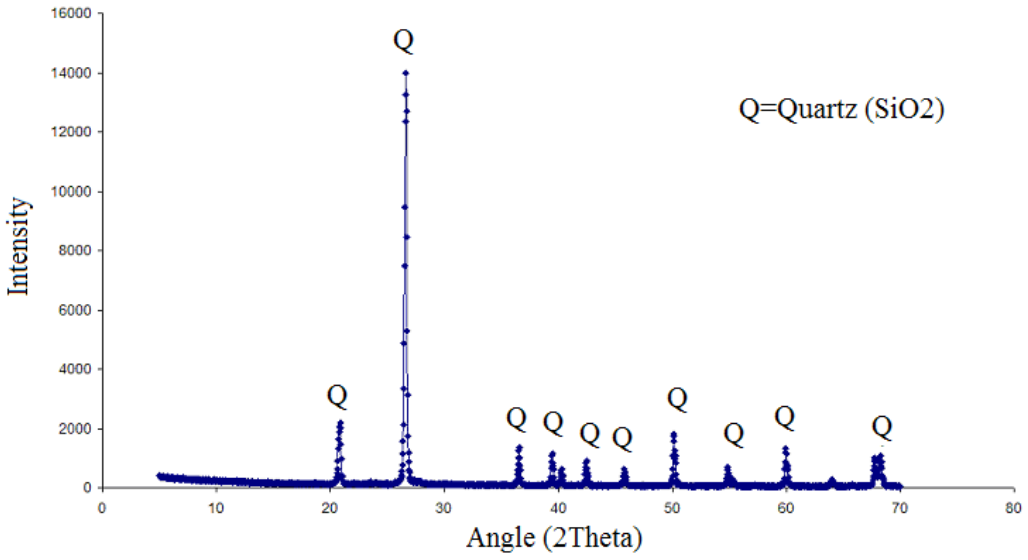


Figure 4.5. XRD analysis of quartz.

According to the X-Ray characterization result of the quartz samples purity of the quartz was very high. In addition to these analyses, Sedigraph was used to measure average partice size distribution to be 15.5 μm. BET (Brunnauer-Emmett-Teller) surface area of the quartz particles were 1.02 m^2/g.

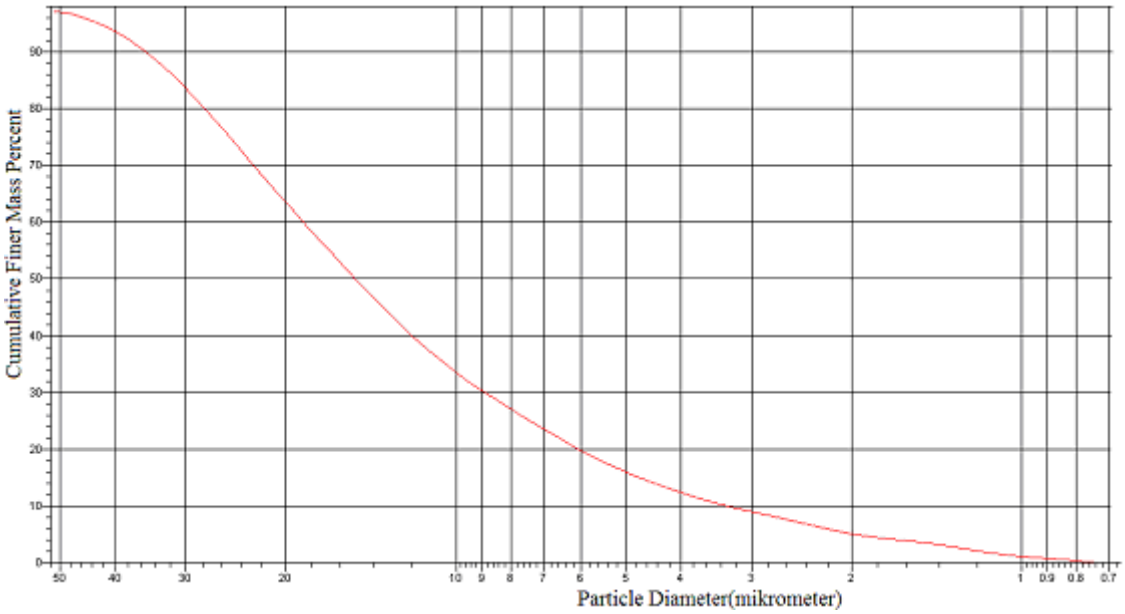
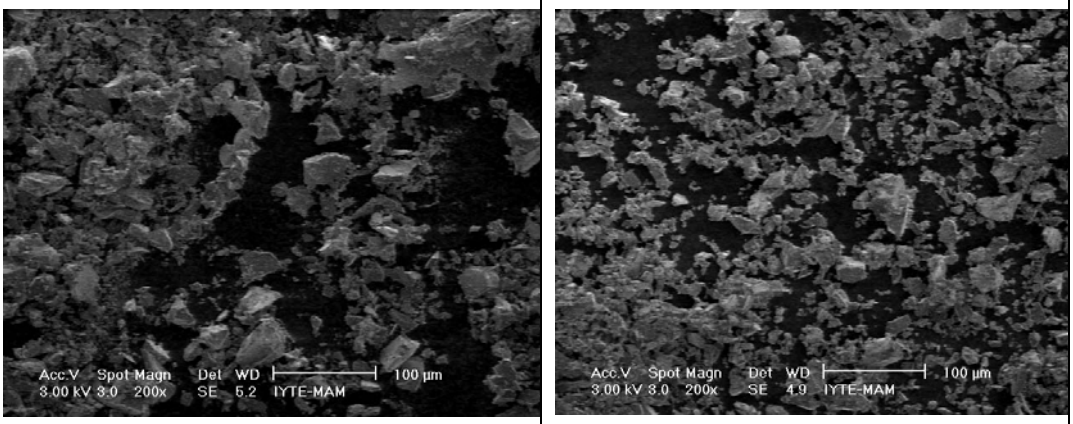


Figure 4.6. Particle size distribution of quartz powder.

4.1.4. Quartz (Kaltun Mining Company, Aydın, Turkey)

Difference between quartz that was obtained by Kaltun mining company and the quartz that was obtained from Kalemaden mining company was their average particle size. Avarage particle size of the quartz obtained by Kaltun mining company was 10.73μm so it was smaller than quartz obtained from Kalemaden mining company. Figure 4.7 shows the SEM pictures of the two types of quartz together.



a) b)

Figure 4.7 SEM image of two types of quartz particles at 200x magnification a) SEM image of quartz (Kale mining co.- 15.5 µm) b) SEM image of quartz (Kaltun mining co.-10.73µm)

4.1.4. Clay-244 (Kalemaden Mining factory, Çanakkale, Turkey);

In this project clay was obtained from Kalemaden mining factory. Characterization of used clay was made by XRD, XRF and sedigraph analysis. Table 4.5 shows the XRF results of the clay samples.

Table 4.5. XRF analysis results of the Clay

Symbol	Weight (%)
SiO2	62.89
Al_2O_3	29.44
K_2O	2.30

Table 4.5 shows that clay has a high amount of silica (SiO_2) and alumina (Al_2O_3).

Average particle size of clay as measured by Sedigraph was 3.31 µm and the BET surface area of the clay was 12.21 m^2/g.

4.1.5. Corn Starch (Piyale Company, Istanbul, Turkey);

Corn starch had quite a narrow particle size distribution around the average particle size of 15micrometers. Its TGA analysis results are shown in Figure 4.8.

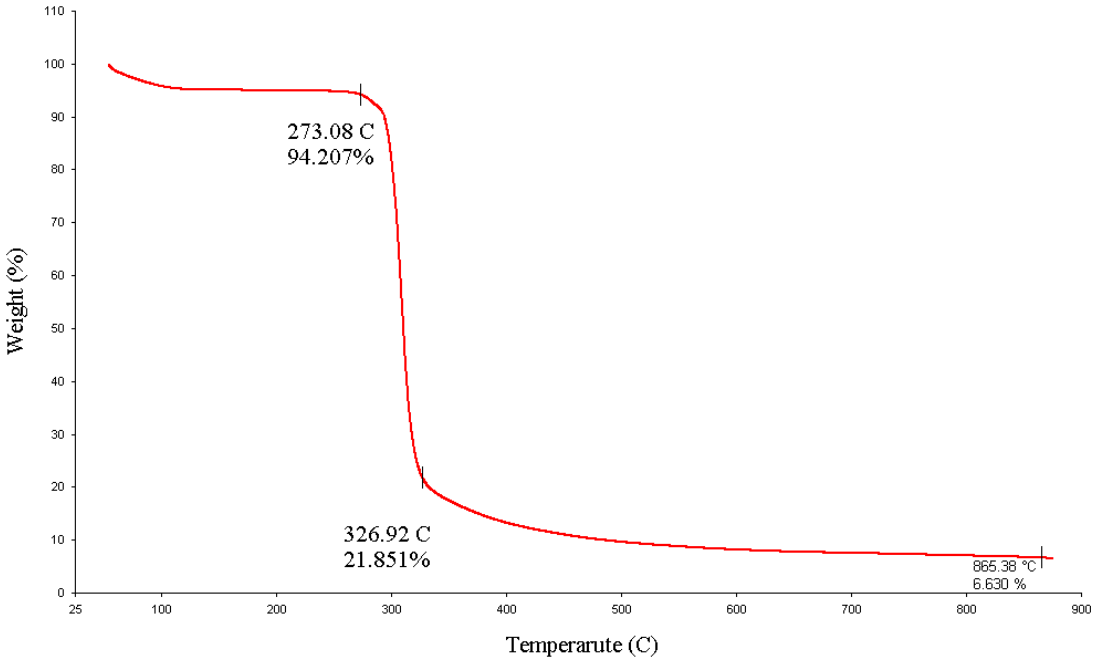


Figure 4.8 TGA analysis of the corn starch

4.2. Results of Analyses of Different Porous Ceramics Produced

Alcoa superground alumina was initially tested to see whether a low firing temperature would produce a porous ceramic that would be used as an air diffuser. Starch additions were made to enhance the porous character of the ceramic. Clay, quartz and starch mixtures followed. Finally mixtures of Bayer alumina, quartz and clay were tested.

4.2.1 Porous Alumina Ceramics Made from Alcoa Alumina by Dry Pressing

At first stage alumina (CT3000SG) was pressed and fired in different operation conditions. After samples were prepared the Archimedes tests and the permeability test of these samples were made (Table 4.6).

Table 4.6. Archimet test results of dry pressed and low fired pellets of supergrounded alumina.

Code	Compaction Pressure (MPa)	Firing Temperature ^{o}C	Firing Time (min)	Porosit (%)
A1	250	1400	120	16.2
A2	100	1400	120	17.8
A3	250	1400	15	24.4
A4	100	1400	15	26.1
A5	250	1200	120	36
A6	100	1200	120	38.4
A7	250	1200	15	40.3
A8	100	1200	15	40.5

Figure 4.9 shows the SEM picture of the the sample that was uniaxially dry-pressed under 100 MPa and fired at 1200 ^{o}C during 15 minutes.

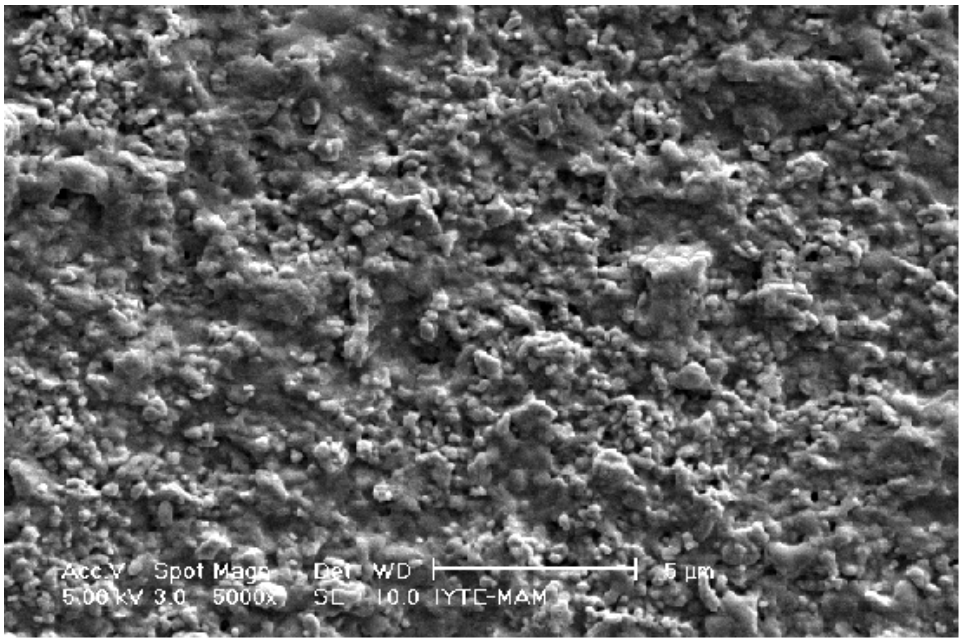


Figure 4.9 SEM images of the sample that was pressed under 100 MPa and fired at 1200^{o}C during 15 minutes.

In this part of the study, although high porous (41%) samples were obtained, pores were not completely open and permeability values were not satisfactory.

4.2.2 Porous Alumina Ceramics Made from Alcoa Alumina and Corn Starch by Slip Casting

At second stage, in order to obtain porous and permeable ceramic, corn starch space holder was used. Slip casting was used for these samples and they were fired at different temperatures. Figure 4.10 shows the SEM photo of the sample that contained %30 corn starch , %70 alumina according to weight fraction and it is fired at 1300 ^{o}C.

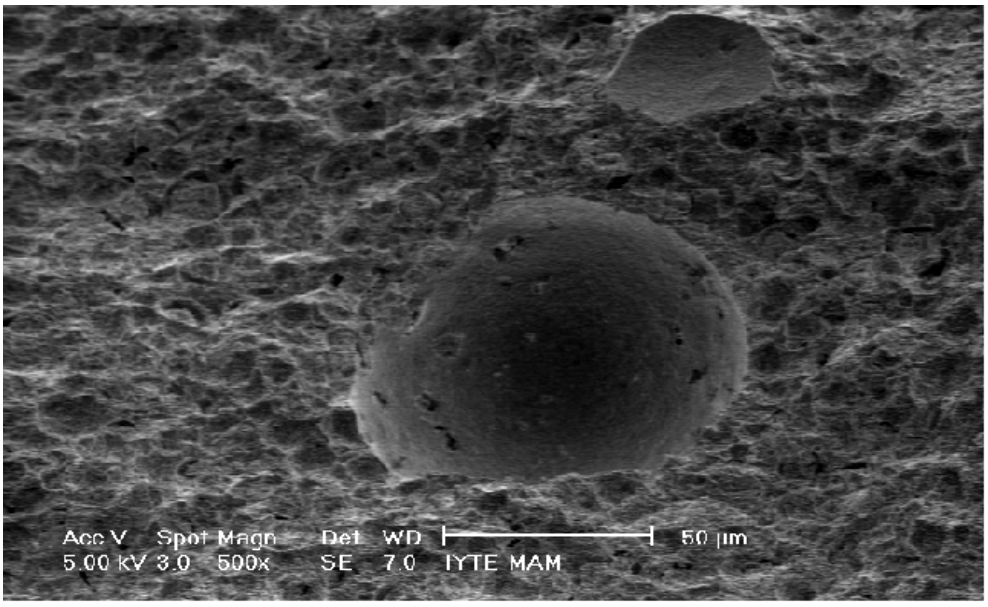


Figure 4.10 SEM images of the samples that contained %30 corn starch , %70 alumina according to weight fraction (fired at 1300^{o}C)

At the same temperatures these samples had higher porosity values than the first ones that contained only superground alumina. However, none of the samples was satisfactorily permeable for the selected operating pressure of 1 bar. This was because of the low particle size of alumina (CT3000SG, average particle size and the BET surface area of the powder are 0.7µm and 7.0m2/g, respectively) and the inefficient use of corn starch that created closed pores. Clay and quartz were also studied to see if any open pores could be produced.

4.2.3 Porous Ceramics Made from Clay, Quartz and Corn Starch by Slip Casting

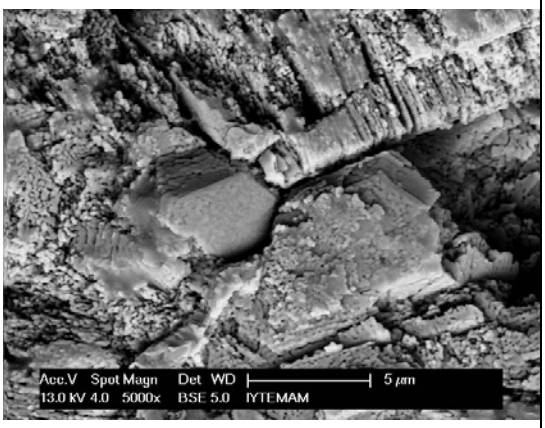
Clay (244) and quartz (kaltun) were used with corn starch. Samples were prepared by slip molding technique. Samples with different compositions were fired at different temperatures to obtain again low permeabilities (see Table 4.7). A few more tests were done to see if larger sized quartz particles would help obtain good permeability but these experiments again failed to provide satisfactory permeabilities.

Table 4.7. Permeable samples that contained quartz, clay and corn starch

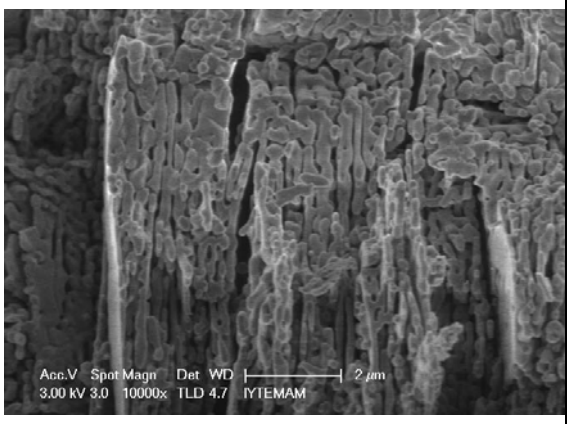
Quartz (Kaltun-10.7 µm)	Clay (244)	Corn Starch (%)	T (°C)	Permeability	Apparent Porosity (%)
50	50	20	1050	Medium	53
50	50	30	1050	Medium	58
50	50	20	1100	Low	51
50	50	30	1100	Medium	56
50	50	35	1100	Medium	57
50	50	30	1150	Very low	52

4.2.4 Small Sized Porous Ceramic Pellets Made from Clay, Quartz and Bayer Alumina by Dry Pressing

In this part of the study Bayer alumina was used to take advantage of its porous character. Because of the structural property of Bayer alumina, it cannot be used to produce a dense ceramic. However this property provides a very big advantage for production of porous ceramics. It produces very thin (200nm) air tubes in the ceramics. Figure 4.11 shows the air tubes of the ceramics that appears because of the structure of the Bayer alumina.



a)



b)

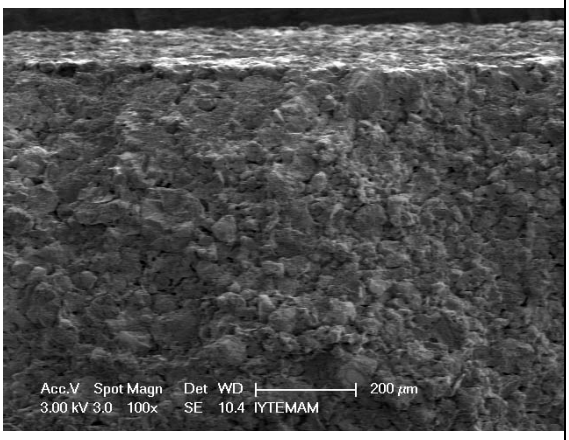
Figure 4.11 SEM images of the samples that contain Bayer alumina (fired at 1300°C). Notice the fine network of pores. a) SEM image of sample S10 at 5000x magnification b) SEM image of sample S13 at 1000x magnification

Bayer alumina, quartz and clay system has high apparent porosity values and high permeability. And also pores are very small sized (nearly 0.2µm). According to the visual permeability results, Table 4.6 shows the apparent porosity, permeability and the XRD test results of the pellet samples.

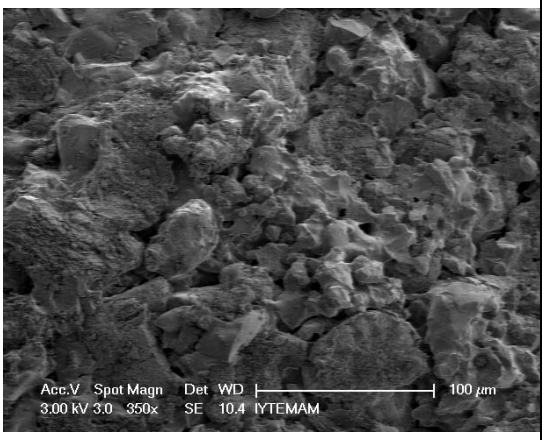
Table 4.8 Results of characterization tests for pellet sized samples

							XRD Peak Intensity Data		
Exp. No	**Bayer Alumina**	**Clay**	**Quartz**	**T (°C)**	**Apparent Porosity(%)**	**Permeability**	**Aluminum Oxide**	**Mullite**	**Quartz**
S1	70	30	0	1300	46	High	171	14	
S2	60	40	0	1300	40	High	180	24	
S3	50	50	0	1300	38	High	137	19	
S4	40	60	0	1300	29	Very low	117	35	
S5	30	70	0	1300	22	Very low	98	40	
S6	60	20	20	1300	43	High	163	161	161
S7	70	20	10	1300	46	High	208	87	87
S8	60	30	10	1300	41	High	160	90	69
S9	70	10	20	1300	48	High	189	89	89
S10	50	30	20	1300	36	High	126	161	76
S11	60	10	30	1300	43	High	176	223	223
S12	50	20	30	1300	39	Medium	156	355	355

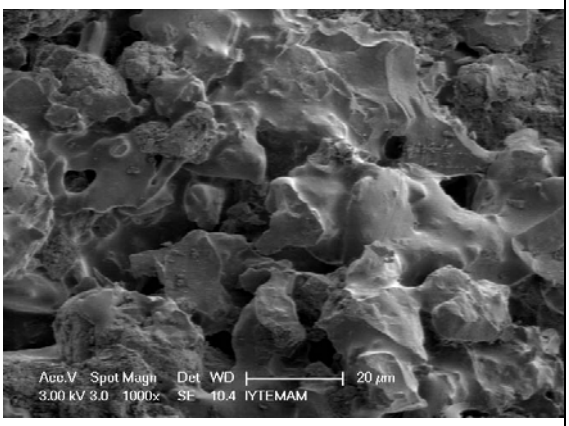
According to the test results, increasing Bayer alumina results in an increase in porosity and also permeability of the samples. Figure 4.12 shows the SEM image of the sample that contained Bayer alumina, quartz and clay together.



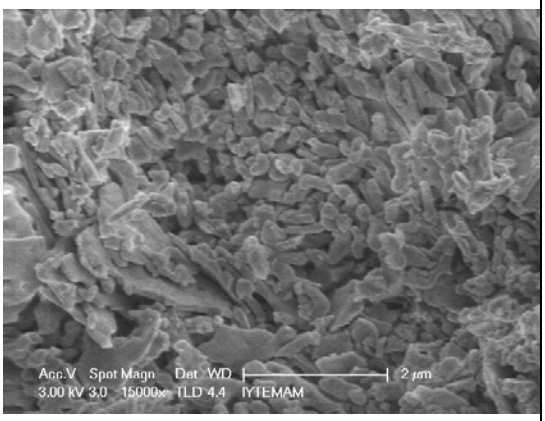
a)



b)



c)



d)

Figure 4.12 SEM images of the sample that contained Bayer alumina, quartz and clay in four different magnifications on one area. a) SEM image of sample S10 at 100x magnification b) SEM image of sample S10 at 350x magnification c) SEM image of sample S10 at 1000x magnification d) SEM image of sample S10 at 1500x magnification

Figure 4.12 shows that the Bayer alumina and quartz particles are partialy sintered and fused together so the small pores appeared around the particles. And also clay helps bond these particles. Figure 4.12 c) clearly shows this type of bond with vitrified glassy bond holding porous alumina particles together.

SEM-EDS analyses results also proved that vitrified area was richer in SiO_2 and porous area was richer in alumina (Figure 4.13. a) and b)). XRD analysis results are shown in Figure 4.14 for most of the small pellet samples. Almost all samples contained varying proportions of quartz, corundum and mullite as expected. In this temperature range of 1300^{o}C formation of mullite was expected.

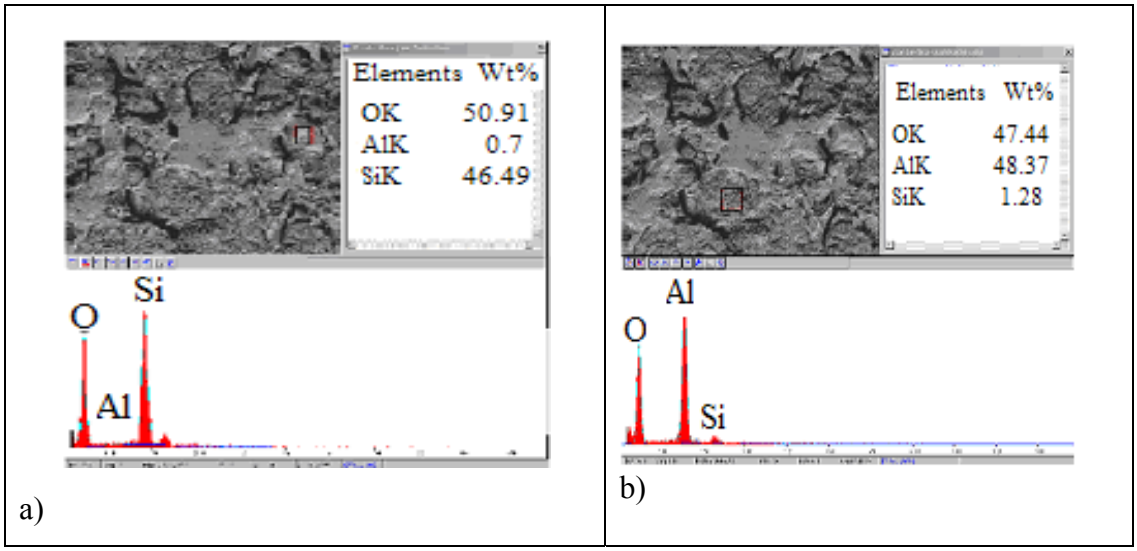


Figure 4.13. SEM-EDS analysis results for sample that contained Bayer alumina, quartz and clay for different points. a) EDX test result of sample S10 b) EDX test result of sample S10

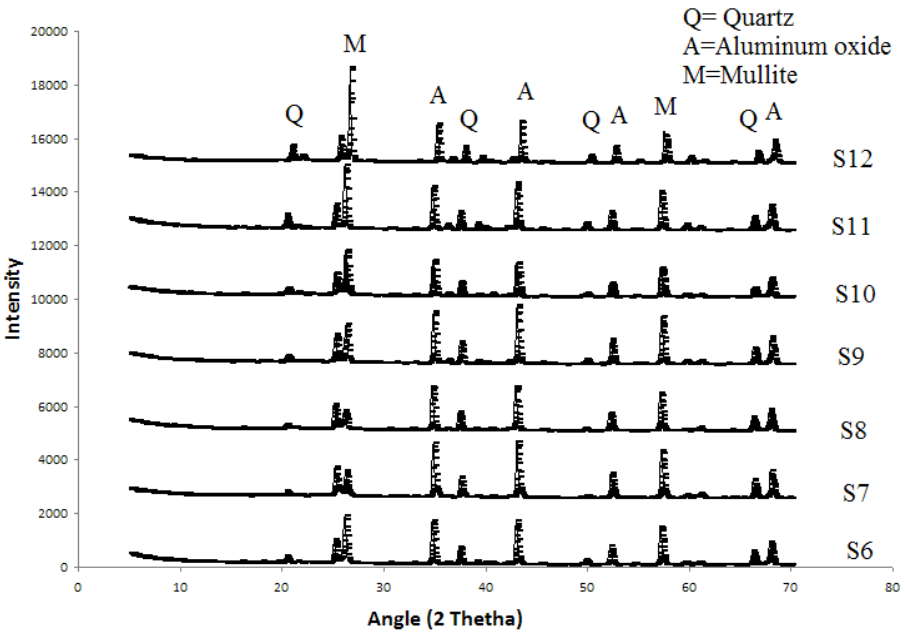


Figure 4.14. XRD test results of pellet samples with Bayer alumina, quartz and clay

In this study samples that contained bayer alumina and clay were also studied (Figure 4.15). Without quartz they had different characteristic properties. Corundum formed and silica in clay completely vitrified due to the absence of a quartz peak. Mullite crystals grew and were observed in the XRD diagram. Figure 4.15 shows the XRD test results of pellet samples with Bayer alumina and clay. Figure 4.16 shows SEM-EDS analysis results for a sample that contained Bayer alumina and clay in different locations. These results indicated that there were vitrified areas rich in silica and porous areas rich in alumina.

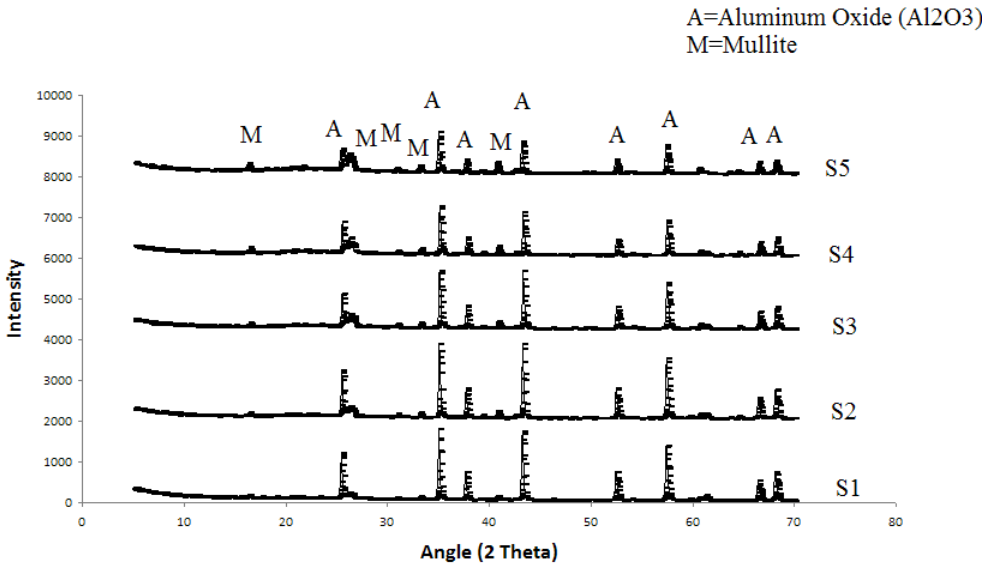


Figure 4.15. XRD test results of pellet samples with Bayer alumina and clay

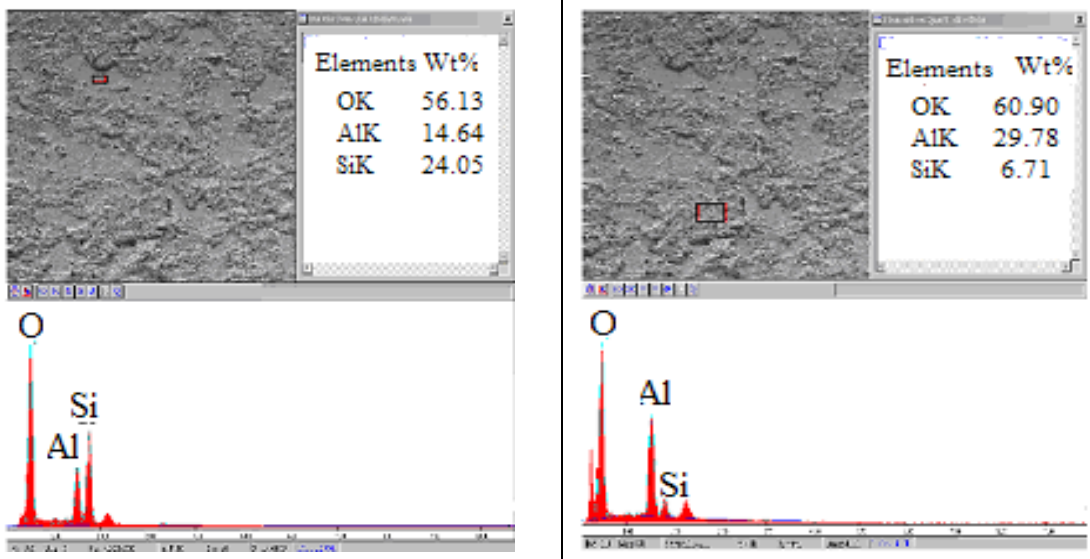


Figure 4.16. SEM-EDS analysis results for sample that contains Bayer alumina and clay for different locations. a) EDX test result of sample S3 b) EDX test result of sample S3

4.2.5 Large Plates of Porous Ceramics Made from Clay, Quartz and Bayer Alumina by Dry Pressing

In this section results of the experiments aimed at producing large sized porous plate type ceramics are presented. The reason for increasing the sample dimensions was to see if the results from smaller pellet samples could be reproduced with larger samples and also to be able to observe the oxygen concentration increases in water when these porous ceramics are used in a air diffuser assembly. Table 4.9 shows results of these experiments and their comparison to the previously produced small pellet samples. Small samples had larger fraction of pores in all samples. This difference could originate from differences in green forming procedure.

Table 4.9. Comparison of pellet samples and big samples according to apparent porosity

Exp. No	Bayer Alumina	Clay	Quartz	T (°C)	Bulk Density (g/cm^3)	Apparent Porosity (%)	Darcy Perm. $x10^{-5}$
L1	70	30	0	1300	1.48	51	61
L2	60	40	0	1300	1.52	41	58
L3	50	50	0	1300	1.68	43	62
L10	50	30	20	1300	1.73	40	55
L13*	50	40	10	1300	1.82	41	54
L14	40	50	10	1300	2.07	16	25
L13-1	50	40	10	1260	1.85	43	56
L13-3	50	40	10	1340	1.73	38	51
S1	70	30	0	1300	1.82	46	-
S2	60	40	0	1300	1.96	40	-
S3	50	50	0	1300	2.04	38	-
S10	50	30	20	1300	1.96	36	-

* L13 and L13-2 are the same samples.

Effect of firing temperature was also investigated. One sample (L13) was fired at three different temperatures. According to the values in Table 4.7, when the firing temperature was increased apparent porosity values decreased. This was an expected result. Because when the firing temperature increases sintering and vitrification between the clay, quartz and Bayer alumina enhances so apparent porosity between them decreases. Pores are closed by the vitrified glassy material that is driven into the pores by capillary action. Figures 4.17 to 4.19 show the SEM image of the samples that were fired at different temperatures. Sampe L13-1 which was fired at the lower temperature of 1260^{o}C was more friable and weaker in compression tests.

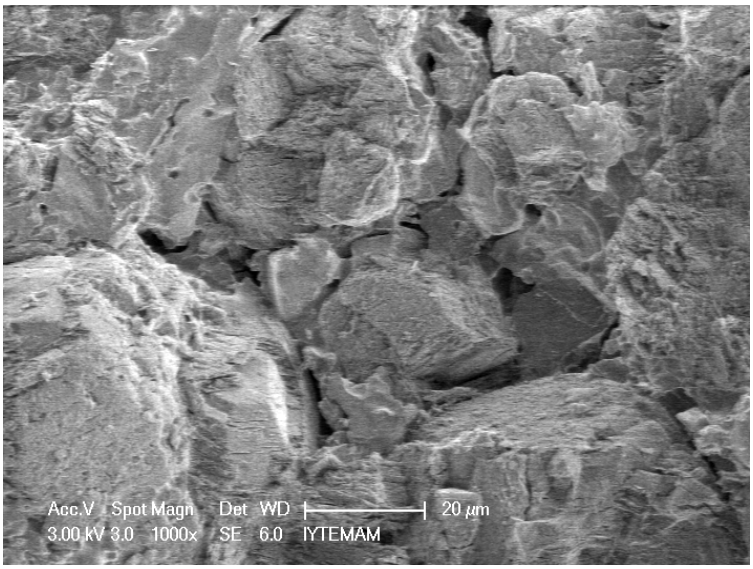


Figure 4.17 SEM image of the fracture surface of the sample L13-1 (1260 ^{o}C)

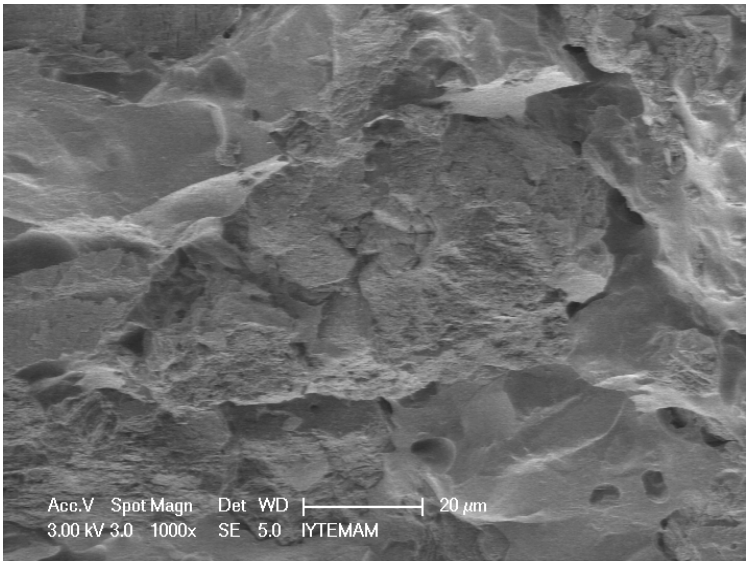


Figure 4.18 SEM image of the fracture surface of the sample L13-2 (1300 ^{o}C)

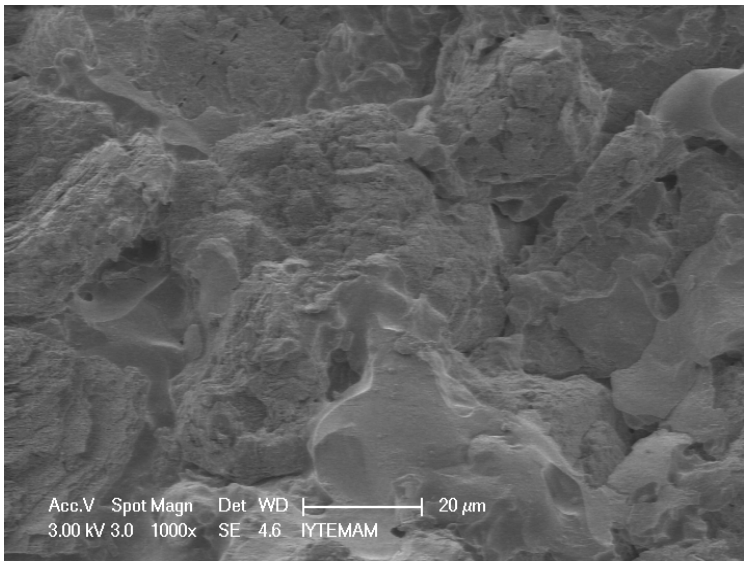


Figure 4.19 SEM image of the fracture surface of the sample L13-3 (1340 ^{o}C)

Powder mixtures were blended in a tumbling ball mill with or without grinding media for different durations and the changes in apparent porosity values of the compressed and fired ceramic plate samples were compared. Table 4.10 shows the apparent porosity values of these samples.

Table 4.10. Mixing conditions and apparent porosity values of the samples.

Exp. No	**Bayer Alumina**	**Clay**	**Quartz**	**T (°C)**	**Grinding media present?**	**Time**	**Apparent Porosity(%)**
L3	50	50	0	1300	Alumina Balls	30 min	39
L3	50	50	0	1300	Alumina Balls	3 min	43
L3	50	50	0	1300	No media	3 min	43

According to the Archimedes test results, duration of milling did not produce a significant difference when grinding media was present. However, the presence and absence of a media made a difference by providing better packing ceramic with less porosity due partially to the presence of a larger fraction of the smaller particles.

4.3. Results of Oxygenation and Permeability Measurements

In this section a pool of water (600x600x600mm) in a glass container like in an aquarium was used as part of the test setup. The purpose was to increase the concentration of oxygen in water by bubbling air into the water through the porous ceramic. Ceramic samples were fixed on a custom made assembly (Figure 4.20) by a water resistant glue sealant. Air was pumped at 1 bar of pressure from underneath the aluminum assembly through the ceramic into the water. A huge number of bubbles were observed to rise in the water. The differences in the concentration of dissolved oxygen in water were measured during 17 minutes of bubbling. Figure 4.21 shows the improvement in oxygenation of water by using porous ceramics that contained only Bayer alumina and clay. The vertical scale in Figures 4.21-23 shows the increase in oxygen concentration achieved as a result of bubbled air through the porous ceramic into the water. The initial dissolved oxygen concentration values were roughly 6mg/l. The results shown in Figures 4.21-23 indicate on the vertical axis the amount of increases achieved in dissolved oxygen concentration. According to Figure 4.21, the highest achieved oxygenation value was obtained in sample L3 which had the highest apparent porosity. A similar diagram is given in Figure 4.22 for ceramics containing all three components of Bayer alumina, quartz and clay. When the Bayer alumina to quartz ratio decreased, oxygenation was reduced.

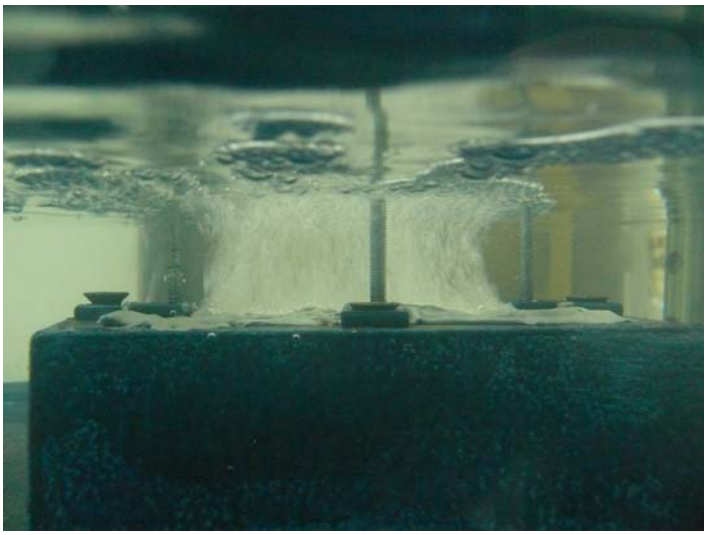


Figure 4.20. Bubbles rising from the porous ceramic into the water.

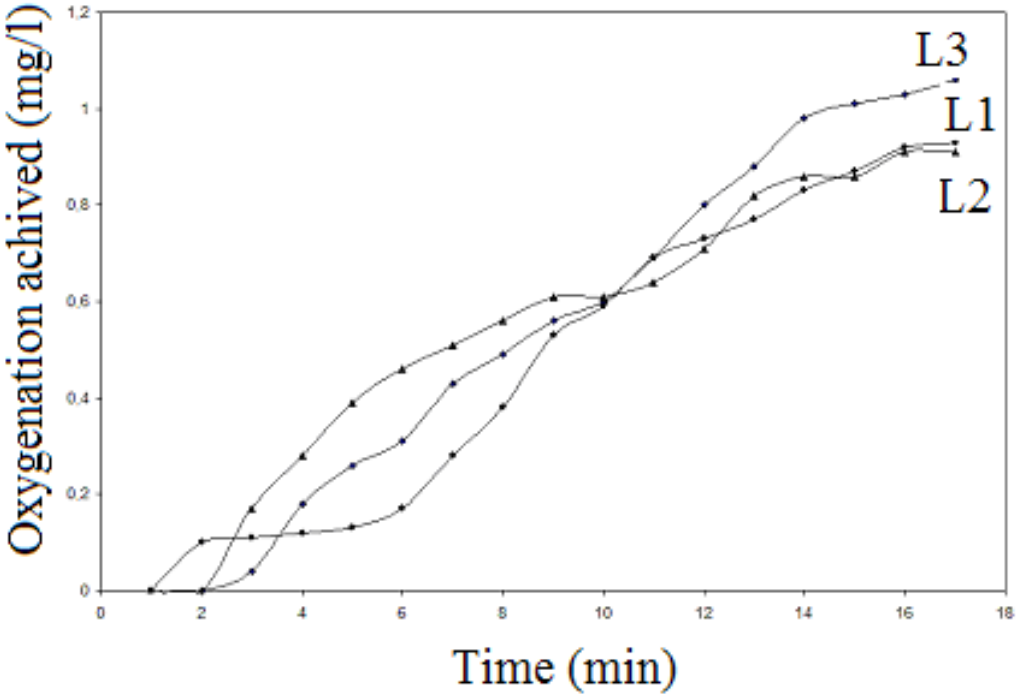


Figure 4.21. Oxygenation of water as a function of time by bubbling air through porous ceramic sample. Ceramic is composed of Bayer alumina and clay.

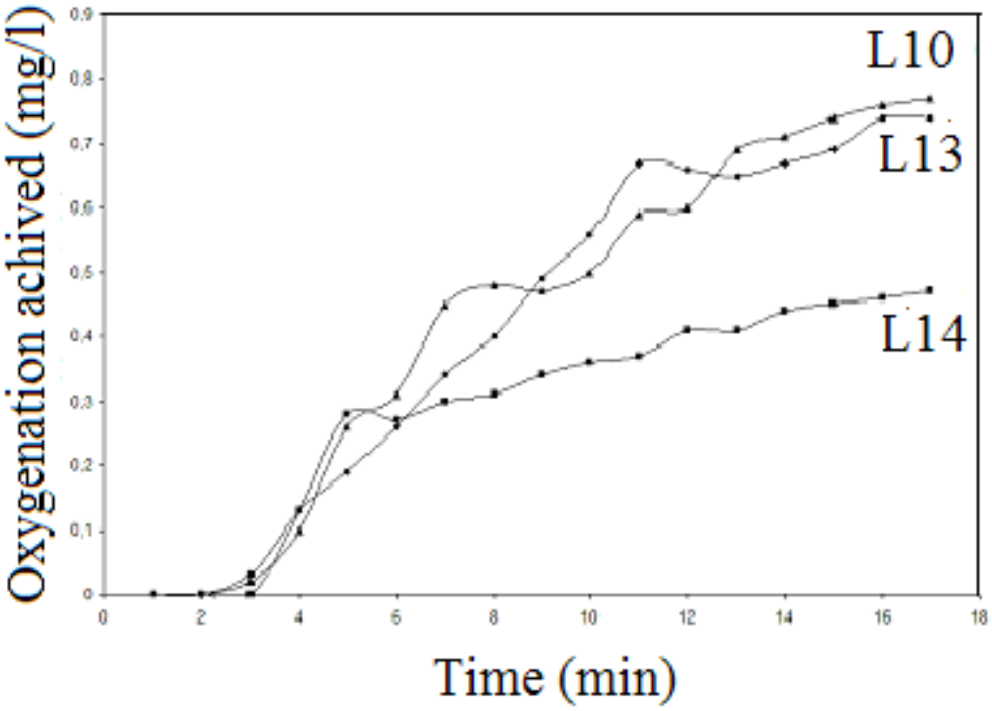


Figure 4.22. Oxygenation of water as a function of time by bubbling air through porous ceramic sample. Ceramic is composed of Bayer alumina, clay and quartz.

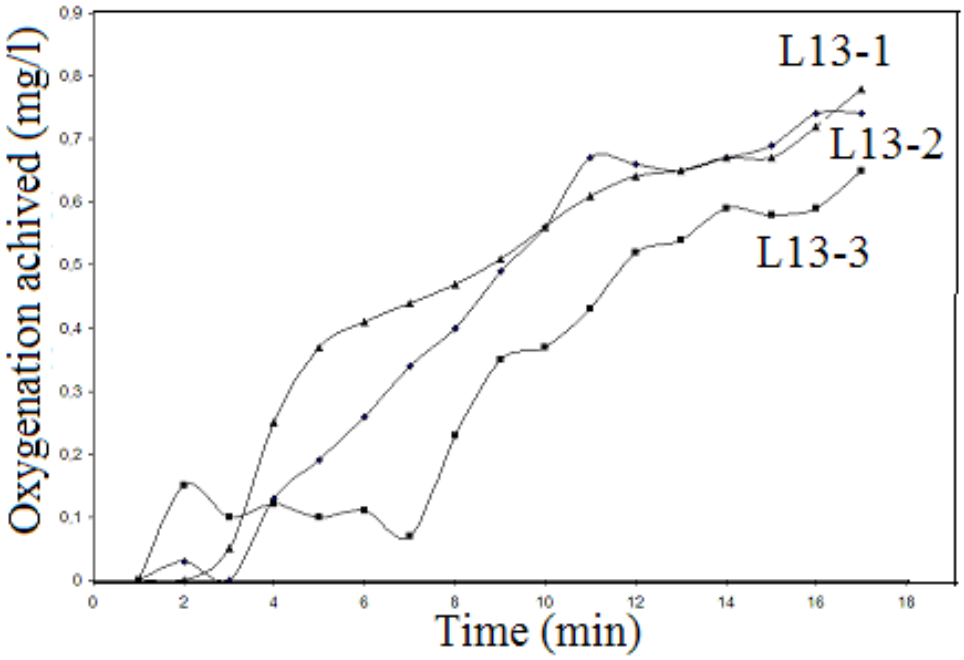


Figure 4.23. Graph of oxygenation differences between the samples that were fired at different temperatures.

Oxygenation depends on apparent porosity. When the apparent porosity value increases, oxygenation also increases. The maximum oxygenation value was observed in sample 10 which has the highest porosity value. Sample L3 had the lowest oxygenation because it was fired at the highest temperature which probably closed many pores.

4.4. Mechanical Test Results of The Samples

In this study mechanical properties of the samples are analysed by using uniaxial compression test. Samples should have some mechanical strength to resist the pressure of air. Compression test results from compression side are shown in Table 4.11.

Table 4.11. Compressive strength values of samples from the compression side

Exp. No	Bayer Alumina	Clay	Quartz	T (C)	Apparent Porosity(%)	Average Compressive Strength (N/mm^2)
L1	70	30	0	1300	51	9.2
L3	50	50	0	1300	43	25.9
L10	50	30	20	1300	50	39.3
L13	50	40	10	1300	41	69.8

In order to determine the compressive strength, there were three replicate samples for each composition. Compressive strength values that are shown in Table 4.11 are the average values of all of the test results. According to these test results, when the porosity increases compressive strength decreases. Quartz additions help increase strength but if more than 10% is added strength was found to be compromised. Figure 4.24 shows the mechanical behaviour of samples that contain Bayer alumina and clay.

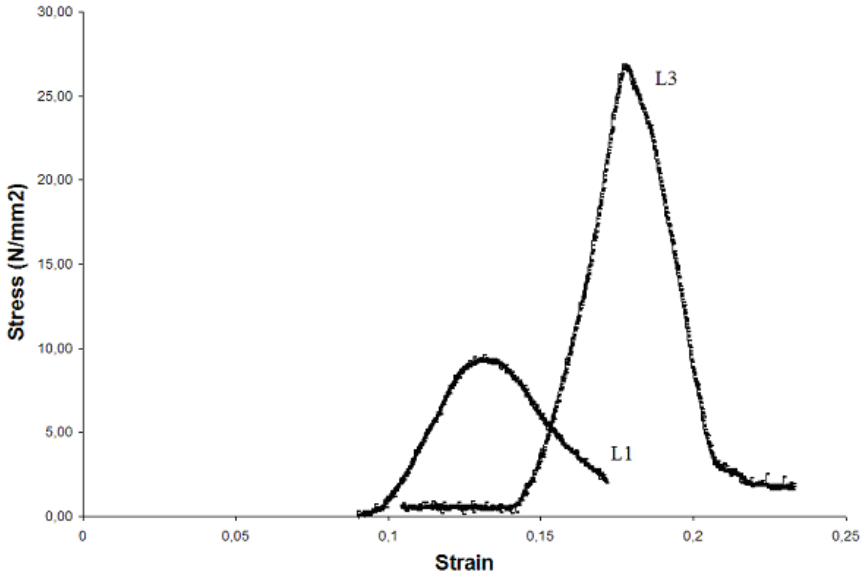


Figure 4.24. Stress-strain behavior of samples that contain Bayer alumina and Clay.

Figure 4.24 proves that increasing porosity cause a decrease in mechanical strength. And also mechanical test results showed that quartz makes the sample more

sturdy. Figure 4.25 shows the mechanical test results of the sample that contained Bayer alumina, clay and quartz.

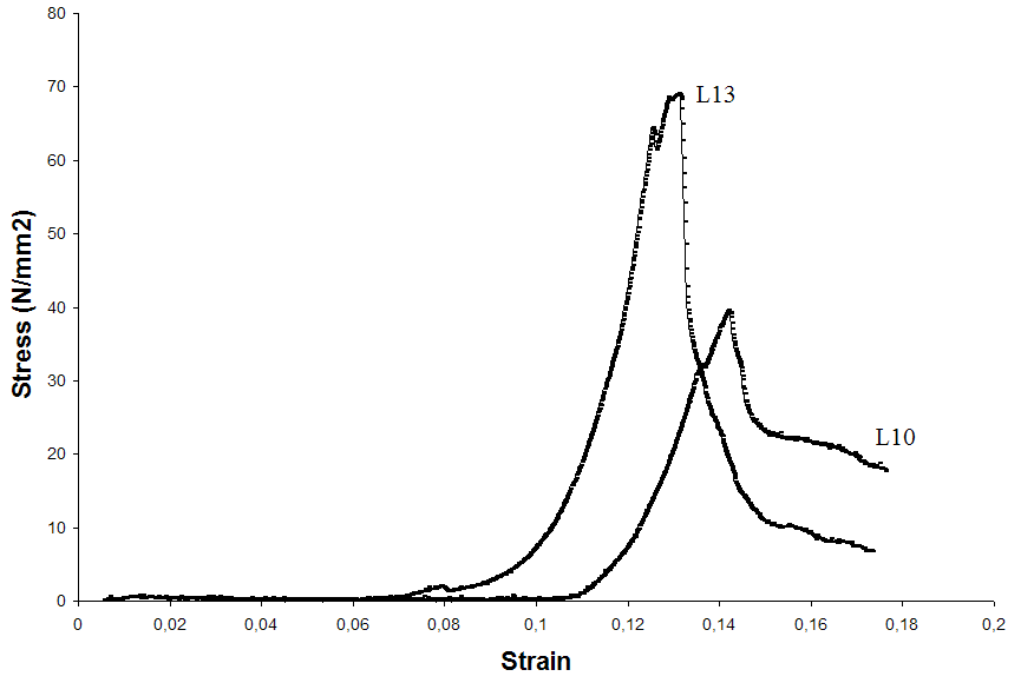


Figure 4.25. Graph of mechanical behaviour of samples that contain Bayer alumina, quartz and Clay.

The values in Figure 4.25 shows that quartz almost double the strength of the samples without quartz. And also increasing porosity causes a decrease in compressive strength.

In this study sample L13 was fired at a different temperature. In that way the affect of firing temperature was investigated. Table 4.12 shows the compressive strength values of the samples that were fired in different temperatures.

Table 4.12. Compressive strength values of the samples that were fired in different temperatures.

Exp. No	Bayer Alumina	Clay	Quartz	T (°C)	Average Compressive Strength (N/mm^2)
L13-1	50	40	10	1260	39.2
L13-2	50	40	10	1300	69.8
L13-3	50	40	10	1340	82.0

For this experiment each of the sample types was tested three times and the average value of the compressive strength was calculated. According to the results in Table 4.12, when the firing temperature increased, strength of the sample was increasing because of the better sintering. Figure 4.26 shows the mechanical behaviour some of the samples. Evidently, increasing firing temperature increases strength of the ceramic samples.

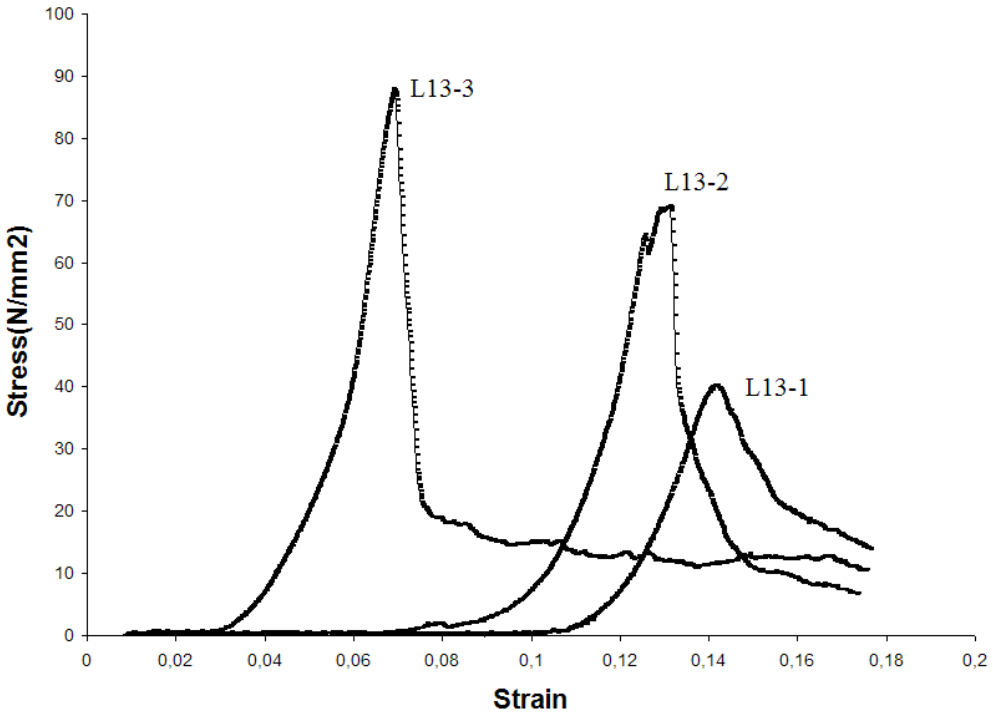


Figure 4.26. Graph of mechanical behaviour of sample L13 that was fired at different firing temperatures.

CHAPTER 5

CONCLUSIONS

A porous ceramic that allows bubbling of air into water at 1 bar of pressure was successfully developed. Many different compositions were tested. The use of superground alumina was not successful because the particle size was too small and the pores were closed thereby forbidding any air transport through the ceramic. Additions of corn starch to this material did not help much because any contribution of porosity was closed porosity and that was useless in air transport. Limited success was accomplished when clay, quartz and corn starch were used but this time the pressure needed to produce a reasonable amount of bubble in water was higher than 1 bar which was the initially set goal for this project. Bayer alumina was used as a replacement for superground Alcoa alumina to help with porosity because these powders are well known to be agglomerated and to offer high amount of porosity. Smaller fraction of quartz was added to help with strength and clay to assist in forming and very good results were obtained. Ceramics made from 50% Bayer alumina and 50% clay provided very good oxygenation of water. However, their strength was not as good as samples made from 50% Bayer alumina, 20% quartz and 30% clay. These latter samples had higher strength and slightly lower oxygenation. A 10% addition of quartz was found to improve strength. The use of these ceramics as air diffusers can help oxygenate water which is needed in a lot of different applications.

Suggestions for future study include the use of smaller sized electrofilter Bayer alumina and more experiments to observe the effects of firing soak time and temperature.

REFERENCES

Acchar, W. Souza, F.B.M. Ramalho, E.G. and W.L. Torquato. 2009. Mechanical characterization of cellular ceramics. *Materials Science and Engineering* A(513-514): 340-343.

Aksay, I.A. and J.A. Pask. 1975. Stable and metastable equilibria in the system SiO_2 Al_2O_3. *Journal of the American Ceramic Society.* 58(11-12): 507-512.

Aluminiumville. 2007. Bayer Process. http://www.aluminiumville.co.uk/bapro.html (accesed May 28,2009).

Canon, J. and T. Sander. 1997. New test method for evaluating permeability of refractory castables. *Refractory Applications.* 2(1): 6 – 7.

Dryden.Aqua,2009...Airation..and..oxygenation..systems..http://www.drydenaqua.com/air_oxygen_diffusers/aeration/airdiffusers/faq/faqq.htm (accesed May 12,2009).

Dong, Y. Diwu, J. Feng, X. Liu, X. and G. Meng. 2007. Phase evolution and sintering characteristics of porous mullite ceramics produced from the flyash-$Al(OH)_3$ coating powders. *Journal of Alloys and Compounds* 460 (1): 651-657.

Erol, M. 2008. Ankara üniversitesi KYM 345 2007-2008 ders notları BL2. http://chem.eng.ankara.edu.tr/345/345not3.pdf (accesed May 13,2009).

Edinburgh University. 2002. Division of engineering materials science and engineering. http://www.cmse.ed.ac.uk/MSE3/Topics/MSE-permeability.pdf (accesed May 10,2009).

Gitzen, Walter H. 1970. *Alumina as a Ceramic Material*. Ohio: Wiley-American Ceramic Society (4).

Innocentini, M.D.M. Rodriguesa, V.P. Romanob, R.C.O. Pileggi, R.G. Silvac, G.M.C. and J.R. Couryc. 2009. Permeability optimization and performance evaluation of hot aerosol filters made using foam incorporated alumina suspension. *Journal of Hazardous Materials* 162(1): 212–22.

Innocentini, M.D.M. Rizzi, A.C. Nascimento, L.A. and V.C. Pandolfelli. 2004. The pressure–decay technique for air permeability evaluation of dense refractory ceramics. *Cement and Concrete Research* 34 (1): 293-298.

Innocentini, M.D.M. and V.C. Pandolfelli. 2001. Permeability of porous ceramics considering the Klinkenberg and inertial effects. *Journal of American Ceramic Society*. 84(5): 941-944.

Isobe, T. Tomita1, T. Kameshima, Y. Nakajima, A. and K. Okada. 2006. Preparation and properties of porous alumina ceramics with oriented cylindrical pores produced by an extrusion method. *Journal of the European Ceramic Society*. 26(1): 957–960.

Isobe, T. Kameshima, Y. Nakajima, A. and K. Okada. 2007. Preparation and properties of porous alumina ceramics with uni-directionally oriented pores by extrusion method using a plastic substance as a pore former. *Journal of the European Ceramic Society*. 27(1): 61–66.

Kingery, W.David., Bowen, H.K.and Donald R. Uhlmann, eds. 1976. *Introduction to Ceramics.* Second Edition. New York: John Wiley &Sons.

Life Science. 2006. The oxygen cycle. http://www.lifesciences.napier.ac.uk/teaching /Env/Ocycle06.htm (accesed May 15,2009).

Lining Water Aeration. 2009. Lake and pond aeration. http://www.livingwateraerati on.com/lapoae1.html (accesed May 15,2009).

Mao, X. Wang, S. and S. Shimai. 2008. Porous ceramics with tri-modal pores prepared by foaming and starch consolidation. *Ceramics International*. 34(1): 107–112.

Nasker, H. and J. Danisch. 1991. *Forming techniques for self-reliant potter*. New York: Friedrich Vieweg & Sohn .

Parkhill, K.L. and J.S Gulliver. 1997. Indirect Measurement of Oxygen Solubility. *Water Resource*. 31 (10) : 2564-2572.

Pondexpo. 2009. Air diffuser. http://www.pondexpo.com/products/aeration/diffuser.php (accesed May 9,2009).

Rahaman, M.N. 2003. *Ceramic Processing and Sintering*. Second Edition. New York: CRC Press .

Reed, J.S. 1995. *Principles of Ceramics Processing*. Second Edition. New York: John Wiley &Sons.

Sadowski, T. and S. Samborski. 2007. Development of damage state in porous ceramics under compression. *Computational Materials Science*. 43 (1): 75-81.

Schierholza, E.L. Gulliverb, J.S. Wilhelmsc, S.C. and H.E. Hennemand. 2006. Gas transfer from air diffusers. *Water Research*. 40 (1): 1018 – 1026.

Sembach. 2007. Dry pressing. http://www.sembach.com/production_dry_pressing_en ,818.html (accesed May 9,2009).

Sepulveda, P. and J. G. P. Binner. 1999. Processing of Cellular Ceramics by Foaming and in situ Polymerisation of Organic Monomers. *Journal of the European Ceramic Society*. 19 (1): 2059-2066.

Shuqiang1, D. Yu-Ping, Z. and J. Dongliang. 2007. Gas permeability behavior of mullite-bonded porous silicon carbide ceramics. *Journal of Materials Science*. 42 (17): 7171- 7175.

Studart, A.R. Gozenbach, U. T. Tervoort, E. and L.J. Gauckler. 2006. Processing of Routes to Macroporous Ceramics: A Review. *The American Ceramic Society*. 89 (6):1771-17789.

Şahin, S. 2000. Boksitlerden Bayer Prosesi ile Alumina Üretiminde Yer Alan Su Giderme İşleminin Teknolojik Esasları. *Journal of Qafqaz University*. 1(6): 177-188.

Tambaş, T. Özgen, S. 2007. Seydişehir Aluminasının Slip Döküm Parametrelerinin Belirlenmesi. *İtü dergisi*. 6(2): 83-94.

TC. Başbakanlık GAP. 2004. TC. Başbakanlık GAP projesi, Bölge kalkınma idaresi başkanlığı 2004. tp://www.gap.gov.tr/Turkish/Tarim/Suurunyt/alabalik.pdf (accesed May 9,2009).

Wikipedia. 2009. Darcy permeability. http://en.wikipedia.org/wiki/Fitzwilliam_Darcy (accesed May 19,2009).

Wikipedia. 2009. Water Oxygenation. http://en.wikipedia.org/wiki/Lake_aeration (accesed May 18,2009).