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Development of glass-ceramics from combination of industrial wastes with boron mining waste

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Yaşamak şakaya gelmez,
büyük bir ciddiyetle yaşayacaksın
bir sincap gibi mesela,
yani, yaşamanın dışında ve ötesinde
hiçbir şey beklemeden,
yani bütün işin gücün yaşamak olacak.

Yaşamayı ciddiye alacaksın,
yani o derecede, öylesine ki,
mesela, kolların bağlı arkadan, sırtın
duvarda,
yahut kocaman gözlüklerin,
beyaz gömleğinle bir laboratuarda
insanlar için ölebileceksin,
hem de yüzünü bile görmediğin insanlar
için,
hem de hiç kimse seni buna
zorlamamışken,
hem de en güzel en gerçek şeyin
yaşamak olduğunu bildiğin halde.

Yani, öylesine ciddiye alacaksın ki
yaşamayı,
yetmişinde bile, mesela, zeytin
dikeceksin,
hem de öyle çocuklara falan kalır diye
değil,
ölmekten korktuğun halde ölüme
inanmadığın için,
yaşamak yani ağır bastığından.

Nazım Hikmet

La vita non è uno scherzo.
Prendila sul serio
come fa lo scoiattolo, ad esempio,
senza aspettarti nulla
dal di fuori o nell'al di là.
Non avrai altro da fare che vivere.

La vita non é uno scherzo.
Prendila sul serio
ma sul serio a tal punto
che messo contro un muro, ad esempio, le mani legate,
o dentro un laboratorio
col camice bianco e grandi occhiali,
tu muoia affinché vivano gli uomini
gli uomini di cui non conoscerai la faccia, e morrai sapendo
che nulla é più bello, più vero della vita.

Prendila sul serio
ma sul serio a tal punto
che a settant'anni, ad esempio, pianterai degli ulivi
non perché restino ai tuoi figli
ma perché non crederai alla morte
pur temendola,
e la vita peserà di più sulla bilancia.

Nazim Hikmet

Alla Bella Bologna…

ABSTRACT

This thesis was aimed to develop efficient utilization methods for highly produced waste materials using glass-ceramic technology. Glass-ceramic materials feature a great potential for environmental clean-up, since they may combine waste stabilization and valorization. In present research, considering the main aim of the thesis, as environment friendly waste utilization, energy consumption was also noticed, in order support environment respecting production techniques. For this concern a controlled fast heating rate, ranging between 40ºC min^{-1} to 2 ºC min^{-1} was applied to studied waste mixtures.

The borate mineral wastes obtained through boron mines and enrichment plants were selected to be the constant starting material in all performed studies. Borate mineral wastes contain high amount of B_2O_3, a very well-known glass forming oxide with a large scale of application areas, also providing lower sintering temperatures. The utilization of borate mineral wastes with glass-ceramic technology was first time studied and primarily not investigated combinations of wastes were incorporated into the research. These wastes consist of; soda lime silica glass, meat bone and meal ash and fly ash. In order to investigate possible and relevant application areas in ceramics, kaolin clay, an essential raw material for ceramic industry was also employed in some studied compositions. Different proportions prepared according to the objected glass-ceramic ternary systems such as; B_2O_3–P_2O_5–SiO_2 (boro-phospho-silicate) and SiO_2-Al_2O_3-CaO (wollastonite).

In order to determine cytotoxicty, cell toxicity analyses applied to some of the studied products, in order to see the effect of boron (a regular daily intake element) in glass structure.

As a result, three different glass-ceramic articles obtained by using powder sintering method via individual sintering processes. Light weight micro porous glass-ceramic from borate mining waste, meat bone and meal ash and kaolin clay was developed. In some compositions in related study, soda lime silica glass waste was used as an additive providing lightweight structure with a density below 0.45 g/cm^3 and a crushing strength of 1.8±0.1 MPa.

In another study within the research, compositions respecting the B_2O_3–P_2O_5–SiO_2 glass-ceramic ternary system were prepared from; borate wastes, meat bone and meal ash and soda lime silica glass waste and sintered up to 950ºC. Low porous, highly crystallized glass-ceramic structures with density ranging between 1.8 ± 0,7 to 2.0 ± 0,3 g/cm^3 and tensile strength ranging between 8,0 ± 2 to 15,0 ± 0,5 MPa were achieved.

Lastly, diopside - wollastonite glass-ceramics (SiO_2-Al_2O_3-CaO) from borate wastes, fly ash and soda lime silica glass waste were successfully obtained with controlled rapid sintering up to 950 and 1050ºC. The wollastonite and diopside crystal sizes were improved by adopting varied combinations of formulations and heating rates.

The properties of the obtained materials show; the products with a uniform pore structure could be useful for thermal and acoustic insulations and can be embedded in lightweight concrete where low porous glass-ceramics can be employed as building blocks or additive in cement and ceramic industries.

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Chapter 1

Boron

1.1 History of Boron

The name “Boron” originates from the Arabic word “Buraq” and it may have been known approximately since 6000 years. Today, it is known that Babylonians used boron as flux in their gold and silver treatments. Archeological researches also showed Egyptians, not far from its missions today, took advantages of boron in mummifying, medical and metallurgic applications.[1]

The first recognized boron ore beds were located in Tibetan lakes, where the name “Tincal” (a former synonym, e.g., tincar) comes from. Boron containing minerals obtained from these lakes were carried to China and, over Himalayans, to India[2]. The usage of boron by Arabian gold and silversmiths in 8th century[2], preoccupies that these minerals were brought there from India by Arabian traders using Indian-Arabic trading routes, which were highly used at those times[3]. Famous explorer Marco Polo was the one who introduced boron from India to Europe first in 13th century[2].

Until the researches in 1808 made by the triumvirate of England’s Sir Humphrey Davy, Joseph Louis Gay-Lussac and Louis-Jacques Thénard from France, boron was considered as a mineral rather than an element. Humphrey Davy prepared boron by reduction of boron trioxide with potassium and by electrolysis of moistened boric acid. The purity of their products was about 50% and named “Boracium”[4]. Louis-Jacques Thénard and Gay-Lussac used iron to reduce boric acid at high temperatures. They oxidized boron with air and proved that boric acid is an oxidation product of boron[5]. Jöns Jakob Berzelius identified boron as an element in 1824[6]. In 1909, William Weintraub produced 99 % pure boron[7]; these “discoveries” lead boron to have a place in periodic table[2]. It took nearly 50 years that the right physical and chemical properties have been examined. High purity boron produced by electrolysis and vapor deposition methods has made such determinations possible.

In 18th century, Sassolite was found in Tuscany, Italy. Sassolite is a boron containing mineral and it occurs from boric acid carrying geyser steam[1]. It was produced thousands of tons per year to meet boric acid demand of Europe till 1950’s. In this period the first known industrial boron enrichment took place in England, Germany and France by converting boric acid into borax.[8]

Turkey, today world’s largest boron producer started its boron mining facilities during Ottoman Empire times in 1865. The first production was borate pandermite (priceite, $4CaO_5B_20_3$ $7H_20$)[8]. After Ottoman Empire’s fall, Turkish Republic took control of the mines and launched a new national mining enterprise called ETI, taking its name from ancient Hittites civilization, known as first modern miners in history. Turkey, first started its modern manufacturing with supplying colemanite ($CaO\bullet 3B_2O_3\bullet 5H_2O$) for European boric acid producers. As a result of exploring new boron mines and increasing technology, today, Turkey produces large variety of boron products through holding 72% of world’s boron resources.[9]

Figure 1.1.1: Pandermite production in Turkey at the end of 1800’s

Around same times with Turkey's boron mining facilities, several colemanite and ulexite deposits were found in California, Nevada (1872) and in Searles lake (1873) U.S.A. The first investors could easily turn these minerals into Borax and increased its commercial value. Today these mines are operated by U.S.A's leading boron producers, U.S Borax (owned by Rio Tinto Group) and Searles Valley Minerals (owned by India's Gujarat-based Nirma Limited). These two companies are still the largest boron producers of U.S.A[10].

Turkey and U.S.A are the top Borate producing countries, followed by China, Peru, Bolivia, Chile, Kazakhstan, Argentina and Iran.

Figure 1.1.2: Borate production in early 1900's at Searles Lake, CA, USA

1.2 Properties of Boron

Boron is a ubiquitous element in rocks, soil, coal, water (in the oceans mostly in the form of borates)[11]. It takes part more than in 230 mineral in nature[9]. It is a metalloid element with an atomic number of 5 and symbolized with letter B. It is located at the top of right hand side of periodic table in group 3A (See Figure 3): surprisingly, its beviour is more similar to silicon than to other metalloids.[12] Boron has two stable isotopes, these are ^{10}B and ^{11}B and it does not generally make ionic bonds, forms stable covalent bonds. Compared to high industrial benefit class elements, so-called competitors, boron's structure is extremely simple. This simple structured element is also considered as one of the most problematic industrial element due to its characteristics in mining and enrichment processes.

Figure 1.2.1: Boron in Periodic Table

Boron is a hard element, after Carbon (diamond), crystalline boron is the second hardest of all the elements on the Mohs scale. In 2009, a team led by Artem Oganov was able to demonstrate the new form of boron contains two structures, B_{12} icosohedra and B_2 pairs. Gamma-boron, as it has been called, is almost as hard as diamond and more heat-resistant than diamond[13].

Chemical characteristics of boron depend on its particle size and morphology, in example; while micron sized amorphous boron can react easily, crystalline boron stays unreactive under similar conditions.

Boron has high heat resistance; its melting point is 2075°C. Only 11 elements have higher melting points than boron, these are C, W, Re, Os, Ta, Mo, Nb, Ir, Ru, Hf, and Tc[14]. At room temperature it is a poor conductor of electricity, but a good conductor at high temperature.

Boron has unique optical properties, it can transmit infrared light; boron mineral ulexite exhibits natural fiber optic properties[15].

1.3 Boron and Environment

Elemental boron is not considered to be toxic for mammals but assimilation of boron compounds has a cumulative toxic effect[16]. Boron containing minerals exhibit high solubility in water, as a consequence, boron compounds can easily merge with hydrological systems and they can be a link to reach organics systems, like plants and animals[17]. When boron merges with plants, animals and drinking water, it would also have effects on human health[18].

Boron can also reach soil through atmospheric deposition, decomposition of organic matter and boron containing products (including boron containing fertilizers). It has been determined that between 1.3 and 4 million tonnes of boron are transmitted to atmosphere only from marine sources each year[19], the origin of which is not completely clear[20]. Boron in oceans generally occurs with an average concentration of 4.5 mg/litre[21] as borates, but the boron amount in fresh water is related with the geochemical nature of the drainage area, proximity to marine coastal regions, and inputs from industrial and municipal effluents.

For humans, boron exposure occurs primarily through the diet and drinking water, and its tolerable intake was set at 0.4 mg/kg body weight per day. However, the last results assessed in different countries, concerning the amount of boron in drinking water, underlines as it is set between 0.1 and 0.3 mg/litre (Table 1.3.1), corresponding to the mean global boron concentration in drinking water. For the general population, the greatest boron exposure comes from the oral intake of food: in the humans and animals, boric acid and borate are absorbed from the gastrointestinal and respiratory tracts, and the mean daily intake of boron in the diet is about 1.2 mg[22]. More than 90% of administered doses of these compounds are absorbed, as evidenced by a rapid excretion in the urine (occurring over a few to several days) [21].

Area	**Samples No.**	**Concentration (mg/litre)**
USA	2595	~1.0
Germany	240 110	~ 0.25 ~ 0.21

United Kingdom	N/A 200	0.05-0.505 0.01-0.45
Chile	N/A	0.31-15.0

Table 1.3.1: Concentrations of Boron in Drinking Water

Soruce: WHO (1998a) Guidelines for drinking-water quality. Second edition. Addendum to Volume 1: Recommendations. Geneva, World Health Organization.

1.4 Boron Uses

The significant progress in technology makes more complicated to comprehend the range of uses of boron. Traces of boron can be seen nearly in every field surrounding daily life, such as; construction, manufacturing, medicine, electronics, pharmaceuticals, telecommunication and aerospace products.

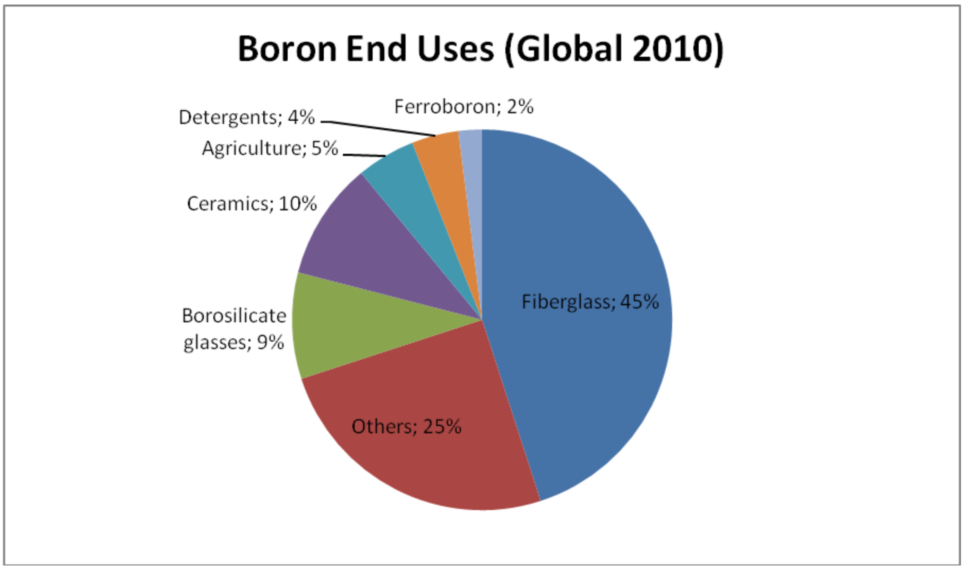
Today, there are more than 300 end uses linked with borates (Figure 1.4.1 represents the global rate of 2010). Approximately 75% of the world's supply is consumed by for four main end uses, which are: glass, agriculture, ceramics and cleaning products (detergents, soaps, bleaches). Their distribution, by the end of 2010, was: 54% glasses, 10% ceramics, 5% agriculture (fertilizers), 4% cleaning products, and 27 % others[23]. These mass boron consuming industries and their main products are reported in Table 1.4.1.[23]

GLASS	Borosilicate glass, Pyrex type glass, Lime-soda glass, Optical glass, Glass-fibres, Glass ceramics, Flat glass, Automotive glass, Sealed beam headlamps, LCD, Cookware, Laboratory-ware
CERAMICS	Ceramic tiles, Frit and Glazings, Earthenware and China Fluxes
DETERGENTS & SOAP	Sodium perborate, Washing powder,Hydrogen peroxide
AGRICULTURE	Fertilizers, Herbicides, Pesticides
METALLURGY	Flux covers in non-ferrous metallurgy, Cover flux in steel production, Metal boron alloys, Ferroboron, Metal boron alloys, Ne-Fe-B magnets
CORROSION INHIBITORS	Antifreeze, Brewing cutting fluids, Heat treatment, Hydraulic fluids
FLAME RETARDATION & WOOD PRESERVATION	Flame proofing of timber board, Plywood cotton textiles, Paper and cellulose insulation, Wire drawing and cables
ADHESIVES	Starch and dextrin based adhesives, Solvent and preservative for casein
ABRASIVES	Borosilicate glass matrix, Boron carbide
OTHERS	Nylon sizing, Paint, Paper, Plastics, Polishes, Refractory , Rubber, Catalysts, Cement and Concrete, Photography, Fire extinguishing, Electrolytic Capacitors, Leather and Skins, Pharmaceuticals, Cosmetics, Buffers in the manufacture of dyestuffs,Dying of nylon carpets, Absorbent to neutrons, Control of nuclear reactions

Table 1.4.1: Mass boron consuming industries and their main products

Since 1950s glass industry has been the main borate consuming market. Today, nearly 54 % of global borate consumption is used in glass industry. In glass, boron is used as an additive: it provides chemical resistance, reduction of thermal expansion, improvement of strength, durability, resistance against vibration, high temperature and thermal shock resistance. Boron effect can be seen evidently in a very widely known example: borosilicate glasses.

The other main aim of using boron in glass is, the ability of using it as a fluxing agent, reducing the viscosity of glass during formation.



Source: The Economics of Boron, 2010

Figure 1.4.1: Boron End uses

Insulation and textile fiberglass industries represent the largest single borate consumption with 45% of total consuming. In fiberglass, boron provides corrosion/heat-resistance, high-strength and improves quality significantly[2]. Mainly in Europe (as agreed by EU through the 20-20-20 targets [a24])

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[a] Due to EU's climate and energy policy released in March 2007, it has decided to combat against climate change and increase the EU's energy security while strengthening its competitiveness. They committed Europe to transforming itself into a highly energy-efficient, low carbon economy. These targets are;

- A reduction in EU greenhouse gas emissions of at least 20% below 1990 levels
- 20% of EU energy consumption to come from renewable resources
- A 20% reduction in primary energy use compared with projected levels, to be achieved by improving energy efficiency.

and developed countries, new buildings require higher standards[25] which will directly affect consumption amount of insulation fiberglass, as well as direct fiberglass using industries such as construction industry.

After glass, ceramic industry is the second largest boron consuming industry. Borates are highly used in frits, enamels, glazes and ceramic tile bodies. In glazes and enamels incorporation of borates increase chemical and wear resistance while reducing thermal expansion. This reduction provides a convenient fit between glaze and clay[26 27]. Lately, a new calcined borate, called E4972, was developed to replace conventional frits used in ceramic glazes. Frits were merged into glazes to obtain the convenient technical and aesthetic properties under short firing of ceramics. E4972 possesses a low solubility, which enables its use in glaze formation [26]. The amount of B_2O_3 used in glazes varies between 8% and 24% and the amount used in enamels is between 17% and 32% by weight.

In terms of economic and environmental benefits, boron lowers the energy consumption by helping to lower the sintering temperature. Boron existing in borates act as a flux and as an inorganic binder in ceramic tile body compositions. In the pressed body, boric acid increases the dry mechanical strength around 40%.

For the porcelain stoneware tiles composition, the main benefits of adding borates include [27]:

- Time reduction of the firing cycle, typically by 10-20%, enabling a better performance of the furnace.

- Reduction of the tile thickness due to a substantial increase (30-80%) in the dry mechanical strength of the unfired tiles. For example, an increase of 25% in dry mechanical strength allows the thickness to be reduced by around 10%.

- Reduction of the body formulation cost by substituting up to 20% feldspar and balancing with lower cost silica to maintain the peak temperature and cycle length. Alternatively, the binding effect of the boric acid can be used to substitute some high quality clay with lower quality, less plastic clay to further increase cost savings.

- Reduction of the firing temperature by more than 25°C, keeping the same cycle length, and thereby producing energy savings.

Boron in the form of Boron Carbide is a vital ingredient in lightweight ceramic armor used in defense industry. In example; boron carbide ceramic plates in Kevlar flak jackets protect soldiers from high-velocity projectiles such as bullets[28].

Late advancements in ceramic industry suggest that the demand for boron in ceramic industry will rise continuously. In recent years, China, Brazil and Turkey are rapidly increasing their ceramic tile and sanitary ware production amount. Together with undeniable impact of European economic crisis that took place in 2010, losses caused by these new competitors can be seen in European ceramic industry. Consumption of borates by the ceramics industry is expected to shift away from Europe to Asia, which accounted for 60% of world demand in 2010[29]. For giving an idea concerning the increasing consumption, the boric acid import of China only from U.S.A jumped from 26.500Mt to 59.900Mt between 2009 and 2010[30].

In agriculture, boron is considered as a must nutrient. As in case of all nutrients, boron requirements differ widely between species, so that deficient tissue levels for one species might already be toxic for another one. In agriculture, boron is highly required for plant growth and must remain available for plant uptake during the growth period. Boric acid and calcium borate are highly used as fertilizers serving nearly in every field of agriculture. Next to its chemical and biological benefits, physical benefits such as solubility in water makes boron compounds available for spraying and irrigation water. Overmuch boron fertilization, can cause toxicity, which studies suggested was more often caused by higher boron levels in irrigation water than those in soil

[31].

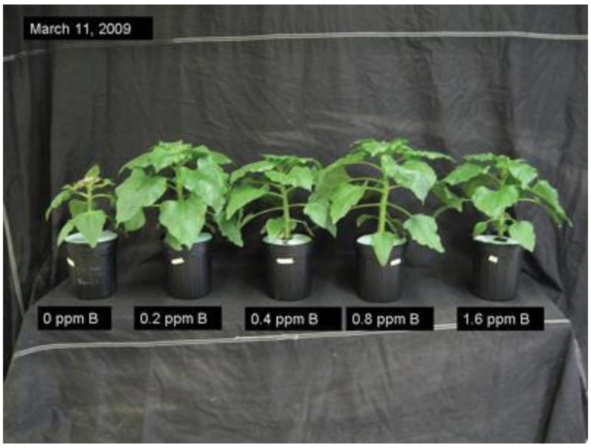

Figure 1.4.2: Comparison of plants height and root growth of sun flowers grown hydroponically with different boron concentrations (left to right, 0, 0.2, 0.4, 0.8, 1.6 ppm B)[32]

There is no doubt that the increase in human population together with life quality will cause a rise on food demand. A simple prevision may give an idea to get the picture about boron demand for next years.

Borates are used as alkaline buffers, enzyme stabilizers, oxygen-based bleaching agents, and water softeners in detergent industry. Peroxygen bonds existing in sodium perborate and perboratetetrahydrate, allows them to be used as oxidizing bleaching agents. Plainly, the high pH value of borax, which is about 9.5, helps it to produce a basic solution in water, thus increasing the effectiveness of bleach and other cleaners. Sodium perborate is considered as an extraordinary bleaching agent known for nearly 100 years. The production of Hydrogen peroxide, an effective and widely known bleaching agent, takes place when sodium perborate undergoes hydrolysis while in contact with water. Due to hydrogen peroxide’s inability of incorporation into detergents, sodium perborate is used as its carrier together with hot water [29].

Hydrogen peroxide and other available oxygen components are highly reactive with organic matter and their deactivation of proteins and enzymes, produces a strong disinfectant effect making them available for detergents used for sanitization.[33]

In metallurgical boron consuming applications, the most famous product is ferroboron with holding 2% of total world borate consumption. Ferroboron (FeB) is an alloy containing boron, ranging between 17.5 wt. % and 24 wt. % together with iron (Fe). It is known as the most low cost additive mainly for steel and some other iron related metal production. Compared to other high-strength steels, ferroboron possess higher strength and lighter weight. The steel industry direct and indirectly consumes more than 50% of the boron produced every year[34].

The main application areas for ferroboron can be listed as: high technology constructions, automotive, neodymium-iron-boron magnets (in computer hard drives and wind turbines[35]), aluminum castings, high conductive copper, nonferrous metals industry.

The ability of adsorbing/capturing neutrons makes boron compounds available to be used in nuclear reactors. In reactors too many neutrons can cause a fission reaction might get out of control with few neutrons, fission reaction stops. Control rods, from boron carbide are employed to control fission reaction by adsorbing neutrons. Furthermore, boric acid is used in the cooling water around reactors to capture leaked neutrons. These properties of boron make it a vital element for nuclear reactors[36].

Boron treatment in is commonly used as a long term wood protecting technique against harmful wood destroying organisms such as wood-decay fungus, termites, carpenter ants and roaches[37]. Several kinds of boron containing solutions acts as preservatives to treat wood, engineered wood composites and other building materials like studs, plywood, joists and rafters[38]. Combined with zinc (zinc borate), barium (barium metaborate) and ammonium (ammonium fluoroborate) borates are used to retard flames and suppress smoke in polymers.

Borates and boric acid based products also act as a flame retardant in cellulose insulation. Before reaching the combustion temperature boron removes the H_2O molecules existing in cellulose and covers the surface of appeared carbon layer thus retards a further fire.

Compared to 2009, in 2010 annual boron products consumption increased approximately 32% to 3.95 Mt. The undeniable effect of industrial growth in Asia and South America shows the boron products consumption will increase rapidly due to new researches and developments.

References

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[1] William G. W., *An Introduction to Boron: History, Sources, Uses, and Chemistry*, Environ Health Perspect 102 (7) (1994) 5-11

[2] Garrett D. E. *Borates: handbook of deposits, processing, properties, and use*. Academic Press.(102 1998) 385–386

[3] Travis N.J., Cocks E.J,.*The Tincal Trail-A History of Borax.*London:Harraps Ltd., (1984)

[4] Davy H. *"An account of some new analytical researches on the nature of certain bodies, particularly the alkalies, phosphorus, sulphur, carbonaceous matter, and the acids hitherto undecomposed: with some general observations on chemical theory".* Philosophical Transactions of the Royal Society of London, 99 (1809) 33–104

[5] Gay Lussac J.L. ,Thenard, L.J., *Sur la décomposition et la recomposition de l'acideboracique,*" Annales de chimie [later: Annales de chemie et de physique], 68 (1808) 169–174

[6] Berzelius,J.,"Undersökning af fluss pats syranochdes smärkvär di gaste föreningar" (Part 2) (Investigation of hydrofluoric acid and of its most noteworthy compounds), *Kongliga Vetenskaps-Academiens Handlingar*, Proceedings of the Royal Science Academy,12 (1824) 46-98

[7] Weintraub E., *Preparation and properties of pure boron*. Transactions of the American Electrochemical Society 16 (1909) 165–184

[8] Sprague R.W. *Boron. Metals and Minerals Annual Review*, Metals Minerals, 2 (1992) 106

[9] EtiMaden AS, 2010 Annual Sectoral report 2010: Ankara, Turkey, EtiMaden AS, 3 –Translated from Turkish-

[10] Vulcan T., *Boron, From Fishing Rods To Flares* www.hardassetsinvestor.com, 2011

[11] World Health Organization/International Programme on Chemical Safety.*Environmental Health Criteria 204, Boron,* (1998) 1-10

[12] Laubengayer A. W., Hurd D. T., Newkirk A. E., Hoard J. L., *Boron. I. Preparation and Properties of Pure Crystalline Boron***.** J. Am. Ceram. Soc., 65 (10), 1924–1931, 1943

---

[13] Artem R. O., *Ionic high-pressure form of elemental boron.*, Nature 457 (2009) 863-867

[14] David R. L., *Properties of the Elements and Inorganic Compounds*; *melting, boiling, and critical temperatures of the elements.*CRC Handbook of Chemistry and Physics, 84th Edition, Section 4, (2003)

[15] Simmons R., Ahsian N., Raven H. *The Book of Stones: Who They Are and What They Teach*. North Atlantic Books. (2007) 421–422

[16] Geugten R. P., *Determination of boron in river water with flameless atomic absorption spectrometry (graphite furnace technique)* Fresen J. Anal. Chem., 3061 (1981) 13-14

[17] WHO, World Health Organization Annual Report 2008

[18] Ross O. Nable, Gary S. Banuelos , Jeffrey G. Paull CSIRO, *Boron toxicity*, Plant and soil, 193 (1997) 181-198

[19] Argust p., *Distribition of Boron in Environment* Biol. Trace. Elem. Res.,66, (1998) 1-3

[20] Anderson D.L., Kilto M. E., McCarthy L., Zoller W.H, *Sources and atmospheric distribution of particule and gas phase boron atmosphere environment*, Atmos. Environ, 28 (1994) 1401-1410,

[21] UNEP United nations environment programme Report 2009 , 43-44

[22] Pieczyńska J., Burnecka J. B., Biernat J., Grajeta H., Żyrnicki W., Żechałko-Czajkowska A., *Boron content in daily meals for preschool children and school youth*, Biol. Trace Elem. Res. 96 (2003) 1-8

[23] EtiMaden AS Annual report 2009, EtiMaden AS,–Translated from Turkish- (2009) 44

[24] http://ec.europa.eu/clima/policies

[25] *Towards a low carbon future, A European Strategic Energy Technology Plan (Set-Plan)* Commision of the European Communities, Brussels, (2007) 723

[26] Industrial Minerals, 2009a, Borates' tile target: Industrial Minerals, no. 501, (2009) 67.

[27] www.etiproducts.com

[28] Industrial Minerals, 2008b, Technical ceramics take off: Industrial Minerals, no. 495, 66. 2008.

[29] Marc A. A, Robert D. C., Jr., *Boron*, USGS mineral year book 2010.

---

[30] U.S. Census Bureau report 2010

[31] Troeh, F.R., Thompson, L.M., *Soils and soil fertility*, IA, Blackwell Publishing, (2005) 489

[32] T.J. Blom, *Light and media in U of G studies*, www.greenhousecanada.com

[33] Rio Tinto Borax, *Bleaching with sodium perborate: Boron*, Rio Tinto Borax, 2005.

[34] Eti Holding Inc, *Pre-feasibility report summaries of boron carbide, boron nitride, ferroboron, frit and glaze, textile glass fibre, zinc borate*, Eti Holding Inc., (2003) 23

[35] Moores S., *Minerals for the digital age*, Industrial Minerals, 513 (2010) 42,

[36] Ceradyne Inc., *Boron products*, Costa Mesa, CA, Ceradyne Inc. http://www.ceradyneboron.com, 2011

[37] Blanchette R. A., A. R. Biggs. *Defense mechanisms of woody plants against fungi*, Spinger-Verlag, (1992) 458

[38] www.borax.com/wood/products2.html

Chapter 2

Borates

2.1 Borates and Their Production

Elemental boron has limited applications; the term, “boron consumption” today is mostly mistaken with the term “borate consumption”. I.e., the global consumption rate of elemental boron was estimated to be 15.000 t/yr in 2010 where only B_2O_3 was 1.5 million t/yr [1] [2]. Borates are defined as “salts or esters of boric acid; a compound containing the radical B_2O_3"[3]. Today, borates are accepted as any compound that contains or supplies B_2O_3 and, therefore, they are priced and sold based on their boric oxide content. Researches show there are more than 300 natural occurring borate minerals. There are also many of non-mineral borates produced in laboratory conditions.

The reason for the existence of many boron containing mineral is related to the ability to form boron-oxygen compounds in many molecular and polymer types. As an effect of rapid crystallization of boron together with silicates and the ability of replacing aluminum or silicon, there are more than 8 Na-borate minerals and approximately 23 Ca-borates with no other cations or anions[4]. Borates linked with calcium, sodium, magnesium and its hydrate compounds has higher economic importance[5]. Enrichment process of borates aims at removal of undesired elements such as Arsenic, Germanium and increasing the weight percentage of B_2O_3 in mineral[6]. Borates are often defined and sold by their boric oxide (the pure form of B_2O_3) or B_2O_3, content, and most statistical data are listed in tons of B_2O_3.

The world’s largest borate reserves are located in Turkey, U.S.A and Russia followed by China, Argentina, Bolivia, Chile, Peru, Kazakhstan, Serbia and Iran. Table 2.1.1 shows the total world boron mineral reserves.

Country	Total Reserves (ThousandTons B_2O_3)	Total Reserves (% B_2O_3)
Turkey[1]	864.500	72
USA[2]	80.000	7
Russia[2]	100.00	8
China[2]	47.000	4
Argentina[2]	9.000	1
Bolivia[3]	19.000	2
Chile[3]	41.000	3
Peru[2]	22.000	2
Kazakhstan[4]	-	-
Serbia[5]	16.200	1
Iran[2]	1.000	0
Total	1.241.000	100

1. EtiMaden, 2010

2. USGS Mineral Commodity Summariers, January 2009

3. USGS Mineral Commodity Summariers, January 2002

4. Due to contradictional statements about Kazakhtan’s reserves it has not reported it table.

5. www.riotinto.com

Table 2.1.1: Total Reserves of Boron Producing Countries

The 90% of the borates used in industry worldwide are sodium and calcium borates, as borax, kernite, colemanite and ulexite[11] .These minerals are mainly produced by Turkey, U.S.A, China, Chile and Argentina. These countries’ production capacities reached 4.8 Mt, containing 2.2Mt of B_2O_3. The world boron production capacities in 2010 are reported in table 2.1.2

Countries	**Production Capacity (Mt)**
Turkey	1,785
USA	1,560
Argentina	196
Bolivia	78
Peru	75
Chile	415
China	545
Russia	151
India	48
TOTAL	4,853

**Etimaden,2010*

Table 2.1.2: The world boron production capacities in 2010

Borate mining, or in other words, “boron mining” works usually takes place as open pit and in some cases as underground mining (Russia). Mass producing boron mines, such as Turkish (Kırka) and American (California), operate their deposits by open pit mining.

Open pit mines are made of benches providing an operating way to machineries and walls less than vertical angle to minimize and danger from rock falls. The range of wall angle and its size depends on the type of mine. The walls of the mines are stepped. The inclined of the mine is called batter and the flat part of the step is known as bench (berm).[7]

Haul roads of the open pit are generally built at the sides of the pit, providing a way for machineries such as trucks carrying ore and waste rock. Generally waste rock is piled up at the surface, near the edge of the open pit called waste dump. Waste dumps are also tiered and stepped, to minimize degradation.[8]

Figure 2.1.1: Open pit Mining Bigadic, Turkey

2.2 World Borate Deposits

Argentina: In South America by the end of 2010, Argentina took the lead in borate production. Argentinean heavy borate deposits are located at Porvenir in Jujuy Province, Sijes and Tincalayu in Salta Province, producing, colemanite, hydroborocite, kernite, tincal, and ulexite. These mines are located at 4,100 m above sea level, the Tincalayu Mine is Argentina's largest open pit operation. The deposit consisted primarily of borax, with rare occurrences of ulexite and 15 other borates[9] Argentina also produces granular deca-and pentahydrate borax, boric acid powder and various grades and sizes of natural boron minerals.[1]

Bolivia: Boron mining in Bolivia started as small enterprises as cooperatives at Andes Plateau producing ulexite together with tincal. The Bolivian Mining Agency (COMIBOL) has invested in Salar de Uyuni salt flats in order to produce boric acid.[1]

Chile: Chile is the second boron producing south American country, in 2010 Chile's boron production decreased 17% compared to previous year. Chile has the world's largest ulexite deposits (30 Mt B_2O_3) and is the leading ulexite producer mostly as boric acid.[10] [1]

China: Despite of having large borate deposits, over 90% of Chinese deposits are low graded, consisting B_2O_3 between 8-12 wt. %. In China, main boron production takes place in northern part of the country at magnesium borate (askarit) deposit and at Qinhai deposit,4,100 m above sea level, hard to operate, similar to Argentinean deposits with consisting related borates (boron lithium potassium). Due to heavy and growing industry, China became import reliant on boron.

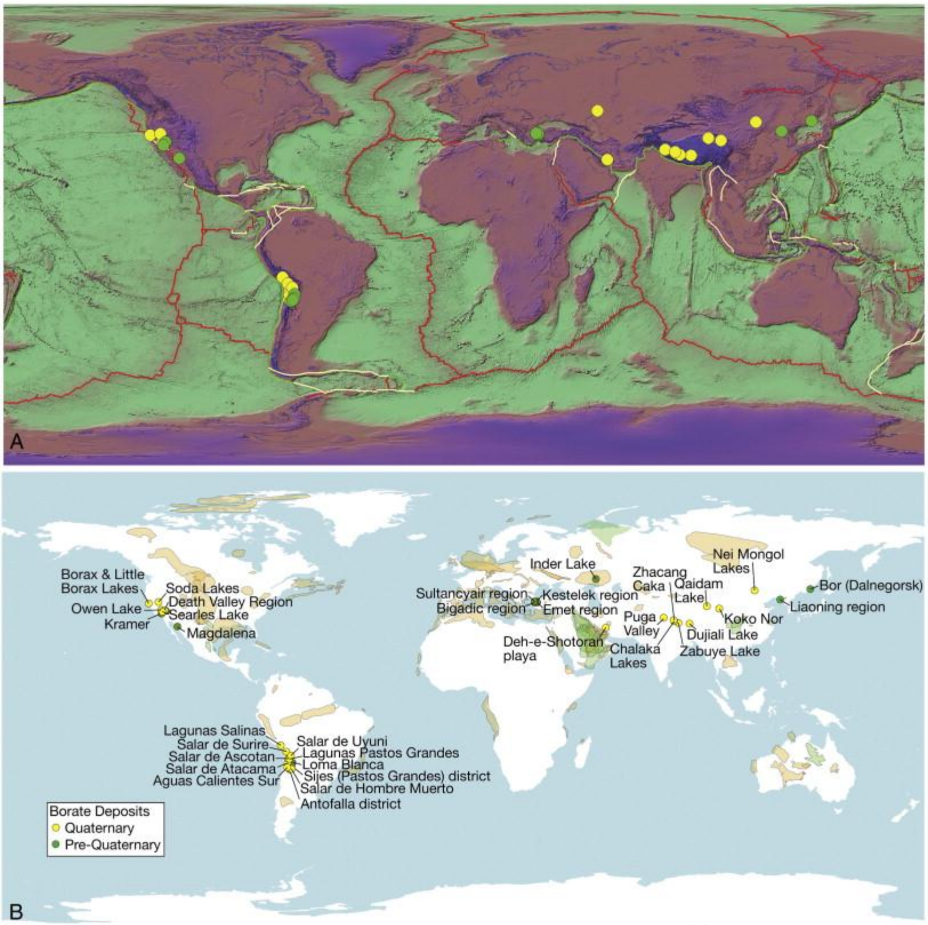

Figure 2.2.1: World Borate Deposits[11]

Between 2000-2007, Chinese boron production increased 7 % however, today some of Chinese deposits are running low, expected to stop production soon.[1 10]

India: India's borate deposits are located at Pithampur, Madya Pardesh and northeast of Mumbai, mainly producing borax and boric acid. Since the Indian reserves cannot meet the domestic requests, similarly in the case of China, also India is a reliable importer of borate products.

Russia: Russia has the world's 3rd largest boron deposit, consisting of low grade of B_2O_3 ranging between 9-12 wt %.

U.S.A: As investigated in "History of Boron" part, USA is one of the first borate extracting countries. This early mining activities, supported with industrial and technologic progress led USA being world's leader borate producer for long time, today passed the chair to Turkey.

The main borate producers of USA are U.S. Borax (Rio Tinto Minerals – United Kingdom) and Searles Valley Minerals (Nirma - India). The largest borate deposits of USA are located at California, operated mainly by surface mining and brine extraction through solution mining mostly associated with compound plants. The tincal and kernit obtained from those deposits has average grades of 25.3% and 31.9% of B_2O_3.The kernite was used for boric acid production and the tincal was used as a feedstock for sodium borate production.[12 10 1]

Turkey: Borate deposits in Turkey are located at north western part of the country controlled by the state owned company Eti Maden A.S., primarily investigated in "History of Boron" part. Turkey is world's largest borate producer with holding nearly 72% of the world's total borate reserves. The main borate production areas are: Bigadic, Emet and Kırka.

In Turkey, the boron deposits exhibit variable B_2O_3 amounts. Kırka, largest borate deposit of Turkey produces 25-26% B_2O_3 containing tincal, similar to Californian deposits[10]. Colemanite, ulexite and probertite (in some areas found merged in each other)[13] gathered from Emet deposit contains 30-32%B_2O_3 while Bigadic produces 28-37% B_2O_3 containing colemanite.

Lately, Turkey started to invest on refined borate production and related compounds rather than raw ores together with increasing research and development facilities in order to build other boron consuming markets.

Country	**Region and Type**	**Total ore**	**Contained B_2O_3**	**B_2O_3 Reserve**	**B_2O_3 Reserve Base**	**B_2O_3 Total Reserve**
Turkey	Bigadic-Balıkesir					
	(Ca-NaCa types)	935545	330	(1030-360)		
	Emet-Kütahya (Ca-	7	200	(890-310)(8-		
	type)	520	3	3)(519-130)		
	Kestelek (Ca-type)	2007	140			
	Kırka (Na-type)			227		
	Subtotal		673			
					624	851
USA	Boron-(Na-type)	113	26			
	Ca-type)	198	20			
	Subtotal	311	46			
	Searles Lake, Death Valley, Hector, Owens Lake, Salton Sea, Four Corners, MuddyMountains,	255	77			
	etc.					
	Subtotal					
		566	123	40	40	80
Russia	Dalnegorsk, etc	700	64	40	60	100
China	Liaoning, Quanhai etc.	480	65	27	9	36
Mexico	Mesa del Amo, Vitro, Tubutama, etc	140	13.5			

Argentina	Loma Blanca, Sijes, Tincalayu, Salars, etc	100	20,5	2	7	9
Chile	Surire, Atacama, etc.	60	76	8	33	41
Serbia	Jarandol, Raska, etc.	40	8	3	-	3
Kazakhstan	Inder, Satimola, etc.	77	5	14	1	15
Bolivia	Salars, Uyuni, etc	20	15	4	15	9
Peru	Salars de Salinas, etc	20	5	4	18	22
Others	Iran, India, Germany, etc.	100	10			
General	Total	4310	1078	369	807	1176

(Roskill, 11. Edition 2006), (Lyday 2006)

Table 2.2.1: World Borate deposits and Estimated B_2O_3 Reserves

2.3 Borate Enrichment

The term “boron enrichment” in mining means increasing the grade of B_2O_3 in borates. The fact making borate more valuable is its B_2O_3 grade thus; boron enrichment is important as boron extraction. The price of a concentrated colemanite nearly doubles the price of the raw colemanite, this also motivates producers to invest more in boron enrichment techniques. Today, industrially, enrichment can increase the grade of B_2O_3 up to 85%, depending on the type.

Boron mines are generally characterized by the presence of enrichment/concentration plants and waste water lakes located close to the extraction area. Depending to the characteristics of the mine, after washing step, boron minerals are crushed (or vice versa) and classified according to the quality (impurities contents), particle size, use fields and economic values (separation, triage and classification processes). Recently, these enrichment/determining processes are also developing together with the increasing rate of the technologic knowledge including techniques, taking the advantages of infra-red, high-tech imaging and ultrasound technologies. After determination of the materials there are still processes to go in order to increase the grade of B_2O_3 of the mine.

Figure 2.2.2: Borate rock crusher (Joyal Shangai Machinery)

Most widely used and efficient enrichment processes can be listed as;

- Gravity separation
- Calcination
- Electrostatic separation
- Magnetic separation
- Mechanical screening
- Froth Flotation

2.3.1 Gravity Separation

Gravity separation is one of the oldest methods in mining activities. In this method gravity is the dominant force. The aim of the gravity separation method is to take advantage of the difference in specific weight of the components to separate them in a low cost-efficient way. With gravity separation method, the grade of B_2O_3 in colemanite can be increased from 36% up to 55% with 65% of efficiency[14].

2.3.2 Calcination

Calcination (also known as calcining) is a thermal process decomposing or phase transiting solid substances when exposed to heat via release of volatile fractions existing in their molecular structure, i.e.; Calcite ($CaCO_3$), fluorite (CaF_2), gypsum ($CaSO_4$. $2H_2O$), colemanite and tincal (borax) ($Na_2B_4O_7$-8H2O). In boron industry this method is also known as “decrepitation method” due to decrepitation of borates in different temperatures. This method is also used to separate the borates even in each other such as ulexite and colemanite[13].

Calcination is a widely used method in colemanite enrichment process: it helps the ore milling and increases the B_2O_3 content. Colemanite decomposes with the release of its five molecules of H_2O between 450 and 500 °C. The temperature of onset of dehydration for colemanite is 262 °C and the first water molecule is lost at 327 °C15 16. Decomposition of colemanite provides release of impurities thus increases weight percentage of the B_2O_3 content. In colemanite, with calcination method the content of B_2O_3 can be increased with 83% efficiency.17 18

2.3.3 Electrostatic Separation

Electrostatic separation is a process that uses electrostatic charges to separate crushed particles of materials also known as high tension separator (roller). This process is mainly used to separate and to sort large amounts of mineral ores in mining or beneficiation plants. Not differently than other methods in borate mining, this process is also used to increase weights percentage amount of B_2O_3. With this method the B_2O_3 amount can be increased 5 to 10%[14].

2.3.4 Magnetic Separation

Magnetic separation is a widely used separation process used in a large spectrum. Minerals with low magnetic characteristics and low susceptibilities could be recovered by high intensity magnetic separators with generating high magnetic fields[19]. Boron recoveries with magnetic separation method are ranging between 41 and 84% depending on the type of the borate.[20] [21]

2.3.5 Mechanical Screening

This method is mainly used in mining and mineral processing industries, also known as screening. Screening is used to separate materials due to their particle sizes, in mining, this method is often used to separate high grade components from impurities such as; clay. In mining industry there are two kinds of mechanical screening: wet and dry screening. In borate production, wet screening is the preferential method. As a result of having significant amount of clay in raw borate mining products, minerals have to be washed before or after screening due to their particle sizes , in order to get rid of clay impurities by spiral classifier or hydrocyclone. There are different kinds of mechanical screening equipment for different purposes: scrubber screens, roller screens, Trommel screens, Circle-throw washing/vibrating equipment. Boron recoveries with mechanical screening method are increasing up to 81% depending on the type of the borate.[22]

2.3.6 Froth Flotation

Froth flotation process is used to separate minerals from gangue in complex structures by taking advantages of differences in hydrophobicity where gravity method is not available. This process is not efficient for all kinds of borates, only ulexite and colemanite can be treated in flotation plants in industrial scale due to their mineral structure. Froth flotation process is a cost reducing method in enrichment of minerals.

2.4 Borate Wastes

For a long time, borate wastes also known as boron wastes, coming mostly from concentrator plants were stored in large deposits after aforementioned enrichment processes. These waste deposits were located near the boron mines. As an example of the amount of these wastes, only in Turkey, which has the largest reserve of borate minerals, the amount of such waste is in the order of 600.000[23] tons in 2002; by the end of 2010 this amount expected to reach 1.5 million tonnes. These wastes consist of clay and carbonates, with lower B_2O_3 content compared to the concentrated minerals and main ore. Wastes gathered from enrichment plants are generally in solid form or pulp[24]. But also waste in liquid form exists, as the water lakes near to the mines, occurs after washing step of the minerals. Before realizing the huge environmental problems that they could represent, these wastes were drained into sea, rivers or in non-populated areas, without any kind of remediation. Recently, the awareness for environment became a real responsibility for mining industry in according to the understanding of issue in international political platforms, as in example from EU[25].

A very important problem is the storage of these kinds of wastes that could be partially solved by using them as “new raw material” in different industrial fields. Waste storage will most probably be used as the resource for the future industry with many advantages in term of solving environmental problem and economic profits. An appropriate evaluation of these wastes, in terms of mineralogical and chemical composition, could allow to better address their re – use, in this way decreasing both the problems originated from their storage, by minimising the wastes disposal and stocking costs, and the final cost of the waste itself.

Various efficient strategies are till now used to manage boron waste. The first simpler strategy, their storing with preferential recovery, is the less efficient and should be going to be given up. The technological level reached in material sciences allowed new recovery methods to use those stored wastes in more efficient ways. Other approaches consist in recovery of valuable minerals from waste water, recovery of valuable minerals from primary and secondary wastes, in which boron minerals occur only in traces.

This last approach is the usage of clay based boron waste in industry, especially in ceramics industry. The boron wastes, concentrator wastes, borax lime wastes, lineal wastes and derivatives wastes, to say, mainly enrichment wastes usually contain large amounts of clays, such as montmorillonite, vermiculite, illite and chlorite[26]. So the final removed clay-based product, considered as “boron waste” (borate waste), contains still a rather large amount of B_2O_3,(depending on the minerals type) the percentage of which is a function of the kind of mine.

As told, the largest amount of boron wastes comes from the boron concentrator plants. The utilization of boron waste can be argued in some main titles as recovery of boron minerals from wastes, safe disposal of boron tailings with suitable methods which will not harm the environment and lastly, direct use of boron tailings in the clay based industry, due to the large amount of clays and carbonates present in this class of waste.

Generally, during the enrichment of boron wastes, several methods which already applied in their premier enrichment are still in use, in order to regain the B_2O_3 which ran into the waste, mechanical distribution, classification, gravity methods, magnetic separation, electrostatic separation, soda (flocculation, flotation, thermal treatment, calcination, decrepitation) and briquetting methods are being used[27]. Besides, lately it has proved that sound waves are an efficient way to remove clay[28].

2.4.1 Waste Waters

The presence of such lakes is necessary for the first mineral enriching operation, that consists in a washing of boron containing minerals, in particular for tincal, colemanite and ulexite (colemanite and ulexite are less soluble in water). The waste lakes, so formed, still contain large amounts of boron minerals ranging between 5-18 % of B_2O_3 that can be further concentrated and extracted, for a direct utilization.

The treatment methods used for the removal of boron from water are grouped into several categories: coagulation and electro-coagulation processes, [29] [30] [31] adsorption[32] and ion-exchange processes[33] [34] [35] and all those processes using membranes systems, such as Donnan dialysis[36], electrodialysis[37] and reverse osmosis (RO). [38]

When paramagnetic and ferromagnetic minerals are present, an effective separation can be made with high-intensity differential magnetic permanent magnet[39] [40].

Due to the fact that different boron minerals can be found as a mixture, further separations treatments are necessary, as in the case of colemanite and ulexite. Calcination is an efficient method which can be used in these circumstances[41]. A thermal treatment, at 450°C for a mix of ulexite and colemanite, allows the first one to gain hardness while colemanite is going to decrepitate for the sudden loss of the five water molecules present in its formula[13].

2.4.2 Utilization and Applications

Due to the high percentage of clays present in most kind of boron waste, scientists are also studying the possibility of their use in the silica based products industry, which can take advantage of the boron mineral included in the clay, that is able to lower the sintering temperatures. At this regard, interesting opportunities are offered by the traditional ceramic industry (wall and floor tiles, glazes, heavy clay ceramics, cement). It has been reported that the use of boron waste in heavy clay ceramics is feasible, “as is”, in small percentages (5-10 %), whereas higher additions may necessitate the optimization of the sintering profile or pre-calcination step for boron waste[42]. The studies in brick industry showed, fritted solid boron waste could be evaluated as a brick product due to exclusive physical and mechanical properties[43]. In ceramic industry, different kinds of wastes have been till now incorporated in tiles and bricks raw materials

The researches on red mud and Kirka Etimine borate waste showed, that the studied composition provides floor tiles characterised by high strength and low water absorption. In a similar study it has been seen boron waste use in ceramic tiles and its glazes. Using it as fluxing agent provides low porous and high strength structure together with providing glass crystals in low temperatures[44]. Boron waste from Kirka Etimine, has been used as masse in tile industry[45]. In several studies it has been experimentally seen that boron waste clay can be used in brick industry as a raw material[46] [47] [48] [49] [47].

Laboratory studies on boron waste utilization in cement industry, showed colemanite addition into cement has an impact on reducing the shrinkage[50]. In related studies it has been found that boron waste through several borates increases the durability while decreasing the mechanical strength.[51] Also separated boron containing clay waste in concrete was investigated by several groups[52] [53]: author would like to state that, none of these researches could have brought an efficient utilization for boron containing wastes employed by cement industry[54] [55] [56].

References

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[1] Marc A. A, Robert D. C., Jr., *Boron,* USGS mineral year book 2010.

[2] U.S Geological Survey , *Mineral Commodity Summaries: Boron,,* U.S Department of the Interior, 2012.

[3] Bates R.L., Jackson J.A., Glossary of Geology, 3rd ed., American Geological Institute, 778, 1987.

[4] Garrett, D. E. *Borates: handbook of deposits, processing, properties, and use*, Academic Press. 6, 1998.

[5] Encyclopædia Britannica *"Borate mineral"*, Online Encyclopædia Britannica Inc., 2012.

[6] Vulcan T., *Boron, From Fishing Rods To Flares,* www.hardassetsinvestor.com, 2011.

[7] Mine Engineer Community, *Open Pit Surface Mine*, 2011.

[8] European Commission Environment, *Mining Waste*, 2011.

[9] Industrial Minerals, 2009b, *Minerals in the mist: Industrial Minerals*, no. 498, March, p. 40.

[10] Eti Maden Annual Boron Report 2010

[11] Warren J. K. , *Evaporites through time: Tectonic, climatic and eustatic controls in marine and nonmarine deposits,* Earth-Science Reviews, 98, 217-268, 2010.

[12] U.S. Geological Survey, *Mineral Commodity Summaries,* January 2012.

[13] ŞenerS., Özbayoğlu G.,*Separation of from colemanite by calcination,* Minerals Eng. 8 (1995) 697–704,

[14] Kaytaz, Y., Doğan, M.Z., Önal, G., Perek, K.T., *Bigadiç ve Kestelek bor atıklarının ısıl işlem, elektrostatik ayırma ve flotasyon ile zenginleştirm e olanaklarının araştırılması*, 2. Endüstriyel Hammaddeler Sempozyumu, Makaleler kitabı, İzmir, *Enrichment of Bigadic and Kestelek boron waste with heating, electrostatic separation and flotation*, II. Industrial Raw Materials Symposium, Papers Booklet, Izmir, Turkey (1997) 76-85.

[15] M.S. Celik, F. Suner , *A thermodynamic analysis of the decrepitation process*, Thermochimi Acta 245 (1995) 167 174

---

[16] B. Cicek; L. Esposito; A. Tucci; E. Bernardo; A. R. Boccaccini; P. A. Bingham: *Microporous glass ceramics from combination of silicate, borate and phosphate wastes,* Advances in Applied Ceramics 111 (2012) 415-421

[17] Erkal F. İ., Girgin, İ., *Etibank Emet kolemanit işletmesi kaba artıklarının konsantre üretimi amacıyla değerlendirilmesi*, 4. Uluslararası Cevher Hazırlama Sempozyumu, *Utilization of Etibank Emet colemanite raw wastes in concentrate production*, IV. International Ore Preparation Symposium, Turkey, 2 (1992) 599-608.

[18] Aytekin, Y., Barduk, M., *Emet kolemanit cevherlerinin dekrepitasyon yoluyla zenginleştirilebilirliğinin araştırılması,* 4. Uluslararası Cevher Hazırlama Sempozyumu, Antalya, *Enrichment of Emet colemanite ore with decrepitation method*, IV. National Ore Preparation Symposium, Turkey 2 (1992) 549-561.

[19] Svoboda, J. *Magnetic Techniques for the Treatment of Minerals,* Kluwer Academic Publishers, London, 2004.

[20] Bilici, U., Akçin, H., Karakoç, G., Doğan, A., *Kestelek konsantratör tesisi ara ürün stoklarının* B_2O_3 *içeriklerinin iyileştirilmesi çalışmaları,* Eti Holding A.Ş., Ankara. B_2O_3 *recovery from Kestelek concentrator mid products,* ETI Holding,Ankara, Turkey (2000).

[21] Özdağ, H., Bozkurt, R., Uçar, A., *Kestelek bor atıklarından borun kazanılması*, 2.Uluslararası Cevher Hazırlama Sempozyumu, İzmir, Turkey (1988) 282-288.

[22] Sönmez, E., Özdağ, H. , *Beneficiation of Emet tailings by water absorption+ mechanical attrition+ magnetic separation,* Changing Scopes in Mineral Processing, Rottterdam, (1996) 143.

[23] C. Yaman and M. Marasoglu: 4thCeramic congress articles book, Anatolian University, Eskisehir, Turkey (1998) 97-102.

[24] C. Yaman, I. International boron symposium report, Kutahya, 2002

[25] T Bentli, I. International boron symposium report, Kutahya, 2002

[26] Karasu, B., Kaya, G., Kozulu, R., *Evaluation of Etibank-Kırka Borax Solid Wastes of Turkey in Wall Tile Glazes*, Abstract Book of 104th Annual Meeting & Exposition of the American Ceramic Society, (2002) 275.

[27] Brian Lewis - *A preliminary report on the relative effectiveness of ultrasonic cleaning versus soaking conversation of clay tablets* – Iraq, 43 1 (1981) 76-78

[28] T. Kavas, *Use of boron waste as a fluxing agent in production of red mud brick*, Building and Environment 41 (2006)1779-1783

---

[29] A.E. Yilmaz, R. Boncukoglu, M.M. Kocakerim, B. Keskinler *The investigation of parameters affecting boron removal by electrocoagulation method*, J. Hazard. Mater 125 (2005) 160-165

[30] A.E Yilmaz. . Boncukoglu, M.M. Kocakerim, *A quantitative comparison between electrocoagulation method and chemical coagulation for boron removal from boron-containing solution*, J. Hazard .Mater. 125 (2007) 475-481

[31] A.E Yilmaz. . R. Boncukoglu, M.M. Kocakerim. *An empirical model for parameters affecting energy consumption in boron removal from boron-containing waste waters by electrocoagulation* J. Hazard.Mater 142 (2007) 101-107

[32] Y. Cengeloglu, A. Tor, G. Aslan. M.Ersoz, S.Gezgin, *Removal of boron from aqueous solution by using neutralized red mud* J. Hazard Mater 142 (2007) 412-417

[33] A.E. Yilmaz, R. Boncukoglu, M.M. Kocakerim M.T Yilmaz, *Adsorption of boron from boron-containing waste waters by ion exchange in a continious reactor*, J. Hazard. Mater (2005) 221-226

[34] R. Boncukoglu, A.E. Yilmaz, M.M. Kocakerim, M. Copur *An empirical model for kinetics of boron removal from boron-containing wastewaters by ion exchange in a batch reactor, Desalination* 160 (2004) 159-166

[35] M. Badruk, N. Kabay, M.Demircioglu, H. Mordogan, U. Ipekoglu, *Removal of boron from wastewater of geothermal power plant by selective ion exchange resigns*. II. Column sorption-elution studies, Sep. Sci. Technol. 34 (1999) 2981-2995

[36] H.F. Ayyildiz, H. Kara, *Boron removal of boron from by ion exchange membranes*, Desalination 180 (2005) 99-108

[37] Z. Yazicigil, Y. Ozeltekin, *Boron removal by electrodialysis with anion-exchange membranes*, Desalination 190 (2006) 71-78

[38] G. Georghiou, I. Pashalidis, *Boron in ground waters of Nicosia (south cyprus) and its treatments by reverse osmosis*, Desalination 215 (2007) 104-110

[39] M. Rodrigues-Pastor. A.F. Ruiz, M.F. Chillion, D.*P. Rico Influence of pH in the elimination of boron by means of reverse osmosis*, Desalination 140 (2001) 145-152

[40] Gh. Iacob, Al. D. Ciochina, O. Bredetean , *High gradue High Gradient Magnetic Separation Ordered Matrices*, Eur Cells Mater 3 (2002) 167-169

---

[41] J.C. Fernandez Caliani, F. Ruiz Muiioza, E. Ganb , *Clay mineral and heavy metal distributions in the lower estuary of Huelva and adjacent Atlantic shelf,* Sci Toral Environ 198 (1997) 181-200

[42] A. Christogerou, T. Kavas, Y. Pontikes, S. Koyas, Y. Tabak, G.N. Angelopoulos, *Use of boron wastes in the production of heavy clay ceramics,* Ceram Inter. 35 (2009) 447-452

[43] Kaya, I. International boron symposium report , Turkey,(2002).

[44] F. Oruç, E. Sabah, Z. E. Erkani, *Evaluation Strategies of Boron Tailings according to Sector,* II. International boron symposium, Eskisehir,Turkey) 2004)

[45] Yaman, C, *Bor Mineral Atıklarının Seramik Endüstrisinde Kullanılabilirliği*, VIII. Ulusal Kil Sempozyumu, Dumlupınar Üniversitesi, Bildiriler Kitabi, Kütahya, 345-352. *Use of Boron Mineral waste in Ceramic Industry,* VIII. National Clay Symosium , Papers Book, Dumlupınar University, Kütahya, Turkey (1997) 345-352

[46] Sönmez, E., Özdağ, H., Özler, A., Sümer, G., *Kırka Boraks İşletmesi Atık Killerinin Seramik Endüstrisinde Kullanılabilirliğinin Araştırılması,* Türkiye XIII. Madencilik Kongresi, TMMOB MadenMühendisleriOdası, İstanbul, 561-566, *Kirka Boron Mine Waste Clay Usage Possiblites in Ceramic Industry,* XIII. Mining Congress, Chamber of Turkish Mining Engineers , Istanbul, Turkey, (1993) 561-566

[47] Sur, H., Yaman, C, Pişkin, S., *Bor Atıklarının İnşaat Tuğlası Üretiminde Kullanılması*, VIII. Ulusal Kil Sempozyumu (Kil'97), Bildiriler Kitabı, 392 Dumlupınar Üniversitesi, Kütahya, 555. *Boron waste re-use possibilities in brick production,* VIII. National Clay Symposium (Kil 97), Abstract Book, , Dumlupinar University, Kutahya, Turkey (1997) 392

[48] Sönmez, E., Yorulmaz, S. *Kırka Boraks İşletmesi Atık Killerinin Tuğla Yapımında Kullanılabilirliğinin Araştırılması,* Endüstriyel Hammaddeler Sempozyumu, TMMOB, Maden Mühendisleri Odası, İzmir, 163-168. *Kirka Boron Mine Waste Clay Re-use possibilities in Brick Industry,* Industrial Raw Materials Symposium, Chamber of Turksih Mining Engineers, Izmir, Turkey (1995) 163-198.

[49] Sönmez, E., Özdağ, H., Özler, A., Sümer, G., *Kırka Boraks İşletmesi Atık Killerinin Seramik Endüstrisinde Kullanılabilirliğinin Araştırılması*, Türkiye XIII.Madencilik Kongresi, 561-566, TMMOB Maden Mühendisleri Odası, İstanbul, 1993. *Kirka Boron Mine Waste Clay Re-use Possibilities in Ceramic Industry,* XIII. Mining Congress, , Chamber of Turkish Mining Engineers, Istanbul, Turkey (1993) 561-566

[50] U.K. Sevim, *Colemanite ore waste concrete with low shrinkage and high split tensile strength,* Materials and structures, 44, (2011) 187-193

---

[51] I.Kula, A Olgun, V.Sevinc, Y. Erdogan , *An investigation on the use of tincal ore waste, fly ash, and coal bottom ash as Portland cement replacement materials,* Concret Res, 32 (2002) 227–232

[52] Targan, Ş., Erdoğan, Y., Olgun, A., & Zeybek, B., Sevinç, V., *Kula Cürufu, Bentonit ve Kolemanit Atıklarının Çimento Üretiminde Değerlendirilmesi*, I. Uluslararası Bor Sempozyumu, Kütahya, 259-266. *The utilization methods for Kula slag, bentonite and colemanite wastes in cement production,* I. International Boron Symposium Report, (2002) 259-266, Kutahya,

[53] Ozdemir M, Ozturk N .U, *Utilization of clay wastes containing boron as cement additives,* Cement and Concrete Res, 3 (2003) 10

[54] Topçu I.B., Boga A.R., *Effect of boron waste on the properties of mortar and concrete*. Waste Manag Res. 28 (2010) 626-33

[55] I.Y. Elbeyli, *Utilization of industrial borax wastes (BW) for Portland cement production* Turkish J. Eng. Env. Sci. 28 (2004) 281 287.

[56] T. Batar, N. S. Koksal, S. E. Yersel, *Production and Characterization of Wall Plaster with Borax and Paper Wastes and Perlite Additives,* Ekoloji 18, 72 (2009) 45-53

Chapter 3

Glass-Ceramics and Their Production

3.1 Glass-Ceramics

Glass-ceramics are polycrystalline materials obtained through controlled crystallization (devitrification) of selected/suitable glass compositions. Due to characteristics of glasses, the decided composition and its heating treatments have to be well studied. Today, not only glass compositions but also different heat treatments are still discussed in respect of producing glass ceramics[1]. There are limited glass composing precursors for glass-ceramics production. Compared to stable and difficult crystallizing parent glasses, some glasses crystallize fast (spontaneous crystallization) and uncontrollably, resulting in undesirable microstructure making impossible to employ a preferred structure[2 3].

Glass-ceramics have a glass (amorphous) phase and typically one or two crystalline phases usually in the range from 30 vol% to 95 vol %. Glass-ceramics share the unique characteristics and advantages of glasses as well as ceramics, exhibiting significant advantages compared to conventional glass or ceramic materials. Glass-ceramics technology provides materials having high mechanical strength and toughness, low (even negative) thermal expansion, high thermal strength. A widely known example for heat resistant glass-ceramic is Li_2O-Al_2O_3-SiO_2 system[4 2].

3.2 Glass Ceramics from Wastes

Thermal treatments of problematic wastes by glass-ceramic technology has been well-documented regarding its effectiveness in immobilising the toxic contents in their glass matrices. These kinds of heat treatment technologies have been widely used for treatment of several wastes usually processed to form glass-ceramic products. These wastes, coming from numerous sources, can be also considered raw materials and comprise, as main examples [2 3 5 6]

- Slag from metallurgical processes (iron and steel production)[7 8 9 6 10 11 12 13 14]
- Coal Ash from Power Stations[15 16 17 18 19 20 21 22 23 24 25 26 27]

- Residues from Urban Incinerators[28] [29] [30] [31] [32] [33] [34] [35] [36] [37]
- Slag from Gasification Processes[38]
- Electric Arc Furnace Dust (Steel Fly Ash)[39] [40]
- Cement Dust[41]
- Ore-Refining Quartz-Feldspar Waste[42]
- Fluorescent Glass Waste[43]
- Sewage Sludge[44] [45]
- Anodising Plant Industrial Waste[46]
- Zinc-Hydrometallurgy Wastes[47] [48] [49] [50]
- Clay-Refining Waste (Kira)[51]

3.3 Crystallisation (devitrification)

The transformation of glass to form glass-ceramic is called crystallization, also known as devitrification. This transformation consists of two parts, called nucleation and growth. Nucleation is the key part in controlling the crystallisation where crystalline glass phases occur. There are two types of nucleation: the first one is volume nucleation, which is commonly used technique for both homogenous and heterogeneous nucleation. The second type is surface nucleation by which is more difficult to control the crystallization. The nucleation process mostly ends with an undesired microstructure setting the characteristics of the glass ceramic. So, it must be never forget that large oriented structure exhibits better mechanical properties. In some parent glass compositions, nucleating agents are needed; these agents can be either metallic or non-metallic due to envisaged characteristics of the glass-ceramic. Nucleation through nucleating agent is called internal nucleation or bulk nucleation[52] [53].

The growth part takes place after obtaining a nucleus matching desired characteristics. The transformation in growth part is movement of atoms/molecules from the glass, across the glass-crystal interface and into the crystal[2], a temperature depending treatment to grow the grains[54]. A typical processing cycle for Li_2O-Al_2O_3-SiO_2 system is given in Figure 9[55].

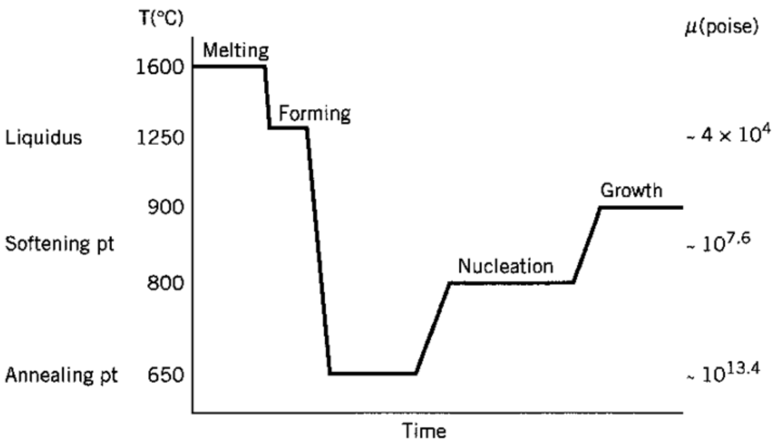

Figure 3.3.1: Processing Cycle of Li_2O-Al_2O_3-SiO_2 Glass-ceramic System

3.4 Glass-Ceramic Production Routes

An increasing amount of investigation on glass-ceramic production has been made in recent years. These processing routes differ from each other in order to obtain unique properties such as expected microstructural or mechanical properties. The glass-ceramic production techniques can be listed as;

- Conventional Method (two-stage)
- Modified Conventional Method (single-stage)
- Petrurgic Method
- Powder Methods
- Sol-Gel Method

References

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[1] Strnad, Z.,*Glass-CeramicMaterials.* Elsevier, Amsterdam (1986).

[2] R. D. Rawlings, J. P. Wu, A. R. Boccaccini, *Glass-ceramics: Their production from wastes*. *A review,* J Mater Sci, 41 (2006) 733-761

[3] Hölland, W.,Beall, G., *Glass-CeramicTechnology*, The American Ceramic Society, Westerville, OH, (2002)

[4] T. Manfredini, G.C. Pellacani and J. M. Rincon, *Glass-Ceramic Materials. Fundamentals and Applications*. Modena, Italy (1997)

[5] C. Ferreira, A. Riberio and L. Ottosen, *Possible applications for municipal solid waste fly ash*, J Hazard Mat, 2003, 96, 201-216.

[6] V.Gomes, C.D.G. De Borba and H.G. Riella *Production and characterization of glass ceramics from steelwork slag,* J Mater Sci, 37 (2002) 2581-2585.

[7] Davies, M. W., Kerrison, B., Gross, W. E., Robson, W. J., and Wichell D. F., *Slagceram: a glass-ceramic from blast-furnace slag*, J Iron Steel I, 208 (1970) 348-370.

[8] Davies, M. W., Hazeldean, G. S. F., Robson, W. J., *Science of Ceramics,* Swedish Institute of Silicate Research, Gothenburg (1970).

[9] Berezhnoi, A. I., *"Glass-Ceramics and Photo-Sitalls"* Trans. from Russian, Plenum Press, New York and London (1970).

[10] Bondarev, K. T. and Pavlushkin, N. M, Slag-Sitall, *A Material of the Future*, in Proc. 9th Int. Congress on Glass, Versailles, France, Scientific and Technical Communications, 2 (1971) 1237-1250.

[11] Ovecoglu, M. L., *Microstructural Characterization and Physical Properties of a Slag-based Glass-ceramic Crystallized at 950 and 1100°C*, J Eur Ceram Soc 18 (1998) 161-168.

[12] Ferreira, E. B., Zanotto, E. D., Scudeller, L. A. M., *Glass and glass-ceramic from basic oxygen furnace (BOF) slag,* Glass Sci Technol 75(2) (2002) 75-86.

[13] Fredericci, C., Zanotto, E. D., Ziemath, E. C., *Crystallization mechanism and properties of a blast furnace slag glass,* J Non-Cryst Solid 273 (2000) 64-75.

[14] El-Alaily, N. A., *Study of some properties of lithium silicate glass and glass ceramics containing blast furnace slag,* Glass Technol 44 (2003) 30-35.

---

[15] De Guire, E. J., Risbud, S. H., *Crystallization and properties of glasses prepared from Illinois coal fly ash,* J Mater Sci 19 (1984) 1760-1766

[16] Cumpston, B., Shadman, F., Risbud, S., *Utilization of coal-ash minerals for technological ceramics*, J Mater Sci 27 (1992) 1781-1784.

[17] Erol, M., Demirler, U., Küçükbayrak, S., Ersoy-Meriçboyu, A., Öveçoğlu, M. L., *Characterization investigations of glass-ceramics developed from Seyitömer thermal power plant fly ash*, J Eur Ceram Soc 23 (2003) 757-763.

[18] Erol, M., Genç, A., Ovecoglu, M. L., Yücelen, E., Küçükbayrak, S., Taptık, Y., *Characterization of a glass-ceramic produced from thermal power plant fly ashes*, J. Eur Cera Soc 20 (2000) 2209-2214.

[19] Leroy, C., Ferro, M. C., Monteiro, R. C. C., Fernandes, M. H. V., *Production of glass-ceramics from coal ashes*, Journal of the European Ceramic Society 21 (2001) 195-202.

[20] Peng, F., Liang, K., Hu, A., Shao, H., *Nano-crystal glass-ceramics obtained by crystallization of vitrified coal fly ash*, Fuel 83:14-15 (2004) 1973-1977.

[21] Ferro, M. C.,Leroy, C., Monteiro, R. C. C., Fernandes, M. H. V., *Fine-grained Glass-ceramics obtained by crystallisation of vitrified coal ashes*, Key Eng Mat 230-232 (2002) 408-411.

[22] Barbieri, L., Lancellotti, I., Manfredini, T., Queralt, I., Rincon, J. Ma., Romero, M., *Design, obtainment and properties of glasses and glass-ceramics from coal fly ash*, Fuel 78 (1999) 271-276.

[23] Kniess, C. T., de Borba, C. D. G., Neves, E., Kuhnen, N. C., Riella, H. G., (2002). *Obtaining and characterizing Li2O-Al2O3-SiO2 glass-ceramics using coal bottom ash as raw material,* Interceram 51 (2002) 140-143.

[24] Boccaccini, A. R.,Bucker, M., Bossert, J., Marszalek, K., *Glass matrix composites from coal fly ash and waste glass*, Waste Manage 17 (1997) 39-45.

[25] Francis, A. A.,Rawlings, R. D., Sweeney, R., Boccaccini, A. R., *Processing of coal ash into glass ceramic products by powder technology and sintering*, Glass Technol 43 (2002) 58-62.

[26] Francis, A. A., Boccaccini, A. R., Rawlings, R. D., *Production of glass-ceramics from coal Ash and waste glass mixtures*, Key Eng Mat 206-213 (2002) 2049-2052.

[27] Kim, J. M., Kim, H. S., *Processing and properties of a glass-ceramic from coal fly ash from a thermal power plant through an economic process,* J Eur Ceram Soc. 24 (2004) 2825-2833.

---

[28] Romero, M., Rawlings, R. D., Rincon, J. Ma. Crystal nucleation and growth in glasses from inorganic wastes from urban incineration, *J. Non-Cryst. Solids*271 (2000) 106-118

[29] Cheng, T. W.,Ueng, T. H., Chen, Y. S., Chiu, J. P., *Production of glass-ceramic from incinerator fly ash*, Ceram Inter 28 (2002) 779-783.

[30] Hjelmar, O.,*Disposal strategies for municipal solid waste incineration residues*, J Hazard Mater 47 (1996) 345-368.

[31] Derie, R., *A new way to stabilize fly ash from municipal incinerators*, Waste Manage 16 (1996) 711-716.

[32] Haugsten, K. E.,Gustavson, B., *Environmental properties of vitrified fly ash from hazardous and municipal waste incineration*, Waste Manage 20 (2000) 167-176.

[33] Nishida, K.,Nagayoshi, Y., Ota, H., Nagasawa, H., *Melting and stone production using MSW incinerated ash*, Waste Manage 21 (2001) 443-449.

[34] Cheng, T. W.,Chen, Y. S., *On formation of* $CaO\text{-}Al_2O_3\text{-}SiO_2$ *glass-ceramics by vitrification of incinerator fly ash*, Chemosphere 51 (2003) 817-824.

[35] Cheng, T. W.,Chen, Y. S., *Characterisation of glass ceramics made from incinerator fly ash*, Ceram Inter 30 (2004) 343-349.

[36] Wiles, C. C.,*Municipal solid waste combustion ash: State-of-the-knowledge*, J Hazard Mater 47 (1996) 325-344

[37] Appendino, P., Ferraris, M., Matekovits, I., Salvo, M., *Production of glass-ceramic bodies from bottom ashes of municipal solid waste incinerators*, J Eur Ceram Soc 24 (2004) 803-810.

[38] Acosta, A., Iglesias, I., Aineto, M., Romero, M., Rincon, J. Ma., *Thermal and sintering characterization of IGCC slag*, J Therm Anal Calorim 67 (2002) 249-255.

[39] Goodwill, J. E.,Schmitt, R. J., *An update of electric arc furnace dust treatment in the United States*, Resource Conservation and Environmental Technologies (1994) 25-34.

[40] Pelino, M., Karamanov, A., Pisciella, P., Crisucci, S., Zonetti, D., *Vitrification of electric arc furnace dusts*, Waste Manage 22 (2002) 945-949.

[41] Morsi, M. M., Khater, G. A., Range, K. J., *Glass ceramics in the system diopside-anorthite-orthoclase prepared by using some industrial waste materials*, Glass Technol 42 (2001) 160-164.

---

[42] Gorokhovsky, A.,Escalante-Garcia, J. I., Gorokhovsky, V., Mescheryakov, D., *InorganicWastes in the Manufacture of Glass and Glass-Ceramics: Quartz-Feldspar Waste of Ore-Refining, Metallurgical Slag, Limestone Dust, and Phosphorus Slurry*, J Am Ceram Soc 85 (2002) 285-287.

[43] Yun, Y. H.,Yoon, C. H., Oh, J. S., Kim, S. B., Kang, B. A., Hwang, K. S., *Waste fluorescent glass and shell derived glass-ceramics*, J Mater Sci 37 (2002) 3211-3215.

[44] Suzuki, S.,Tanaka, M., Kaneko, T., Glass-ceramic from sewage sludge ash, *Journal of Materials Science* 32 (1997) 1775-1779.

[45] Park, Y. J., Moon, S. O., Heo, J., *Crystalline phase control of glass ceramics obtained from sewage sludge fly ash*, Ceram Inter 29 (2003) 223-227.

[46] Diaz, C., Salgado, S., Jordan, R., Cruz, E., Zayas, M. E., *Glass-Ceramics nade from anodizing plant industrial waste,* Am Ceram Soc Bull 82 (2003) 9601-9604

[47] Pelino, M., Cantalini, C., Rincon, J. Ma., *Preparation and properties of glass-ceramic materials obtained by recycling goethite industrial waste,* J Mater Sci 32 (1997) 4655-4660.

[48] Romero, M. and Rincon, J. Ma., *Surface and bulk crystallization of glass-ceramic in the* Na_2O*-CaO-ZnO-PbO-*Fe_2O_3*-*Al_2O_3*-*SiO_2 *system derived from a goethite waste*, J Am Ceram Soc, 82 (1999) 1313-1317

[49] Marabini, A. M., Plescia, P., Maccari, D., Burragato, F., Pelino, M., *New materials from industrial and mining wastes: glass-ceramics and glass- and rock-woolfibre*, Int. J Miner Process 53 (1998) 121-134.

[50] Romero, M., Rincon, J. Ma., Preparation and properties of high iron oxide content glasses obtained from industrial wastes, J Eur Ceram Soc 18 (1998) 153-160.

[51] Toya, T.,Tamura, Y., Kameshima, Y., Okada, K., *Preparation and properties of CaO-MgO-*Al_2O_3*-*SiO_2 *glass-ceramics from kaolin clay refining waste (Kira) and dolomite*, Ceram Inter, 30 (2004) 983-989

[52] Beall, G. H., *Design and properties of glass-ceramics. A. Review*. Mater. Sci. 22 (1992) 91–119

[53] Höland W., Rheinberger V. and Schweiger M. A *Control of nucleation in glass ceramics* Phil. Trans. R. Soc. Lond 361 (2003) 575-589

[54] Beall, G. H. *Glass-ceramics: recent development and application. in nucleation and crystallization in glasses and liquids (ed. M. C. Weinberg).*

Ceramic Transactions Series, Westerville, Ohio. The American Ceramic Society.30 (1993) 241–266.

[55] A. D. Rollett *Microstructure properties: II Crystallization of Glass,* Lecture Notes 2002

Chapter 4

Materials and Characterisation

4.1 Aim of the Study

It is a present fact that no manufacturing or industrial process can exist without emission of some level of unwanted by-products, i.e. wastes. The consequent environmental damage is obviously enhanced by the associated consumption of natural resources, which are increasingly limited in supply. Glass-ceramic technology can provide a positive contribution to the reduction of negative impacts to the environment, since added-value products can be developed using inorganic wastes, thus coupling waste reduction and rational (re)use of natural raw materials. Wastes usually processed to form glass-ceramic products come from numerous sources.

Borate and phosphate wastes, less studied as secondary raw materials in comparison with SLS scrap glass and fly ash, require brief introduction in the context of the present investigation.

The extraction of commercially valuable borate minerals, such as colemanite ($CaO•3B_2O_3•5H_2O$), ulexite ($Na_2O•2CaO•5B_2O_3•2H_2O$) and borax ($Na_2O•2B_2O_3•10H_2O$), generates a large amount of boron-containing waste. These consist of clay and carbonates, with a lower B_2O_3 content compared to the main ore. Various potential applications of these wastes have been considered for the building materials industry, i.e. in formulations for cements and bricks. Most reports in the literature show that borate wastes (BW) cannot be used efficiently as additive in the aforementioned industrial products due to the rather high amount of water emitted during the required thermal treatment.

The phosphate waste used in this study, meat and bone meal (MBM) ash, also known as “bone ash”; is a residue from incineration of meat and bone meal, featuring high percentages of P_2O_5 and CaO. This residue is available in very large quantities; the total production of MBM in the European Union exceeds 3,500,000 tons/year. As an example, in France 850,000 tons of MBM are produced each year, but only 45% is used in cement plants, while the other 55% does not presently have any established applications. [1]

In ceramic and cement industry, fly ash was investigated in numerous studies. The current annual production of coal ash worldwide is estimated to be around 600 million tons, with fly ash constituting about 500 million tons at 75–80% of the total ash produced[2]. Thus, the amount of coal waste (fly ash), released by factories and thermal power plants has been increasing throughout the world, and the disposal of the large amount of fly ash has become a serious environmental problem. The present day utilization of ash on worldwide basis is ranging between 3% and 57%, yet the world average only amounts to 16% of the total ash[2]. A substantial amount of ash is still disposed of in landfills and/or lagoons at a significant cost for the utilizing companies and thus for the consumers.

The thesis is dedicated to the development of glass-ceramic from a combination of wastes not previously investigated: i) borate and phosphate containing wastes, ii)common recycled soda-lime-silica (SLS) glass, iii)fly ash.

Three different studies were carried out:

- Micro porous glass ceramics from combination of borate, phosphate and silicate wastes
- Dense glass-ceramic production from borate and silica wastes and its cytotoxic characterization
- Wollastonite glass-ceramics from fly ash and boron containing wastes

4.2 Materials

As addressed in the aim title of the introduction part, this thesis is focused on obtaining three different products through aforementioned wastes where borate waste was constant at all studies. The used wastes, in addition to BW, are;

- Borate waste (BW) from the borate mine waste deposits in Bigadic (Turkey);
- Meat bone and meal (MBM) ashes, from Glanford Power Station near Scunthorpe in Lincolnshire, UK;
- SLS glass waste from municipal recycling (provided by SASIL Life, Biella, Italy).

In every product mentioned, wastes were treated separately, with different instruments in different conditions. Particle sizes, applied thermal treatments and used methods were varied in each product in order to achieve the expected structure and explore the alternative methods. For a better understanding of the each research, production steps will be explained and examined separately for each product.

The constant material BW used in all studies was selected from three different borate wastes gathered from ulexite and colemanite concentrator plants located next the borate mines in Turkey. After chemical analyses, it has been decided to use, in all studies, the high B_2O_3 containing waste, from Bigadic colemanite enrichment plant. The chemical compositions of the used materials are presented in Table 4.2;

	FA	BW	SLG	MBM	Kaolin Clay
SiO2	49,4	16,1	71,6	2.3	54
Na2O	0,9	0,22	13,5	8.7	
K2O	1,4	0,51	0,4	3.5	
MgO	1,6	6,91	3,9	1.3	
CaO	8,9	26,41	9	46.4	
SrO		1,23			
Al2O3	22,7	0,89	1	0.2	46
Fe2O3	7,4	0,11	0,1		
TiO2	1,1			3.6	
SO3	0			34.0	
P2O5	0				
B2O3	0	19,67			
others	5,3		0,5		
LOI	1,3	27,98			

Table 4.2 Details of the chemical compositions of the used materials

4.2.1 Materials for producing micro porous glass ceramics from combination of borate, phosphate and silicate wastes

Cellular ceramics, or ceramic foams, constitute a typology of ceramic products of growing interest due to their industrial use as insulators, membranes for separation processes in the chemical industry and foamed filters, for hot gas cleanup and molten metal processing[3]. For the production of these kinds of materials, different techniques are used connected to the application areas, i.e. sol–gel methods, polymeric sponge method, control of sintering conditions to achieve a partial densification, reaction sintering, direct foaming, pyrolysis of organic additives and bubbles generation in slurries or in a green body, during specific thermal treatments[4]. A limited number of papers, to date, report the production of glass-ceramic foams. Most are in the field of biomaterials[5,6,7] and other papers concern foams from inorganic wastes[8,9,10] . Such foams could be very attractive, considering the possibility of confining toxic components in an ecologically harmless, leach-resistant glass-ceramic matrix phase in the form of a foamed material with tailored high porosity, suitable for various purposes.

The evolution of non-toxic gas in a silicate-glass matrix upon thermal decomposition of BW is potentially advantageous, for a foaming process. If a glassy phase with an appropriate viscosity is available. It is also known that the foaming of glass occurs when gaseous species originate by decomposition or oxidation of a pyroplastic mass, not too viscous to feature a modest expansion nor excessively fluid to release the gases[11]. The calcite present in BW, as an example, may be very useful as a foaming agent if the softening temperature of the glass in which it is embedded is not higher than its decomposition temperature, as in the case of CRT glasses[12]. Starting from the aforementioned BW and phosphate waste, a glassy phase was expected to be developed by the combined action of borate and phosphate compounds, well known to provide glasses with low characteristic temperatures[13]; the addition of kaolin clay provided silica and alumina. Recycled SLS glass was chosen as an extra additive essentially to modify the features of the developed glassy phase. The presence of more than one oxide, acting as a glass network former, was expected to promote crystallisation, i.e. the obtainment of porous glass ceramics, taking into account the high tendency towards phase separation of glasses containing multiple glass formers[13]. For the optimised combination of wastes, additives and thermal treatments, high porous glass ceramics with homogeneous microstructure were effectively obtained. Such positive results may promote the large scale reutilisation of the selected wastes in the formation of structural foams.

4.2.2 Materials for producing of dense glass-ceramic from borate and silica wastes and for its cytotoxic characterization

Distinctively from the previous study, in this research soda lime silica glass (SLS) waste was used as a main additive together with BW and MBM ash in different proportions and heating rates. SLS wastes, that usually contain 70% SiO_2, 10% Na_2O and 10% Ca_2O, is one of the most important waste materials considering not only its amount of production, but also its natural and economic gains. It is collected from windowpanes, bottles (containers) and glass products through various industries (glass packaging and other waste glass from municipal, commercial or industrial sources, mixed municipal solid waste and bulky waste etc.). In 2009, 11.5 million tons of packaging glass waste were collected from all the 27 European countries, including Norway, Switzerland and Turkey. Packaging glass recycle ratio is 65% in EU countries[14].

Various researches are published on the re-use possibilities of waste glasses, especially when there are colored glasses that are hard to separate, and these researches are generally focused on utilizing them in glass[15], ceramic[16], glass-ceramic[17], porcelain[18] and in cement industry[19].

The main objective of the present study is to obtain a glass-ceramic structure by favoring crystallization with rapid firing at relatively low temperature through using well known glass forming oxides and to obtain a previously uninvestigated dense glass-ceramics from combination of three different wastes.

As Mentioned in chapter 3, beside of being a highly preferred and gainful waste utilization technique, glass-ceramic option has its own boundaries too. In glass- ceramic technology, the toxic components can be encapsulated in the material's glass matrix phase, but on the other side, boron within a glass forming oxide B_2O_3, can be toxic after reaching previously mentioned amounts. In this research this effect will be studied through cytotoxicity analyses on sintered samples.

4.2.3 Materials for producing wollastonite glass ceramics from fly ash borate wastes

Fly ash is a side product obtained from the combustion of coal in power plants (energy production). The physical and chemical characteristics of fly ash depend on the type of coal used and the combustion conditions; due to these variable characteristics, fly ash is considered as an environmental pollutant, as well as a waste and a potential raw material. In energy production, fly ash is a waste material, but also a resource waiting to be utilized in the coal industry. Fly ash has been examined numerous times by the thermal electricity production industry in order to find efficient re-use strategies: in last 15 years, significant developments have been achieved by research and development studies.

Today, fly ash is being used by the cement industry as an additive in concrete production as well as ceramic industry. In ceramic industry fly ash utilization together with clay has been studied and efficient strategies developed for the production of dry pressed ceramic tiles[20] [21].

This research is focused on the re-use and utilization possibility of fly ash (FA) obtained from power plant in Greece, together with previously investigated waste materials, BW and SLS . After examining the researches made on FA utilization technologies, it has been seen that FA containing high amounts of SiO_2, CaO, and Al_2O_3 can be used as a suitable raw material for glass-ceramic production. The objective of the research was to study a possible starting composition respecting the CaO- SiO_2- Al_2O_3 (wollastonite) glass-ceramic ternary system, with a heat treatment studied in aforementioned researches, thus comparing the results in order to achieve glass ceramics with better characteristics which also can be used in construction industry.

4.3 Characterisation

4.3.1 Inductively Coupled Plasma (ICP)

Inductive coupling plasma is an efficient instrument for chemical composition analyses, compared to other methods ICP analyses are considered more economic and sensitive in several aspects.

In inductively coupling plasma analyses, a high-frequency current is sent to load the coils which surrounds a torch, with conductive argon gas being swirled through the torch, a spark is applied to the gas causing some electrons to be stripped from their argon atoms. These electrons then caught up in the magnetic field and accelerated by it. Adding energy to the electrons by this manner is known “inductive coupling”. The Argon gas passing through this coil forms the argon plasma, reaching a temperature of 6000 to 11000°C. By high temperature plasma, excited electrons carried by a secondary gas emit energy at a given wavelength, as they return to ground state after excitation. Nearly all elements in examined sample create its own wavelength specific to its own. At the end, a spectrometer analyses the spectra of the emitted lights of the examined elements, resulting sensitive analyses possible.
Emission spectrometry using an ICP light source is known as "ICP Emission Spectrometry."

All the chemical analyses in this research are done with inductively coupled plasma optical emission spectroscopy model; 3200 XL Perkin Elmer, USA

4.3.2 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive highly preferred analyse technique mainly used for phase identification of crystalline materials, minerals or inorganic compounds. XRD also can be used to examine unit cell dimensions.

In this method, the analysed material has to be finely grounded and homogenized. X-rays are produced in a device called an ***X-ray tube***. (Figure 4.3.2.1) It consists of an evacuated chamber with a filament at one end of the tube(cathode) and a metal target at the other end (anadode).

Electrical current is run through the tungsten filament, causing it to glow and emit electrons. A large voltage difference is placed between the cathode and the anode, causing the electrons to move at high velocity from the filament to the anode target resulting inner outer shell transfer of the electrons. These electronic transitions results in the generation of X-rays. [22]

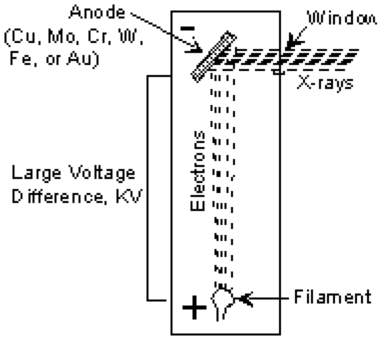

Figure 4.3.2.1 - X-Ray Tube

The generated X-rays are concentrated and directed towards on the sample. Due to Bragg's Law ($n\lambda=2d \sin \theta$) when a monochromatic X-ray beam with wavelength *lambda* is projected onto a crystalline material at an angle *theta*, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number *n* of wavelengths. In other words, this law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample.

These diffracted X-rays are then detected, processed than noted. By scanning the sample through a range of 2θangles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacing allows identification of the mineral because each mineral has a set of unique d-spacing. Typically, this is achieved by comparison of d-spacing with standard reference patterns. [23]

X-ray powder diffraction is also used for;

- Characterization of crystalline materials
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- Determination of unit cell dimensions
- Measurement of sample purity

With specialized techniques, XRD can be used to:

- Determine crystal structures using rietveld refinement
- Determine of modal amounts of minerals (quantitative analysis)
- Characterize thin films samples
- Make textural measurements, such as the orientation of grains, in a polycrystalline sample[23]

Phase characterization of the starting materials was performed by Philips PW3830, NL; phase identification was achieved by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA).

4.3.3 Heating Microscopy (Hot Stage Microscopy)

Heating microscopy is also known as hot stage or thermal microscopy, a combined system of microscopy and thermal analyses. This technique provides a better understanding concerning the sintering behaviors of the materials, such as determining the melting point and changes in volume while sintering, plus, enabling the simultaneous comparison of the sintering behaviors of the samples.

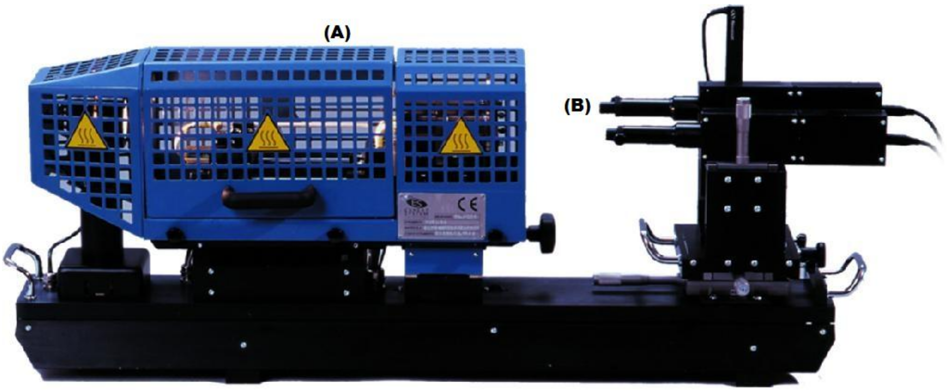

Figure 4.3.3.1 - Heating Microscope- Expert system solutions, A) Hot stage, B) Microscope

Hot Stage Microscope
Misura 3.32
www.expertsystemsolutions.com
tech@expertsystemsolutions.com

Codice:	00153L	**Tipo prova:**	Provino doppio
Descrizione:	B2	**Temperatura min.:**	28 °C
Data:	02/03/2012	**Temperatura max.:**	1137 °C

Figure 4.3.3.2 - A comparison between two samples accessed with heating microscopy

The heating microscopy analyses in this research are made by, Expert system solutions-Heating microscope HSM MO, Italy.

4.3.4 Density

The densities in this research are measured with pycnometer and by averaging mass by geometrical volume methods.

Pycnometer is a container usually made of glass or metal, used to determine the density of the insoluble, irregular, porous solid materials .While determining the density of the material with pycnometer, the mass of solid is determined by weighing. While measuring the denstiy, the sample is first placed in a pycnometer filled with a liquid of known density such as water, the volume of the liquid which will overflow is equal to the volume of the solid. The density measurements in this research was made by Micromeritics AccuPyc 1330,GA, USA.

The mass of the overflown liquid is defined as the difference between the sum of the mass of the pycnometer filled with liquid, plus the mass of the solid and the mass of the pycnometer filled with liquid after the solid has been placed inside. The volume associated to this mass is determined from the known density of the liquid. The density of the solid is determined from these measurements of mass and volume.[24]

Density is the ratio of the mass of a body to its volume.

$$d = M/V$$

M: The mass of the empty pycnometer

Mw : The mass of the pycnometer filled with water at t°C.

d: The density of water at t°C

V:Volume of the pycnometer

$$V = (Mw - M)/d \quad 1$$

M_L: The mass of the pycnometer when filled with the liquid.

d_L: The density of the liquid

$$d_L = (M_L - M)/V = d(M_L - M)/(Mw - M) \quad 2$$

M_S: The mass of the solid
$M_L{'}_S$: The mass of the pycnometer containing the sample and filled with the liquid.

The mass of the liquid displaced is;

$$\mathbf{M_{L'} + M_s - M_{L's}} \quad 3$$

When the volume of the solid is equal to the ratio of the mass of the liquid displaced to d', the density of this liquid at t°C,
The mass of the solid at that temparature;

$$\mathbf{(M_{L'} + M_s - M_{L's})/d'} \quad 4$$
$$\mathbf{d_s = M_s d'/(M_{L'} + M_s - M_{L's})} \quad 5$$

4.3.5 Mechanical Strength

To determine the mechanical characteristics of the sintered samples, worldwide used testing equipment Instron is used. Method of instron is subjecting a selected sample from the material or component to forces either tensile (pull), compressive (crushing), bending, torsion (twisting), frictional, peel resistance. The testing machine measures the forces applied to the sample and determines the behavior of the material. In this research compression and split tensile strengths of the materials are studied. Split tensile strength of some samples are measured with Brazilian testing method, the required details about this method will be examined in part 6.3

Figure 4.3.5.1 - Instron

To measure compression strength with instron, sample is placed on a receptacle between two pressing arms. In small samples (less than 3cm of diameter), in order to prevent surface cracks which may cause rubbing with the load arm’s surface, the surface of the arms has to be covered with a plastic patch. This patch must not be over 2 mm, due to the possibility of miscalculation by stress absorbing ability of the patch. When the sample is placed, loading begins till the maximum stress that the sample can sustain (crush of the sample) load rates can be read through the monitor of the instron in order to calculate by dividing the maximum load by the original cross-sectional area of the sample. In this research, to obtain a valid result, 20 samples from each composition are tested by means of Instron 1121 UTS and Instron 4204, MA, USA.

4.3.6 Scanning Electron Microcopy (SEM)

The objective of the scanning electron microscopy (SEM) is to magnify and focus on the studied solid surface in high magnifications when the other lens holding microscopes are not enough. The external morphology, elemental map, crystalline structure and crystalline shapes of the examined sample can be determined/imaged through SEM. Instead of glass lenses, in SEM, electromagnets
are used to focus beam of high-energy electrons and to generate a variety of signals at the targeted area, this areas (mainly range between 1 cm to 5 microns in width) can be imaged in a scanning mode using conventional SEM techniques (20X to 30,000X)
A SEM equipped with an Energy-Dispersive X-Ray Spectroscopy (EDS) can help on determining the chemical composition of the scanned area, or to determine the crystals in case of complex and unknown structures

For a dependable analyse in SEM, samples must be conductive and electrically grounded in order to prevent accumulation, thus to obtain higher resolution, to provide this sample is coated with gold and combined to is receptacle with copper band, in some cases liquid carbon is also used to for a better conductivity.
The scanning electron microscopy used in this study was; Zeiss EVO 40 D, Germany and Quanta FEI 200, Netherlands equipped with an energy dispersive X-ray analysis attachment (EDS, Inca, Oxford Instruments, UK).

4.3.7 Light Microscopy

Light microscope is a widely used optical microscope providing high-resolution images of a variety of specimens. In recent years this imaging technology is highly improved. It is called light microscope because to identify small objects, it employs light from a source . The light is reflected from a specimen with a condenser lens, then is passed through other lenses (2 or more depending on the microscope) placed at end of the tube, each magnify the image.

In light microscopy, resolution, illumination and contrast is as important magnification. Resolution can be improved using different types of lenses developed for specific purposes, lighting and contrast can be also improved using led, florescent modifications such as dark field, phase contrast, and differential interference contrast. [25] The light microscope used in this study was LM Zeiss, Primo Vert, Germany.

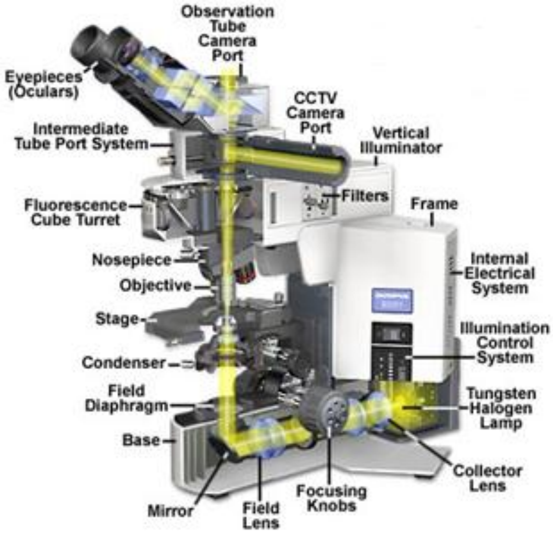

Figure 4.3.7.1 Light microscope optical pathways[26]

4.3.8 Cytotoxity

In materials, cytotoxity test is mainly used for testing bio-compatibility and toxicity of the materials as well as measuring their intolerance levels. In cytotoxicity tests, due to the fact that toxic chemicals affect parent functions of cells which are common to all cells, toxicity can be measured by measuring cellular damage.

Depending on the aim of the test various methods can be followed, in materials testing, there are two main basic analyses. The first one is to measure cellular metabolic activity. The metabolic function is assessed through measuring cellular ATP levels or mitochondrial activity. Cellular damage lowers metabolic activity and enables to comment about the toxicity level of the examined material.

The other analyse mainly used is the measurement of membrane integrity. The cell membrane is consisted of an outer system covering the cell which contains transporters, receptors and secretion pathways. Membrane integrity is determined by measuring lactate dehyrogenase (LDH) in the extracellular medium. This enzyme is present in the cytosol, and only can be measured when the cell is damaged. Due to level of the damage, the cell spread can be either slow or stopped. The detailed information (parallel to research) about cyctotoxity analyses will be in part 6.2

4.3.9 Surface Roughness

Surface roughness, also known as "roughness" is a measurement technique of examining surface texture, this method is mainly used in determining the surface interaction characteristics of materials in their usage area. The large deviations on the surface represents rough surfaces which in many cases an expected feature such as in wearing and friction, while smooth surfaces are preferred in high surface interaction applications, such as various types of biomaterials. Roughness measurement can be also made in nanometric scale in order determine long term behaviors of the materials (cracks, corrosion etc.) and also to prevent un expected results. [27]

In this Research optical determination technique is used with Taylor Hobson, CCI MP - 3D Optical Profiler, UK. To determine surface characteristics, a beam of electromagnetic radiation is reflected off from surface, depending on the surface roughness, radiation of a certain wavelength can be reflected speculary while another wavelength reflects diffusely, this specular and diffuse reflections helps to map the surface the sample.

References

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[1] Syndicat des Industries Francaises de Co-Produits Animaux (SIFCO), http://www.sifco.fr/index.html

[2] Joshi RC, Lothia RP. *Fly ash in concrete: production, properties and uses* Advances in Concrete Technology. Gordon and Breach Science Publishers 2 (1997).

[3] L.M. Sheppard: *Porous Materials,* The American Ceramic Society, Westerville, OH., 31 (1993) 3-25.

[4] R.A. Lopes and A.M. Segadaes *Microstructure, permeability and mechanical behavior of ceramic foams,* Mater. Sci. Eng. A., 209 (1996) 149–155.

[5] E. de Sousa, C.R. Rambo, D. Hotza, A.P. Novaes de Oliveira, T. Fey and P. Greil, *Microstructure and properties of LZSA glass-ceramic foams* Mater. Sci. Eng., 476 (2008) 89-97.

[6] M.F. Gorriti, J.M.P. Lopez and A.R. Boccaccini, *In vitro Study of the Antibacterial Activity of Bioactive Glass-ceramic Scaffolds,* Adv. Eng. Mater., 11 (2009) B67-B70.

[7] R. Huang, J. Pan and A.R. Boccaccini, *A two-scale model for simultaneous sintering and crystallization of glass-ceramic scaffolds for tissue engineering,* Acta Biomater., 4 (2008) 1095-1103.

[8] D.U. Tulyaganov, H.R. Fernandes, S. Agathopoulos , J.M.F. *Ferreira, Low temperature synthesis of anorthite based glass-ceramics via sintering and crystallization of glass-powder compacts*. J. Porous Mater, 13 (2006) 133-139(7).

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[9] J.P. Wu, A.R. Boccaccini, P.D. Lee, M.J. Kershaw, R.D. Rawlings, *Glass ceramic foams from coal ash and waste glass: production and characterisation,* Adv. Appl. Ceram., 105 (2006) 32-39.

[10] E. Bernardo, *Micro- and Macro-cellular Sintered Glass-ceramics from Wastes*, J. Eur. Ceram. Soc., 27 (2007) 2415-2422.

[11] G. Scarinci, G. Brusatin, E. Bernardo: *Production Technology of Glass Foam, Cellular Ceramics. Structure, Manufacturing, Properties and Applications,*Wiley-VCH, Weinheim, (2005) 158-176

[12] E. Bernardo G. Scarinci, S. Hreglich, *Foam glass as a way of recycling glasses from cathode ray tubes.* Glass Sci. Technol., 78, (2005) 7-11

[13] J.E. Shelby: *Introduction to Glass Science and Technology*, The Royal Society of Chemistry, Cambridge, (2005) 67, 77, 93-100.

[14] http://www.feve.org/ The EU association for container glass annual statistics 2009

[15] W.M. Brown, K.J.D. Mackenzie, *Process design for the production of a ceramic-like body from recycled waste glass* J. Mater. Sci. ,17 (1982) 2164–2183

[16] R.V. Manukyan, N.S. Davydova, *Use of waste in the ceramic industry,* Glass and Ceram., 53 (7–8) (1996) 247–248

[17] E. Bernardo, R. Dal Maschio, *Glass–ceramics from vitrified sewage sludge pyrolysis residues and waste glasses* Waste Manage, 31 (2011) 2245-2252

[18] A. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi, *Fired Porcelain using Wasted Glasses as a Fluxing* , J Eur Ceram Soc ,24 (2004) 83–92

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[19] F. Matteucci, M. Dondi, G. Guarini, *Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles,* Ceram Int. 28 (2002) 873–880

[20] R. Sokolar, L. Smetanova *Dry pressed ceramic tiles based on fly ash–clay body: influence of fly ash granulometry and pentasodium triphosphate addition* Ceram Inter, 36 (1) (2010) 215–221

[21] I. Queralt, X. Querol, A. López-Soler, F. Plana *Use of coal fly ash for ceramics: a case study for a large Spanish power station* Fuel, 76 (8) (1997), 787–791

[22] Stephen A. Nelson X-Ray Crystallography,19.10.2011, http://www.tulane.edu

[23] Barbara L Dutrow, Louisiana State University ,Christine M. Clark, Eastern Michigan University X-ray Powder Diffraction (XRD), www.carleton.edu

[24] Cenco Physics Selected Experiments in Physics (No. 71990-184), Copyright, Sargent-Welch Scientific Company (2003)

[25] David R. Caprette, Rice University, 7 Sept 1995 http://www.ruf.rice.edu

[26] Olympus micrsocopy reseource center http://www.olympusmicro.com

[27] Degarmo, E. Paul; Black, J T.; Kohser, Ronald A. *Materials and Processes in Manufacturing* (9th ed.), Wiley, (2003) 223

Chapter 5

Experimental Procedure

5.1 Experimental procedure for producing micro porous glass-ceramics from combination of borate, phosphate and silicate wastes

The wastes used in the preparation of the studied mixtures were borate waste (BW) and meat bone and meal (MBM) ashes. Their chemical composition, determined with inductively coupled plasma optical emission spectroscopy (ICP-OES model 3200 XL Perkin Elmer, USA), is reported in Table 4.2. Pure kaolin clay and, in some compositions, SLS glass waste were used as additives. The raw materials used in this study except BW were previously studied by the ceramic and related industries numerous times, while, due to the limited knowledge of BW used in this study, BW has been examined and analysed more in detail than the other selected materials in every step of the research in order to observe its characteristics under conditions variations. The raw materials were used after dry ball milling and sieving to a maximum dimension of 150 µm, the starting SLS glass powder, used in some compositions was finer, having an average particle size of 50 µm. Both BW and kaolin clay were used after calcination in an electric laboratory oven at 500°C for 180 min.

Phase characterization of the starting materials was performed by means of X-ray diffraction (Philips PW3830, NL); phase identification was achieved by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). The thermal characterization of BW powder (< 150µm particle size) and MBM ash (< 150µm particle size) was investigated by heating microscopy (Expert system solutions-Heating microscope HSM), up to 970°C and 1350°C, respectively, adopting a heating rate of 5°Cmin^{-1}.

BW and MBM ash wastes were mixed first with only kaolin clay, giving origin to the formulation labelled "Mix A", as reported in Table 5.1.1; such basic formulation was modified adding 8 and 16 wt% of SLS glass giving origin to further mixes, labelled "Mix B" and "Mix C" respectively, also reported in Table 5.1.1.

Formulations of the tested mixes*, wt%				
	BW	MBM ash	SLS glass	Kaolin clay
Mix A	36	20		44
Mix B	34	18	8	40
Mix C	30.5	16	16	37.5

Table 5.1.1 - Details of the formulations for porous glass-ceramics.

In order to promote the homogeneity of the formulations, the starting powders were milled with ethanol in zirconia jar mill for 35 min. After drying in oven at 100°C for 60 min, the powders were sieved at 150 µm sieve, moisturized with 5 wt.% H_2O and uniaxially pressed at 50 MPa to form cylinders with a diameter of 20 mm and a height of about 9 mm, without using any binder.

Firing of samples was performed up to the maximum temperature of 1050°C and adopting very different heating rates, from 2 to 40 °Cmin^{-1}. Natural cooling was applied after a dwell of 30 min at the maximum temperature. Details of the thermal treatments investigated are reported in Table 5.1.2.

Mix	Sample	Heating rate, $Cmin^{-1}$	Remarks	Density, gcm^{-3} [Porosity]	Crushing strength, MPa
A	A1	2	Microporous body	1.52 ± 0.7 [44%]	8.7 ± 1.3
	A2	10	Microporous body		
	A3	20	Microporous body		
	A4	40	Cracked sample		
B	B1	2	Microporous body	1.28± 0.6	
	B2	10	Microporous body		
	B3	20	Microporous body	1.18±0.4	
	B4	40	Cracked sample		
C	C1	10	Inhomogenous Foam		
	C2	20	Foam	0.44 ±0.03 [84%]	1.8 ± 0.1
	C3	40	Cracked sample		

5.1.2 Details of the adopted combinations of formulation and heating rate.

The phase composition of the fired materials was determined by X-ray diffraction (XRD) analysis (PW3830, Philips, NL). Phase identification was achieved by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). For quantitative determinations, powdered specimens were diluted with 10 wt% of corundum NIST 676, acting as an internal standard, and carefully side loaded to minimize preferred orientation. The data were collected in the angular range 2θ=10-80° with steps of 0.02° and 5 s/step; Rietveld refinements were performed using GSAS.[1] The microstructure of the fired materials was analysed by scanning electron microscopy (SEM, Zeiss EVO 40, D) equipped with an energy dispersive X-ray analysis attachment (EDS, Inca, Oxford Instruments, UK).

The bulk density of fired materials was inferred by averaging masses by geometrical volumes. For a selected composition small blocks of about 10 mm × 10 mm × 8 mm were cut from larger disc samples (31 mm diameter) and used for bulk density measurements and compressive testing (by means of Instron 1121 UTS, Instron, Danvers, MA) with a cross-head speed of 1 mm/min. True density determinations were performed by means of a gas pycnometer (Micromeritics AccuPyc 1330, Norcross, GA) on powdered blocks.

5.2 Experimental procedure for producing dense glass-ceramic from borate and silica wastes and its cytotoxic characterization

The three wastes, BW, MBM ash and SLS, were used as starting materials to prepare the tested mixes. As in the previous study, chemical compositions of the used wastes were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES model 3200 XL Perkin Elmer, USA), is reported in Table 4.2. The phase composition of the starting material and of the studied mixes, after the thermal treatments, was determined by X-ray powder diffraction analysis (Philips PW3830, NL); phase identification was achieved by means of the Match! program package (Crystal Impact GbR, Bonn, Germany), supported by data from PDF-2 database (ICDD-International Centre for Diffraction Data, Newtown Square, PA). The thermal characterization of the starting materials was performed with the use of a heating microscopy (Expert system solutions-Heating microscope HSM, IT)

Two different mixes were prepared. The first one, labeled A, contains 30wt% of MBM, 30wt% of BW and 40wt% of SLG. Due to the presence of crystalline phases such as calcite ($CaCO_3$) and colemanite ($CaO{\cdot}3B_2O_3{\cdot}5H_2$) in BW, that would have released gases during the following heating step, the BW material were calcined at 500°C. The calcined BW and MBM ash are milled below 150µm. SLG glass is milled below 50µm **(**Retcsh PM 100 Germany).

Compared to the annual production amounts and re-use capacities of the selected wastes, BW has the highest amount of production. For this reason, in the second studied composition, labelled “B”, always respecting the glass-ceramic ternary system, the amount of BW was increased up to its highest possible limit. As a final result, B samples contained 40wt% of BW and 30wt% of MBM ash and SLG. It is known that colemanite ($CaO.3B_2O_3.5H_2O$), present in the studied BW, decomposes with the release of five molecules of H_2O between 450 and 500°C, by transforming into a fine particulate material, less than 0.2 mm in size.[2] The temperature of onset of dehydration for colemanite is 262°C and the first water molecule is lost at 327°C, which coincides approximately with the onset of decrepitating. The last crystal water loss takes place at 412°C.[3] Several studies underline that the calcination step of colemanite has an impact similar to that of the milling process.[4 5] According to the main aim of the study, this impact is used to replace calcination, an energy consuming process. As a result, differently from A samples, the BW waste used in B samples was not calcined.

The sintering tests were performed on compacted specimens, uniaxially pressed in form of discs of 10mm diameter and 4.5 mm in height, under a load of 5.10^4 N. Specimens of both the mixes were sintered at 950°C by using different heating rates. A fast sintering, characterised by heating rate of 16.5°C/min up to the maximum heating temperature of 950°C, the sintered samples are labelled with a tag “F”. The samples fired with the same heating cycle, but with 1 hour of dwell time at 950°C, are labelled with a tag “H”. A rather rapid cooling, about 1 hour to reach room temperature, was adopted for both.

A slow sintering, characterised by heating rate of 2.6 °C/min up to the maximum temperature of 950°C, with a 3 hours of dwell and natural cooling.

The sintered samples are labelled with “S”. In Table 5.2.1, the details of the different sintering treatments are reported.

Mix	Sample	Heating rate °C/min	Tmax / Soaking time	Cooling	Density g/cm^3	σ_d MPa
A	AF	16.5	950°C / 1min	Fast, 1 hour	1.76	18.40
	AH	16.5	950°C / 1h	Fast, 1 hour	1.97	12.98
	AS	2.6	950°C / 3h	Slow, natural cooling	2.07	14.02
B	BF	16.5	950°C / 1min	Fast, 1 hour	2.04	7.88
	BH	16.5	950°C / 1h	Fast, 1 hour	2.02	14.37
	BS	2.6	950°C / 3h	Slow, natural cooling	1.96	15.00

Table 5.2.1 - Details of the adopted combinations of formulation and heating rate and their physical and mechanical characteristics

The bulk density of fired materials was inferred by averaging masses by geometrical volumes. The mechanical strength of the different sintered samples was measured by Brazilian test method. This method is also known as “diametric compression” and “indirect (splitting) tensile test”, an indirect experimental method to measure the tensile strength of materials.[6] For each composition, ten sintered discs were tested by using a universal machine (Instron 4204, Instron, Danvers, Ma, USA).

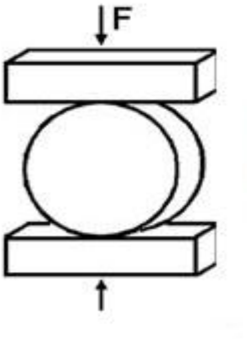

Figure 5.2.1. Brazilian test principle

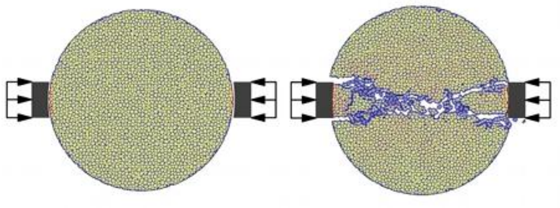

Figure 5.2.2 Dynamic of Brazilian Test [7]

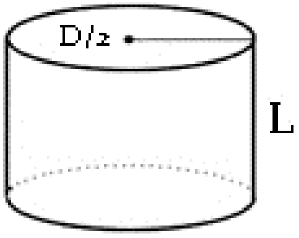

Figure 5.2.3 Sample prepared for Brazilian Test

$$\sigma_t = 2P/ \pi DL$$

P: Load at failure

D: Diameter of the specimen (disc)

L: thickness of the disc

The morphology of sintered samples were investigated by means of light (LM Zeiss, Primo Vert, Germany) and scanning electron microscopy (SEM), (Quanta FEI 200, Netherlands).

Surface roughness analyses of the sintered samples were performed by 3D surface profilometer (Taylor Hobson Precision Ltd, UK). In order to perform the cell toxicity analyses, the surfaces which to be cell seeded has to meet the required profile for the cell growth. These analyses were done in order to determine the surface structure of the sintered samples.

To evaluate the cell toxicity of two different waste materials compared with a reference, MEF (mouse embryonic fibroblasts, Fig. 5.2.4) cells (provided from Prof. Fabry, Biophysics Erlangen, Germany) were used. These cells was cultured at 37 °C in a humidified atmosphere of 95 % air and 5 % CO2, in RPMI 1640 (Gibco, Germany) containing 10 vol.% fetal bovine serum (FBS, Sigma-Aldrich, Germany) and 1 vol.% penicillin/streptomycin (Sigma-Aldrich, Germany). Cells were grown for 48 hours to confluence in 75 cm2 culture flasks (Nunc, Denmark), before harvested using Trypsin/EDTA (Sigma, Germany), counted by a hemocytometer (Roth, Germany) and diluted to a final concentration of 100,000 cells/ml.

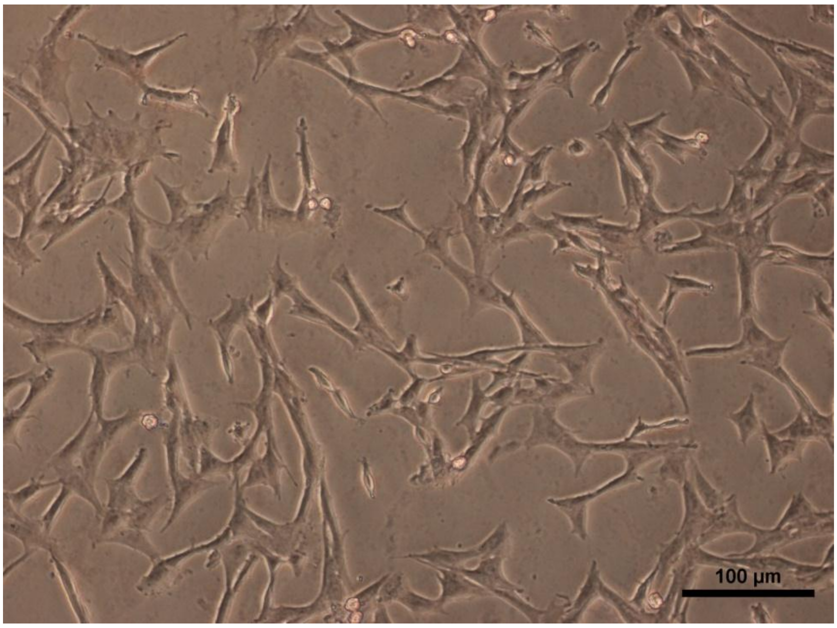

Fig. 5.2.4: Light microscopic image of MEF cells.

Before cell seeding, material samples were cleaned by soaking in Extran (Merck, Germany) and sodium dodecyl sulphate (SDS, Sigma, Germany) solutions. Afterwards they were sterilized at 134 °C in an autoclave (Systec, Germany) and placed in a 48-well cell culture plate (Greiner, Germany).

LDH (Lactate dehydrogenase activity)-activity gives a measurement of the amount of attached cells on the analysed materials. Therefore, the toxicology kit from Sigma was used. LDH reduces NAD+, which catalyses the conversion of tetrazolium to a coloured formazan derivative. A commercially available lactate dehydrogenase (LDH) quantification kit (TOX7, Sigma-Aldrich) was used to quantify cell proliferation by enzyme activity in cell lysate. Cells cultured in 48-well plates were washed with phosphate buffered saline (PBS) solution and lysed with lysis buffer for 10 minutes (1 ml/well). The lysate solutions were centrifuged for 5 min at 1000 rpm and 100 µl from the supernatant solutions was transferred to a 98-well plate. 30 µl of Master-mix was added to each well containing equal amounts of: substrate solution, dye solution and cofactor solution for LDH assay. The plates were left for 30 minutes in the dark and the reaction was stopped with 40 µl HCl 1 N per well.

The dye was measured using a spectrophotometer (SPECORD 40 BU, analytikjena, Germany) at 490 nm.

For measuring the mitochondrial activity and assessing the influence of different materials on the viability of MEF cells after 48 hours of culture, a WST-8 assay (Sigma-Aldrich) was used. After a cultivation period of 24 hours, the mitochondrial activity MEF cells was measured by the conversion of tetrazolium (WST-8, Sigma) to formazan by mitochondrial enzymes. Culture media was removed from the 48-well wells plates and the cells were washed with PBS. After addition of 100 µl of solution containing 99 µl culture medium and 1 µl WST-8 in each well, the plates were incubated for 1 h. Subsequently, the solution was given in a 98-well plates (50 µl in each well) to measure the absorbance at 450 nm.

Cell morphology

After 24 hours the cultures were washed with PBS. Cells were fixed with a solution containing 3 vol.% glutaraldehyde (Sigma, Germany) and 3 vol.% paraformaldehyde (Sigma, Germany) in 0.2 M sodium cacodylate buffer (pH 7.4) and rinsed three times with PBS. For cell observation using scanning electron microscopy (Quanta FEI 200, Netherlands), all samples were dehydrated in a graded ethanol series (10, 30, 50, 75, 90, 95, 98 and 100 vol.%). Samples were maintained at 100 vol.% ethanol and critical-point dried. The samples were sputtered with gold before being examined by scanning electron microscopy (SEM).

Statistics

Results are presented as mean value ± standard deviation of four replicates of each sample type. Statistical evaluation was performed by one-way analysis of variance (ANOVA) with a level of statistical significance of $P = 0.05$ (Origin 6.1G, Origin Lab. Corp., USA). All results were normalized to REF (=100%).

5.3 Experimental procedure for producing wollastonite glass-ceramics from fly ash and boron containing wastes

The waste materials are selected to generate low porous glass-ceramic structure respecting SiO_2-Al_2O_3-CaO (wollastonite) glass-ceramic system. Chemical compositions of the used wastes were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES model 3200 XL Perkin Elmer, USA), and are reported in Table 4.2

The phase composition of the starting material and of the studied mixes, after the thermal treatments, was determined by X-ray powder diffraction analysis (Philips PW3830, NL).

The thermal characteristics of the raw materials and compositions were studied with heating microscopy (Expert system solutions-Heating microscope HSM) by adopting the same thermal cycle used for sintering.

It is expected the amounts of Al_2O_3 present in FA and B_2O_3 in BW will provide positive effect on glass structure as glass network former and lower the sintering temperature while CaO has a modifying effect. On the other hand, traces of ZrO and BaO are expected to lower the viscosity. Fe_2O_3 in FA is an intermediate character which can stabilize the glass structure and can generate porosity between 850-950 °C caused by Fe_2O_3 transformation. Ternary system respecting these compositions point a high chemical stability due to the amount of alkalines present in wastes.

In order to meet the required proportions for a wollastonite glass-ceramic system, two compositions were prepared. These compositions are named B and B2. Composition B was consisting of 30 wt % FA, 30 wt % BW and 40% SLG, where B2 was 30 wt % FA, 20 wt % BW and 50% SLG. The reason for decreasing the BW amount in composition B2 was to obtain more closer proportions to the requirements of the wollastonite glass-ceramic ternary system. The weight percentage of the compositions are reported in table 5.3.1.

As in previous studies, the used boron waste is calcined at 500°C. All waste materials used milled below 100μm **(**Retsch PM 100 Germany).

Formulations of the tested mixes* wt%			
B	30	30	40
B2	30	20	50

- *BW is calcined*

Table 5.3.1 The weight percentage of the prepared compositions

Samples' firing was performed up to maximum temperature of 950 and 1050 °C and adopting different heating rates from 5.5 °C/min to 21 °C/min. Half of each compositions was sintered with a holding time of 1 hour while the natural cooling was applied to the other half. Holding time was applied in order to observe the sintering effect, providing better properties in case of ceramics, and to observe the characteristics of the expected crystals, their sizes, and amorphous wt% of the sintered samples.

The samples prepared with composition B without holding time with a heating rate of 21 °C/min. were labeled as FB, same rate with 1 hour of holding time were labeled as FBH and slow sintered samples with a heating rate of 5.5 °C/min. were labeled as BS. Same labeling also applied for composition B2 (FB2,FB2H, FBS), Table 5.3.2 shows the heating rates and sample codes.

The sample FB95 was sintered up to 950°C with a heating rate of 21 °C/min. in order to observe its microstructural characteristics at a relatively lower temperature and, as in previous studies, to examine the effects of fast sintering, an environment friendly technique. The researches at 950°C were suspended after observing poor crystals on SEM results of the sintered samples. Sample BS was sintered with a heating rate of 5.5°C/min., in order to study and compare effects of fast sintering.

Sample	Comp.	Heating rate (°C/min)	Max. Temp. (° C)	Holding Time
FB95	B	21	950	NO
FB	B	21	1050	NO
FBH	B	21	1050	1 hour at 1050
FB2	B2	21	1050	NO
FB2H	B2	21	1050	1 hour at 1050
BS	B	5.5	1050	1 hour at 1050
BS2	B2	5.5	1050	1 hour at 1050

Table 5.3.2 Heating rates and sample codes

References

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[1] A.C. Larson, R.B. Von Dreele, General Structural Analysis System (GSAS), Los Alamos National Laboratory Report, LAUR., (1994) 86-748.

[2] S. Piskin: *Thermal properties of hydrated boron minerals,* Doctoral Dissertation, Istanbul Technical University, (1983)

[3] M.S. Celik, F. Suner: *A thermodynamic analysis of the decrepitation process,* Thermochim Acta, 245 (1995) 167174

[4] Ö. Yildiz, *The effect of heat treatment on colemanite processing: a ceramics application* Powder Technol., 2004 142 7-12.

[5] M.S. Celik, F. Suner: *Thermodynamic Analysis of Decrepitation of Boron Minerals,* Thermochim. Acta, 245 (1995) 167–174.

[6] M.K. Fahad: *Stresses and Failure in the Diametral Compression Test*, J. Mater Sci, 31 (1996) 3723-3729

[7] D'Addetta, G. A., Ramm, E., Diebels, S., Ehlers, W. *A particle center based homogenization strategy for particle assemblies*, Engng. Comp., 21 (2004) 360–383.

Chapter 6

Results and Discussions

6.1 Micro porous glass-ceramics from combination of borate, phosphate and silicate wastes

Colemanite ($CaO.3B_2O_3.5H_2O$), present in BW, is known to decompose with a rapid release of its five molecules of water in the range 450-500 °C, by transforming into a fine particulate material, less than 0.2 mm in size[1]. For this reason, several studies underline that the calcination step of colemanite has an impact similar to that of the milling process[2,3]. In order to exploit this "auto-milling" and promote homogenisation, BW and kaolin clay were used after mixing and calcination at 600°C. From heating microscopy observations it was found that BW began to melt at 880°C. On the contrary, MBM ash did not melt and had no significant change, except for a slight expansion of 1%, in the temperature range of 900-1200 °C.

The XRD analyses of the studied wastes are reported in Fig. 6.1.1. BW (Fig. 6.1.1a) contains, as main crystal phases, colemanite (PDF#74-2336) and calcite ($CaCO_3$) (PDF#05-0586). The presence of minerals similar to colemanite, but having a different CaO/B_2O_3 ratio, such as olshanskyite ($3CaO.2B_2O_3.9H_2O$) (PDF#22-0144)and another calcium borate hydrate ($2CaO.3B_2O_3.5H_2O$,PDF#22-0146), is also probable, mainly considering the peaks at $2\theta \cong 16°$, $2\theta \cong 29°$ and $2\theta \cong 32°$. Traces of saponite $[(Ca,Na)_{0,3}(Mg,Fe^{+2})_3(Si,Al)_4O_{10}(OH)_2\cdot 4(H_2O)]$, gypsum ($CaSO_4\cdot 2H_2O$) and illite $[(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ cannot be excluded, because their peaks overlap with those of the main crystal phases.

MBM ash has a much simpler phase assemblage (see Fig.6.1.1b), consisting of hydroxyapatite ($Ca_5(PO_4)_3(OH)$, (PDF#73-0294) and traces of beta-phase tri-calcium phosphate (β-TCP, $Ca_3(PO_4)_2$), also known as whitlockite (PDF#09-0169).

After the thermal treatment of BW/MBM ash/kaolin clay mixture, the original phase composition changes (see Fig.6.1.1b), owing to calcite decomposition, providing both CaO and CO_2 gas, useful for obtaining porous bodies. Hydroxyapatite, from MBM ash, is still present, but accompanied by a significant amount of anorthite, $CaAl_2Si_2O_8$ ($CaO\cdot Al_2O_3\cdot 2SiO_2$) (PDF#86-1706). The presence of such newly formed phase is consistent with recent observations regarding the thermal behaviour of kaolin minerals when coupled with Ca-rich substances, including Ca-rich glasses[4] as metakaolinite ($Al_2O_3\cdot 2SiO_2$), from kaolin dehydration, interacts with Ca^{2+} ions, forming calcium feldspar (anorthite). The other components are likely involved in the formation of a glassy phase.

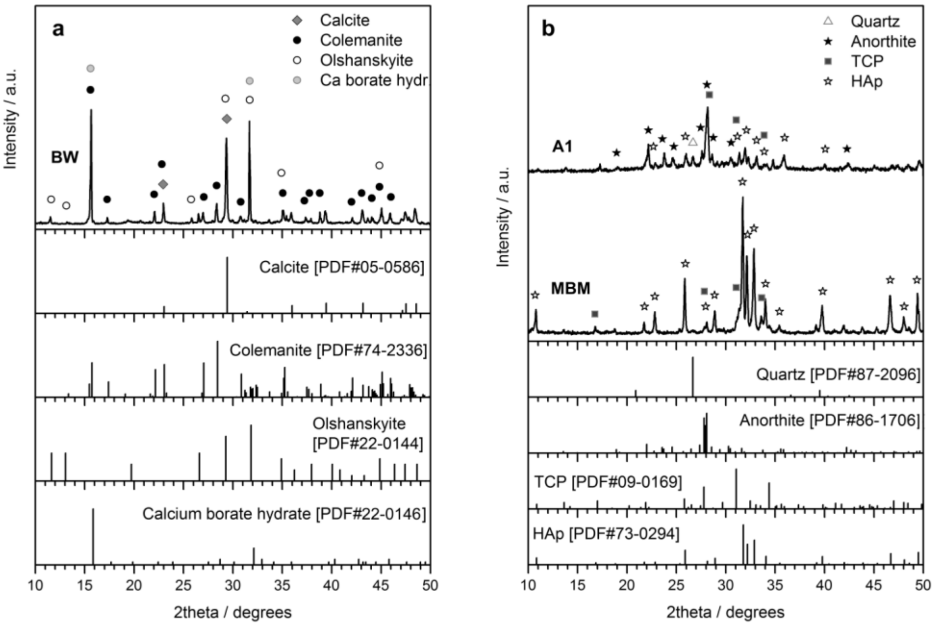


Figure 6.1.1 - X-ray diffraction patterns of the starting wastes and of sample A1 (fired mixture of BW, MBM and kaolin clay).

To better understand the phase reactions, for selected fired samples, quantitative X-ray diffraction analysis were also performed, the results of which are reported in Table 6.1.1

Formulation	A1	B1	B3
Heating rate, °Cmin^{-1}	2	2	20
Crystal phases, wt.%			
Quartz	1.0(1)	0.9(1)	0.2(1)
Anorthite	43.5(3)	44.2(2)	26.6(3)
Hydroxyapatite	7.2(2)	10.5(2)	8.5(2)
Whitlockite	14.1(3)	8.1(3)	7.4(3)
Amorphous phase	34.2(1)	36.3(8)	57.3(9)

Table 6.1.1 - Quantitative X-ray diffraction analysis results of selected samples.

The crystallization of anorthite in samples A1 and B1, subjected to the same heating rate of 2 °C min^{-1}, is similar. The distribution of further phases, however, may be interpreted on the basis of a different origin of CaO, reacting with clay residue to yield anorthite. In fact, CaO may originate: *i)* from the decomposition of calcite, *ii)* from the decomposition of hydroxyapatite into whitlockite ($2Ca_5(PO_4)_3OH \rightarrow 3Ca_3(PO_4)_2+CaO+H_2O$), *iii)* from the glass. The increased content of hydroxyapatite compared to whitlockite, when passing from A1 to B1, is the reasonable effect of the fact that CaO was extracted from the glass rather than by decomposition of hydroxyapatite. Due to the lower content of MBM ash, hydroxyapatite should be present in a lower amount in mix B, compared to mix A. Anorthite formation is greatly conditioned by the heating rate, as testified by the comparison of samples B1 and B3: the slow heating rate of 2 °Cmin^{-1}, used for B1, determined longer times at high temperature, 50 min, for passing from 950 °C, a temperature around which anorthite is reported to precipitate,[5] to 1050 °C. This condition in turn favoured the interdiffusion of ions and crystallisation phenomena.

The basic formulation, Mix A, was originally developed to form ternary B_2O_3-P_2O_5-SiO_2 glasses, yielding particularly porous bodies, i.e. the so-called "gas-ceramics" from Corning Inc.[5].The molar balance among the network formers is very close to the reference glasses, however, the presence of network modifiers, and typically CaO, complicated the achievement of homogeneous foams. The remarkable formation of anorthite greatly increased the apparent viscosity, so that the CO_2 released from the decomposition of calcite, in BW, did not cause a significant expansion.

Fig. 6.2 illustrates some microstructural details of the porous glass-ceramics developed from the selected mixtures of wastes. Mix A, when treated with the slow heating rate of 2 °Cmin^{-1}, led to microporous samples that were not particularly homogeneous (Fig. 6.1.2a). The precipitation of many microcrystals, visible in the high magnification image of Fig. 6.1.2b, justifies such poor homogeneity. The introduction of SLS glass, in Mix B, as illustrated by Fig. 6.1.2c, enhanced the viscous flow, leading to the formation of many pores with a more rounded shape. In any case, due to the slow heating, even in the presence of glass additive, the samples cannot be regarded as "foams", but simply microporous bodies, since the pores are all quite isolated and separated by relatively thick struts. The increase of heating rate, owing to the above discussed effect of limiting the crystallization (mainly of anorthite phase), greatly favoured the development of pores. The porosity increased with increasing glass addition, from A2, (Fig. 6.1.2d) to B2 (Fig. 6.1.2e) and C1 (Fig. 6.1.2f). Samples B2 and C1 were clearly foamed, but again with poor homogeneity. B2, in fact, exhibited great differences in pore size along the thickness, whereas C1 showed quite large struts, in turn featuring many micropores, known to be detrimental to the mechanical properties.**Error! Bookmark not defined.**

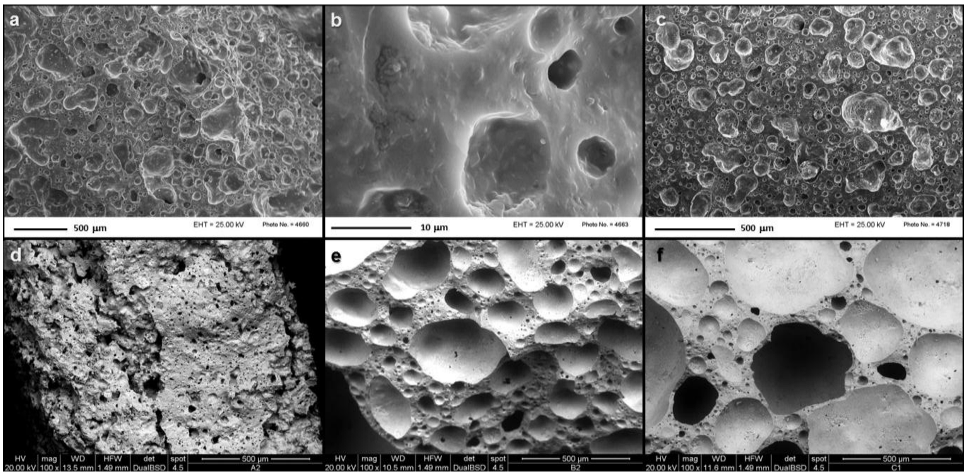


Figure 6.1. 2 - SEM micrographs of fracture surfaces of selected porous glass-ceramic samples: a, b) A1; c) B1; d) A2; e) B2; f) C1.

To improve the foaming process, the application of faster heating rates, typical of the firing of most industrial ceramic products, was tested. The use of a heating rate of 40 °Cmin^{-1} was very disadvantageous, leading to cracked samples (Fig. 6.1.3), for every formulation, from A4 (without glass) to C3 (comprising 20 wt.% glass).

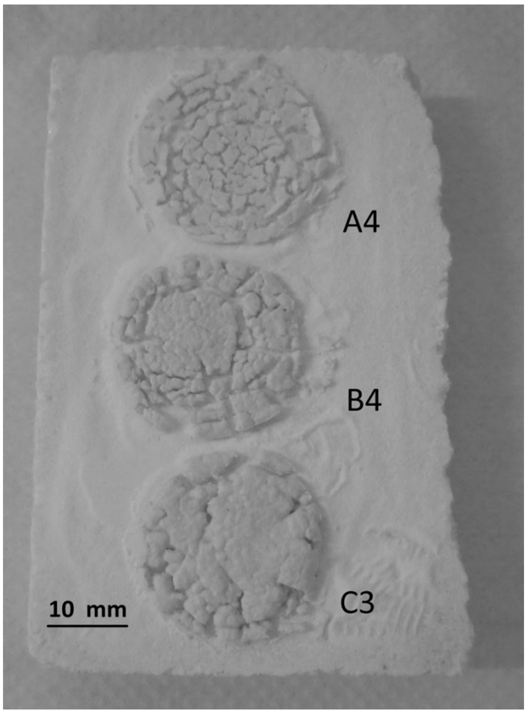


Figure 6.1.3 - Macroscopic appearance of samples A4, B4 and C3 after the thermal treatment with 40 °C min^{-1}heating rate.

A likely reason for this behaviour is represented by non-uniform heating. In fact, very high heating rates determine a temperature gradient from the hotter surface to the centre of the samples, with consequent differential sintering and foaming. The foaming of the internal zone probably occurred slightly after the foaming of the surface, where the pores first developed had enough time to collapse, causing the samples to “explode”. As shown by Fig. 3, sample C3, featuring more glass, appeared more "foamy" and less cracked; this could be interpreted on the basis of a higher ability to accommodate the volume changes associated to the release of CO_2, due to increased viscous phase.

The intermediate heating rate of 20 °Cmin^{-1} was finally used for all the formulations. Samples A3 and B3, with no glass and with limited glass content respectively, were still poorly foamed or inhomogeneous. Sample C2, on the other hand, consisted of a white foam with uniform pore structure: as shown in Fig. 6.1.4a, the struts are thin, exhibiting limited microporosity. As illustrated by the micrograph in Fig. 6.1.4b and by the XRD patterns in Fig. 6.1.5, the foam is still crystalline with anorthite being the main crystal phase and hydroxyapatite and whitlockite being secondary phases. Formulation A yielded more crystallized samples, as demonstrated by the higher intensities of the diffraction peaks in Fig. 6.1.5a. Furthermore, both the formulation A and B were quite stable, in their crystallization, when passing from 10 to 40 °Cmin^{-1} (the quantitative data reported for the heating at 20 °C min^{-1}, in Table 6.1.3, may be considered valid also for the other heating rates). On the other hand, formulation C, characterised by the presence of a larger amount of SLS glass, is more influenced by the heating rate. C3 sample, heated at 40 °C min^{-1}, is characterised by a rather low crystallization, as can be inferred by the height of the peaks in Fig. 6.1.5b, whereas C2 sample, heated at 20 °Cmin^{-1}, was quite similar to samples B2 and B4.

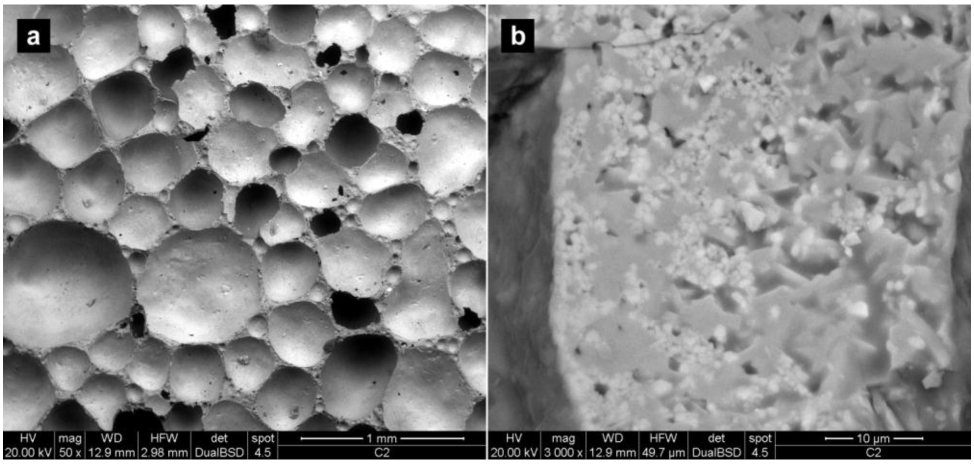


Figure 6.1.4 - SEM micrographs of sample C2, 20 °C min^{-1} heating rate, characterised by optimized foaming, a) surface, b) high magnification detail of a cell strut, evidencing lot of microcrystals.

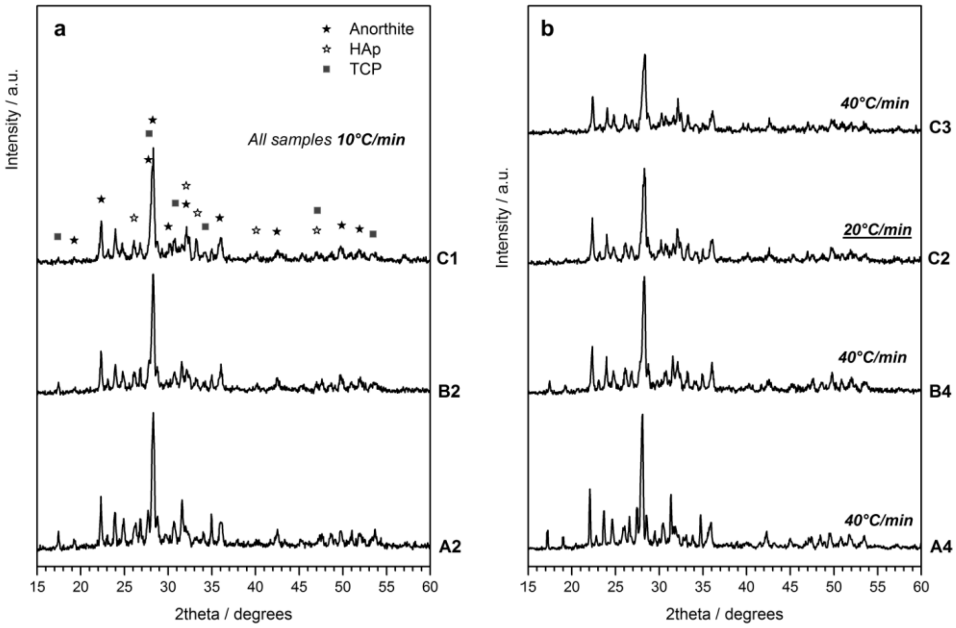


Figure 6.1.5 - X-ray diffraction patterns of the studied glass-ceramics.

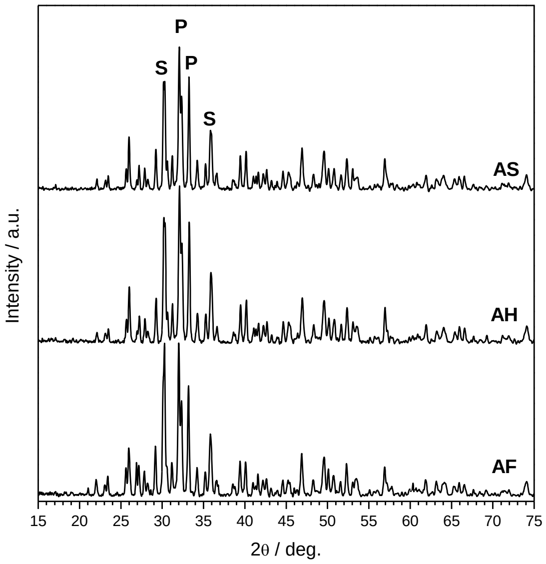
The crushing strength of 1.8 MPa, obtained for the foamed C2 sample, is of the same order of magnitude as most glass foams reported in literature.**Error! Bookmark not defined.** It should be remembered that glass foams are no longer merely used for both thermal and acoustic insulation, in the form of panels, but they are now used also for lightweight concrete manufacturing, in the form of loose aggregates or granules.**Error! Bookmark not defined.** The comparison with microporous A1 sample is interesting in the view of this latest application. A1, due to its superior compressive strength, almost 9 MPa, could be applied in lightweight concrete structures subjected to moderate loads, featuring moderate thermal insulation ability (concretes of this type generally feature aggregates with strength from 7 to 18 MPa). C2 formulation could be useful for actual thermally insulating concrete, to be used as insulating filler or coating (concretes of this type generally comprise aggregates with modest strength and density below 0.8 gcm^{-3})[6]. Cellular glasses have been reported to be less susceptible to the alkali-silica reaction, generally involving aggregates featuring amorphous silica, than monolithic glasses[7]. The materials here presented, being partially crystalline, are thought to be even more chemically resistant; specific determinations of the behaviour of optimised foams in concrete will be the object of future investigations

6.2 Dense glass-ceramic from borate and silica wastes and its cytotoxic characterization

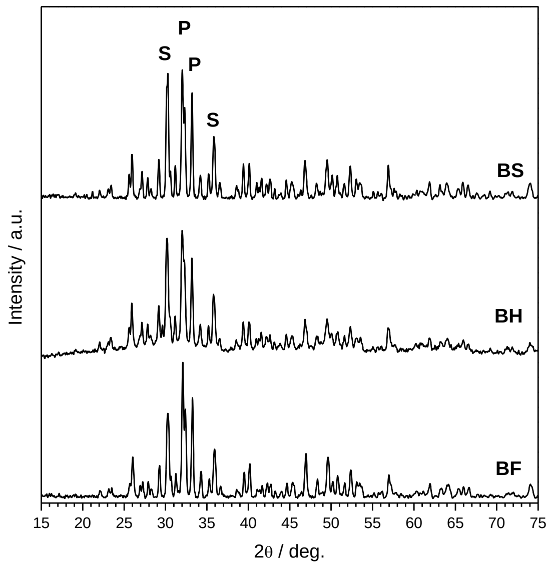
The different amounts of wastes used in the two mixes were chosen to generate the B_2O_3: P_2O_5: SiO_2 ternary system and to meet the rates of the amounts of the system. The aim was to enable controlled crystallization on selected wastes, providing a high chemical durability and strength. The reason for this high chemical durability should be assured by the presence of SiO_2 glass matrix in glass-ceramic structure which protects the crystals from chemical reactions.

The XRD patterns of the mixtures after firing, in different conditions, are reported in Fig. 6.2.1. The crystallinity of the samples, owing to the almost flat background and the number of peaks, is reputed to be substantial. As a general trend, the main peaks can be grouped into two groups, labelled as “S” and “P” in both Fig.6.2.1a and 6.2.1b. The “P” peaks are almost constant, in terms of intensity, whereas “S” peaks are quite variable. For A samples, shown in Fig. 6.2.1a, “S” peaks decrease when passing from fast treatment (AF, 950 °C for 1 min, after rapid heating) to slow treatment (AS, 950 °C for 3 h, after slow heating). Interestingly, for B samples, shown in Fig.6.2.1b, “S” peaks exhibit an opposite trend. Finally, the most crystallized samples for the two formulations, as testified by Fig.6.2.1c, are very similar.

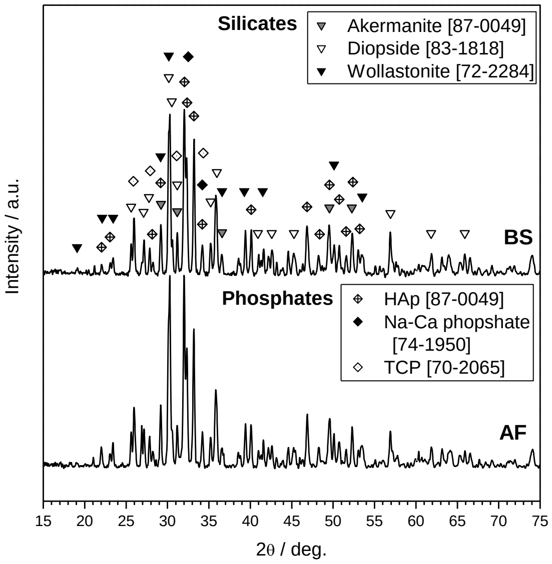
Fig.6.2.1c shows that the two groups of main peaks are attributable to two distinct types of compounds. While "S" peaks are due to the contribution of silicate phases, such as diopside ($CaMgSi_2O_6$, PDF#83-1818) and wollastonite (β-$CaSiO_3$, PDF#72-2284), "P" peaks are due to hydroxyapatite (HAp, PDF#86-0740). Also minor peaks are associated to a combination of silicates, such as akermanite ($Ca_2MgSi_2O_7$, PDF#87-0049), and phosphates, such as tricalcium phosphate ($Ca_3(PO_3)_2$, PDF#70-2065) and Na-Ca phosphate ($NaCaPO_3$, PDF#74-1950). Phosphates represent unreacted phases, being already present in MBM waste; the absence of practical variations, comparing A and B samples, is consistent with the fact that the two formulations comprise the same amount of MBM. The different balance, in A and B formulations, among BW and soda-lime glass, has an impact on the crystallization of silicates. A higher content of soda-lime glass (samples A) promotes a substantial crystallization in short firing times, likely attributable to interaction between glass and CaO and MgO oxides from BW; longer firing treatments evidently favour some dissolution of the silicates, operated by secondary components of the same BW. On the contrary, a lower content of soda-lime glass (samples B) promotes a progressive crystallization.



(a)



(b)



(c)

Figure 6.2.1 Diffraction pattern of samples from MBM/BW/soda-lime glass mixtures: a) A samples; b) B samples; c) comparison among most crystallized samples and phase identification.

Optical analyses performed with light microscope. In these analyses differently from samples sintered up to 950 °C, samples sintered up to 1050 °C indicated a foamy structure with closed pores with smooth, glassy surface. The reason for this might be the melting temperature of colemanite 950-1050 °C and the difference in dimension with viscosity of matrices.

Figures shown below represent light microscope images of sintered samples;

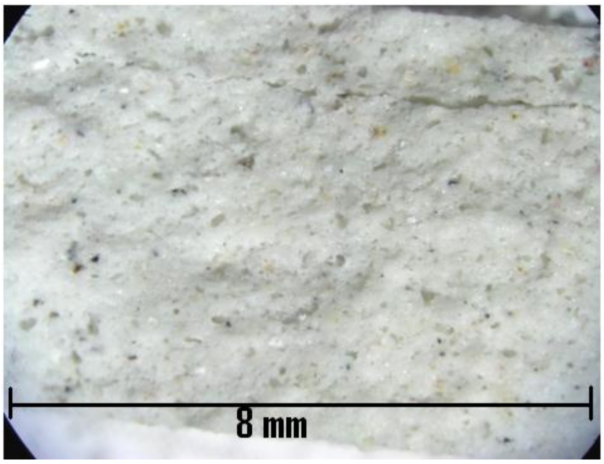


Figure 6.2.2 - Light microscope image of AF

Figure 6.2.2 represents the light microscopy image of sample AF which was milled under 150 µm. As an effect of mentioned particle size, brown points derived from SLG can be observed. The crack on the upside of image is probably caused by pressing conditions.

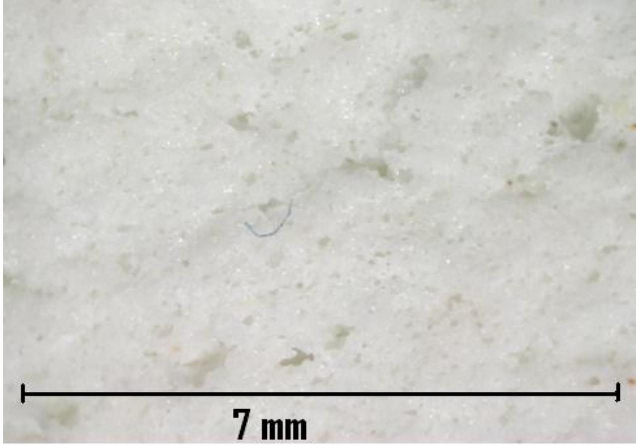


Figure 6.2.3 - Light microscope image of AH

Figure 6.2.3 represents the light microscopy image of sample AH. Differently from sample AF, AH was milled under 100 µm like the following samples. As an effect of mentioned milling, impurities in brown color disappeared. Due to 1 hour of holding time more porous structure were observed. The pores are mostly shapeless and dimensions ranging between 0.3 and 0.8 mm.

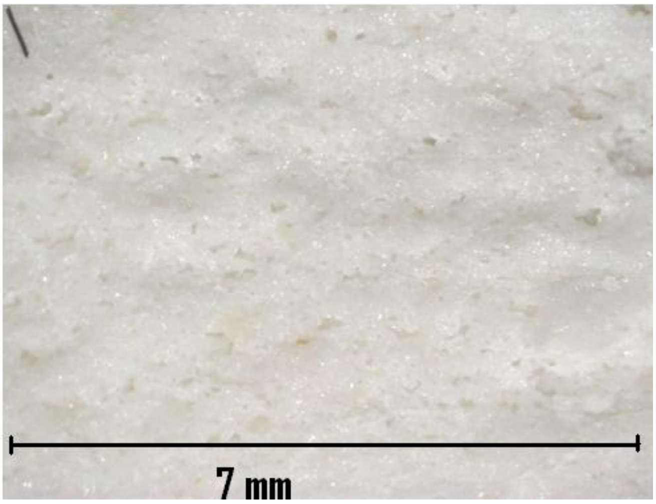


Figure 6.2.4 - Light microscope image of AS

Figure 6.2.4 represents the light microscopy image of sample AS. As an effect of slow sintering, low porosity and shapeless pores ranging between 0.1 and 0.9 mm can be observed.

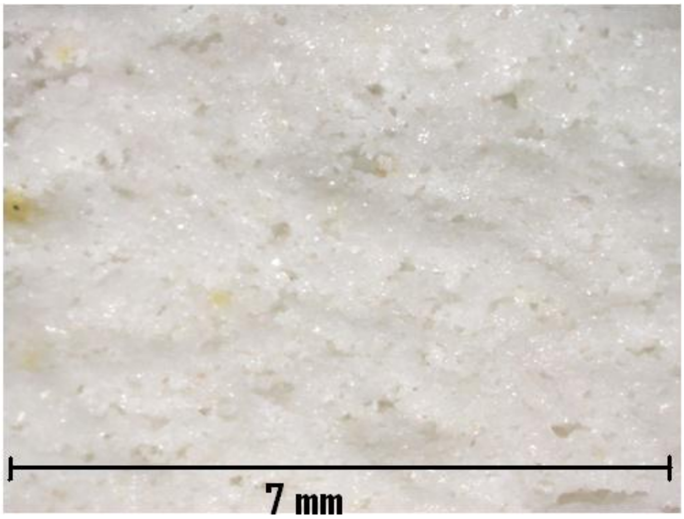


Figure 6.2.5 - Light microscope image of BF

Figure 6.2.5 represents the light microscopy image of sample BF. Differently from AF more porosity ranging between 0.6 and 0.1 can be observed. The brown point on the left side of image is again trace from SLG.

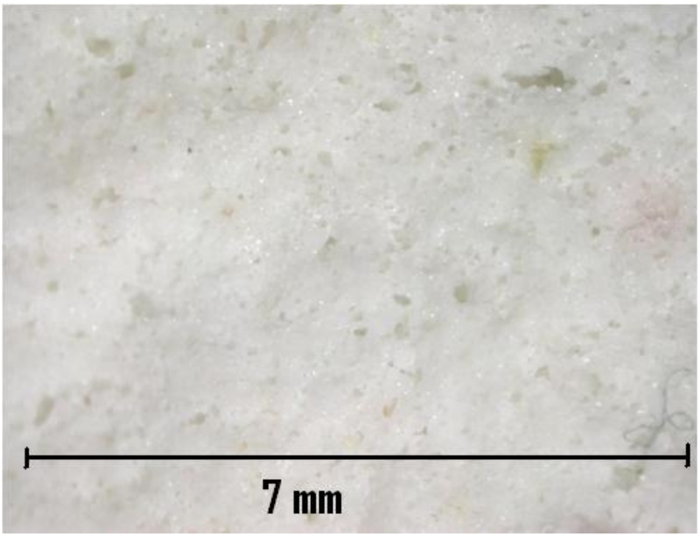


Figure 6.2.6 - Light microscope image of BH

Figure 6.2.6 represents the light microscopy image of sample BH. As an effect of one hour holding time, a porous structure like sample AH with shapeless pores ranging between 0.1 and 0.08 mm can be observed.

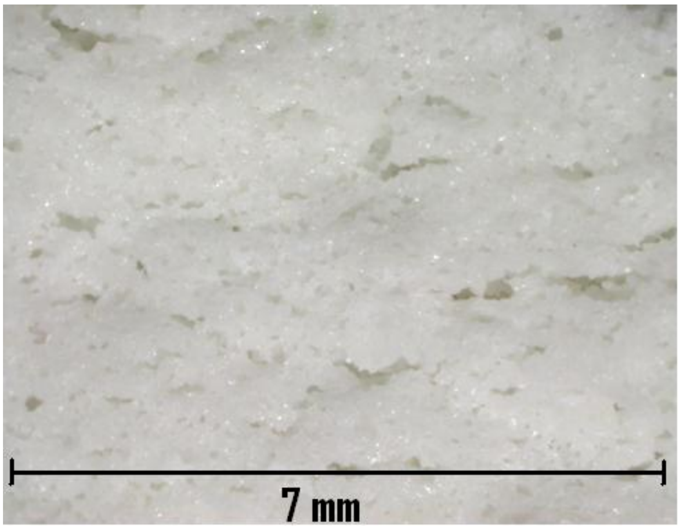
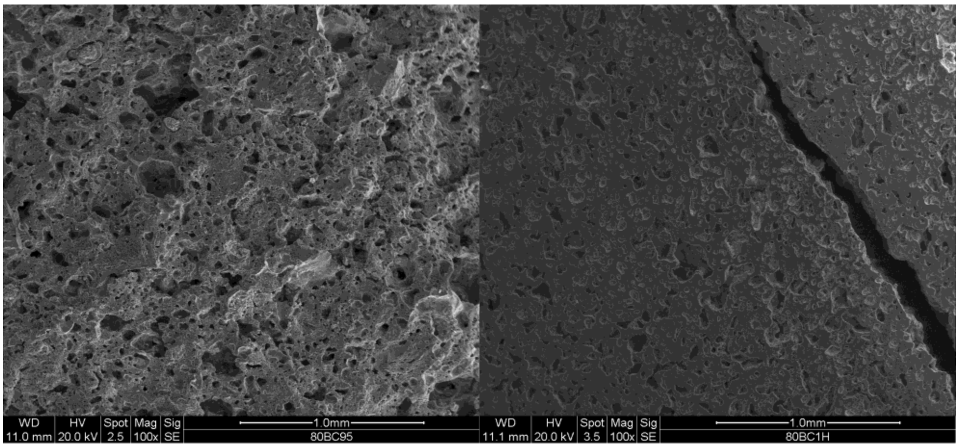


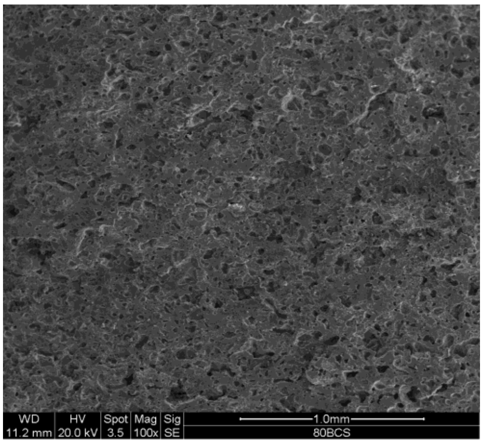
Figure 6.2.7 - Light microscope image of BS

Figure 6.2.7 represents the light microscopy image of sample BS. Compared to the other slow sintered sample AS, in BS more porosity (like cracks) can be observed with dimensions ranging between 0.1 and 0.9 mm.

For the mix A samples, the density values increase with the soaking time at 950 °C (Table 2) as a result of progressive crystallization. SEM observations (Fig. 6.2.8) point out as sample AF presents a higher porosity, in comparison with AH and AS, characterized by a larger range of pore sizes. In addition, while for AH and AS the pores are usually rather round, the short soaking time adopted for AF samples did not allow to develop an amount of low viscosity liquid phase able to create spherical pores. In all samples, during sintering between 400-450 °C, calcite (a foaming agent) in BW turns into wollastonite, $CaSiO_3$, together with SiO_2 carried from SLS. As a result, the decomposition of calcite in the temperature range of 750-900 °C can not take place; CO_2 release in a more viscous phase is prevented, and this can lead up to a high porous or foamy structure.

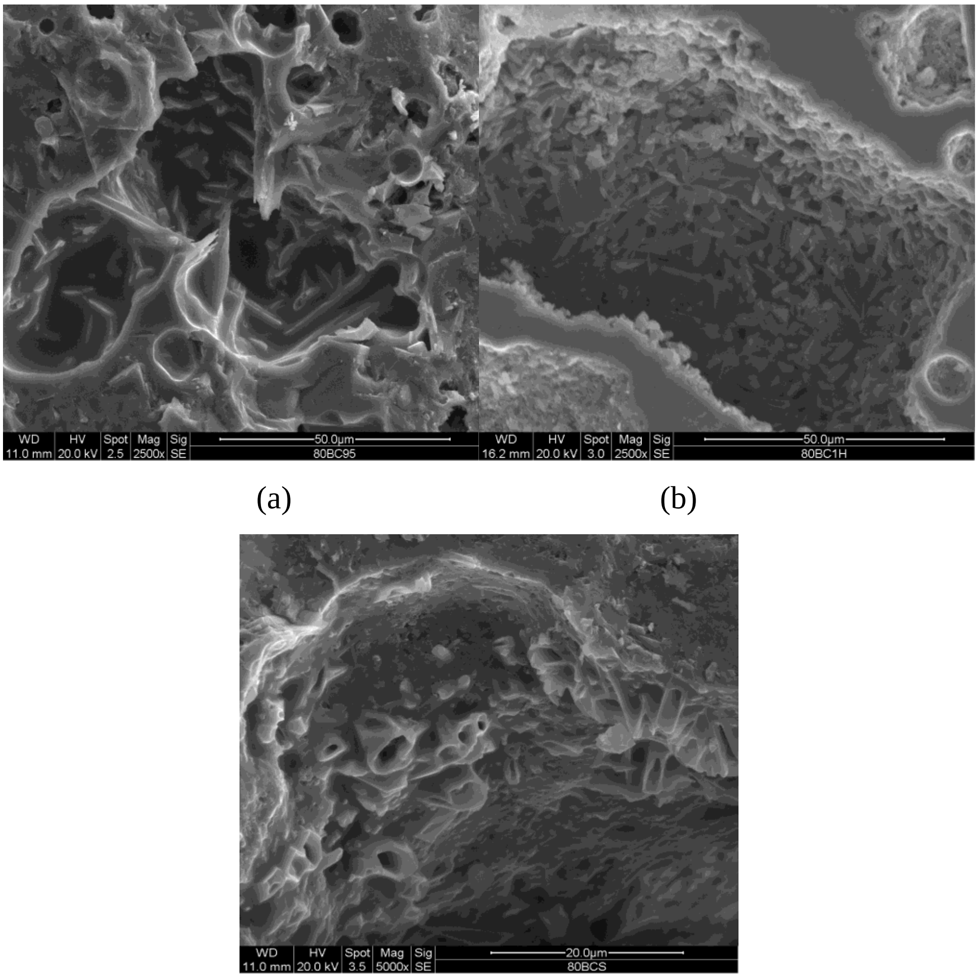


(a) (b)



(c)

Figure. 6.2.8 - SEM micrographs of a) AF, b) AH and c) AS samples.



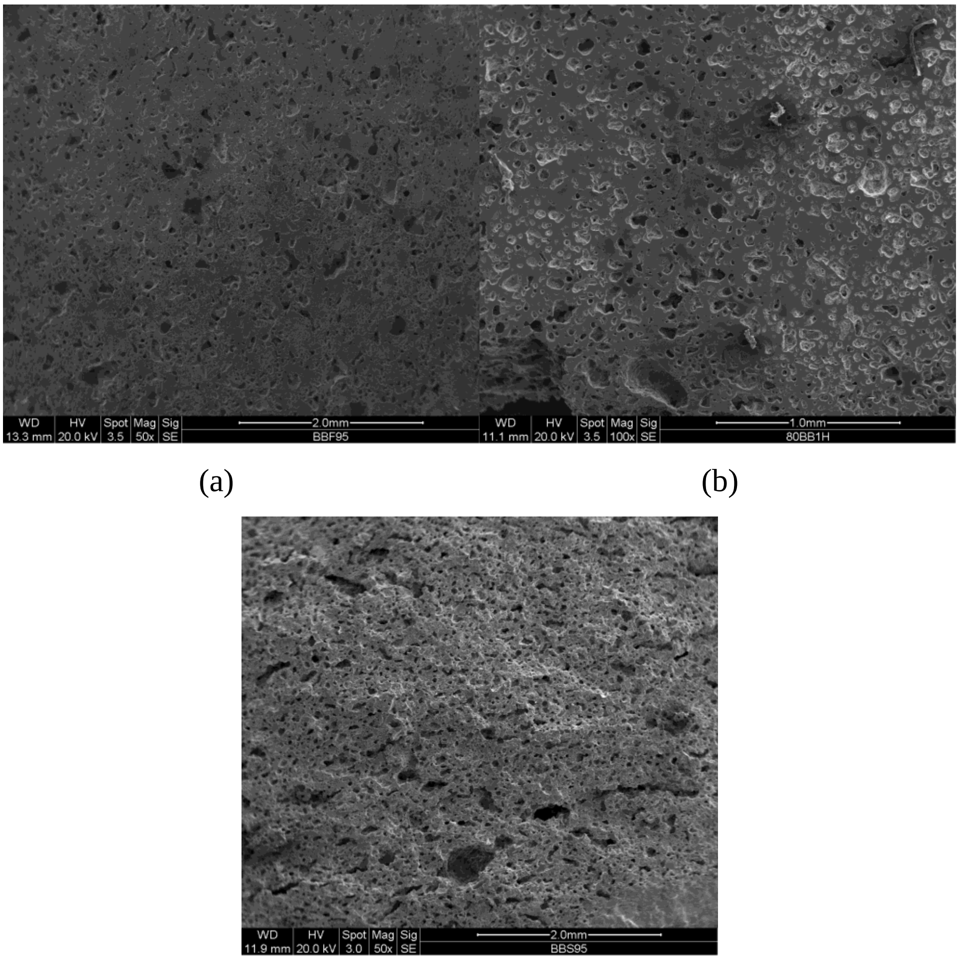
(a) (b)

(c)

Fig. 6.2.9 - SEM micrographs of a) AF, b) AH and c) AS samples

For all the three thermal cycles, as reported by the XRD results, a rather high crystallization is observed (Fig. 6.2.9). It is interesting to note as, for AF, elongated tubular crystals of wollastonite are observed, that are very probably responsible of the found increased mechanical properties.

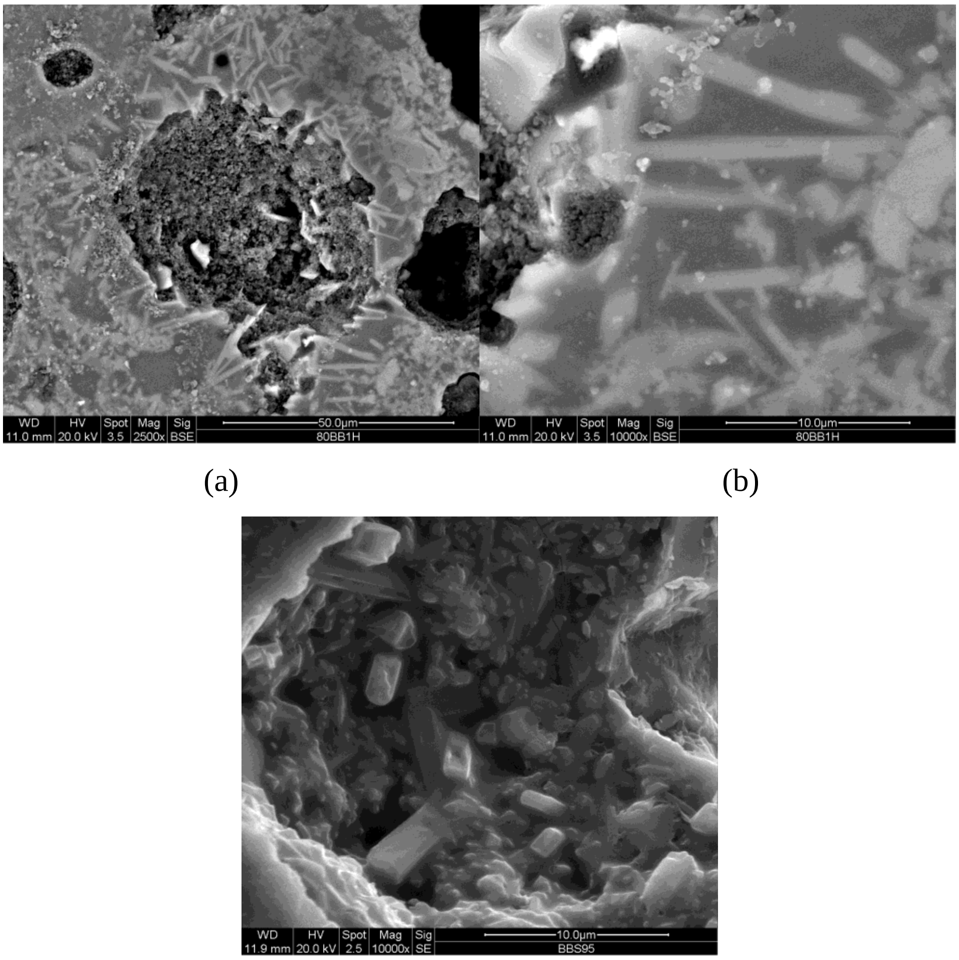
For the mix B samples, the density values slowly decrease with the soaking time at 950 °C (Table 2). While no large differences in terms of porosity, essentially closed pores, are observed between BF and BH samples (Fig. 6.2.10a and b), the microstructure of sample BS (Fig.6.2.10c) is characterized by a diffuse and large interconnected porosity.



(a) (b)

(c)

Figure 6.2.10 - SEM micrographs of a) BF, b) BH and c) BS samples



(a) (b)

(c)

Figure 6.2.11 - SEM micrographs of a) polished surface of BH, b) particular of a) and c) particular of the inside of a pore in BS sample.

Backscattered SEM images of polished surface of BH are shown in figure 6.2.11a and b. A homogeneous distribution of wollastonite crystals was found together with diopside crystals, mainly located inside the pores, as observed in Fig. 6.2.11c.

The tensile strength of sintered samples was ranging between 7.88 to 18.40 MPa, mechanical properties of the studied samples values in agreement with other studies[891011]. Differently from BF, the fast sintered sample AF possessed more crystals. Owing to these crystals, the tensile strength of AF was measured 18 MPa with a density of 1.76g/cm^3, whereas BF was 7.88 MPa with a density of 2.0476 g/cm^3. AB and AH, sintered with the same holding time, were quite similar, in their crystallization. The measured tensile strength of AH, 12.98 MPa, is lower than BH with 14.37 MPa of strength. The densities of AH and

BH were 1.97 g/cm^3 and 2.02 g/cm^3 similar to each other. On the other hand, S labelled (i.e. characterised by the slow sintering) samples, AS and BS, exhibited a relatively high strength as a result of long sintering time. The tensile strength of AS was 14.02 MPa with 2.07 g/cm^3 density, while BS was 15.00 MPa with a density of 1.96 g/cm^3.

Figures 6.2.12 and 6.2.17 represent 2 dimensional surface images of the sample BH and sintered SLG. With the support of the related analyses reported in figures 6.2.16-21, it has been seen, in BH, that pores were ranging between 10 µm to 25 µm, with an average depth of 2 µm, while in SLG they ranged from 10 µm to 50 µm with an average depth of 2 µm, meeting the required standards of surface structure for cell feeding.

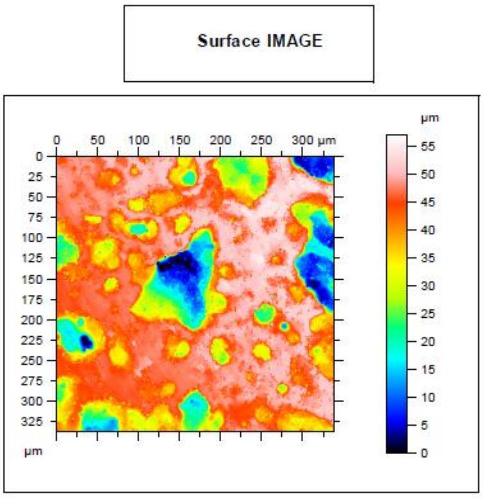


Figure 6.2.12 - 2D surface image of the sample BH

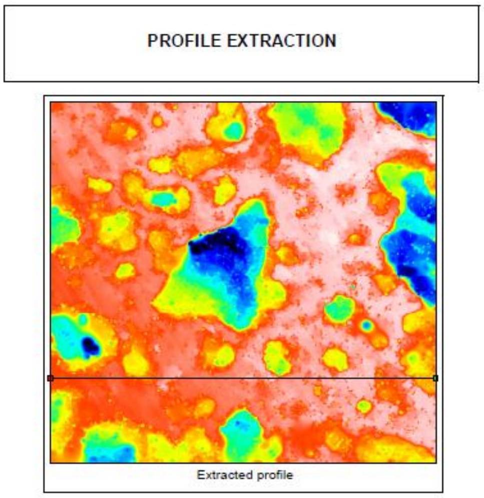
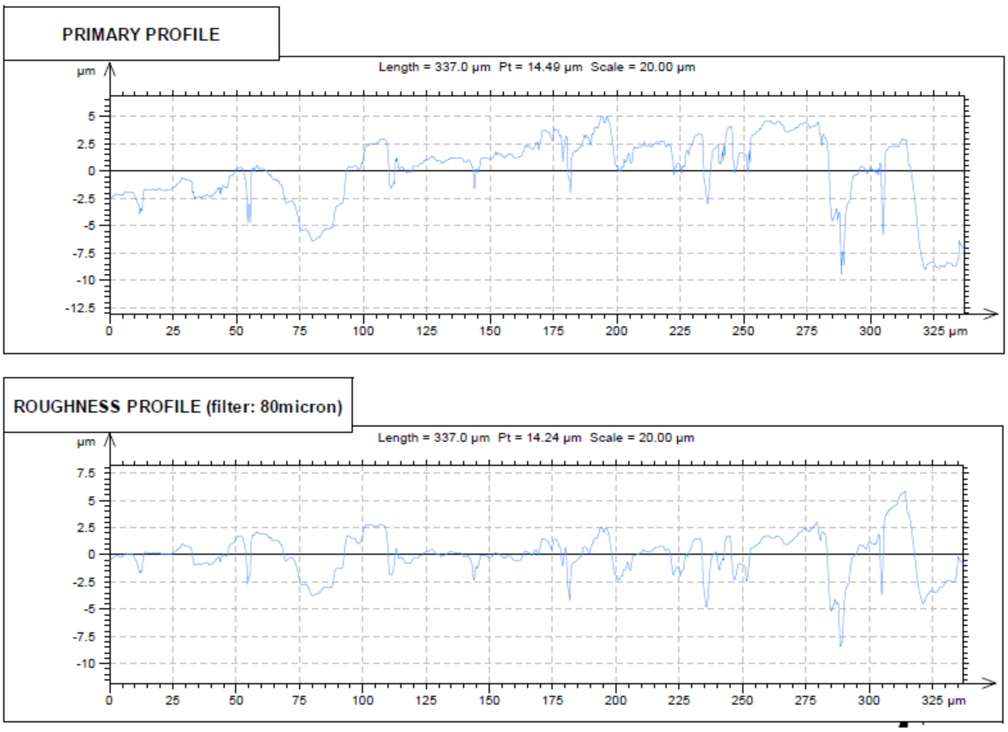


Figure 6.2.13 - Extracted 2D profile sample BH



6.2.14 - Primary profile and roughness profile (with 80 mm filter) of the sample BH

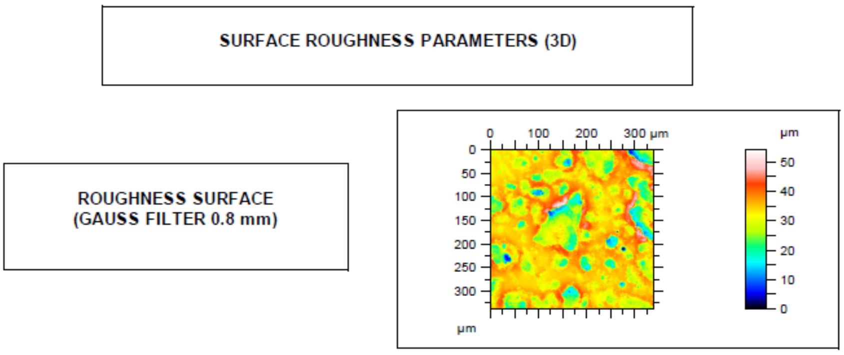


Figure 6.2.15 - 3D surface roughness parameters of BH with gauss filter

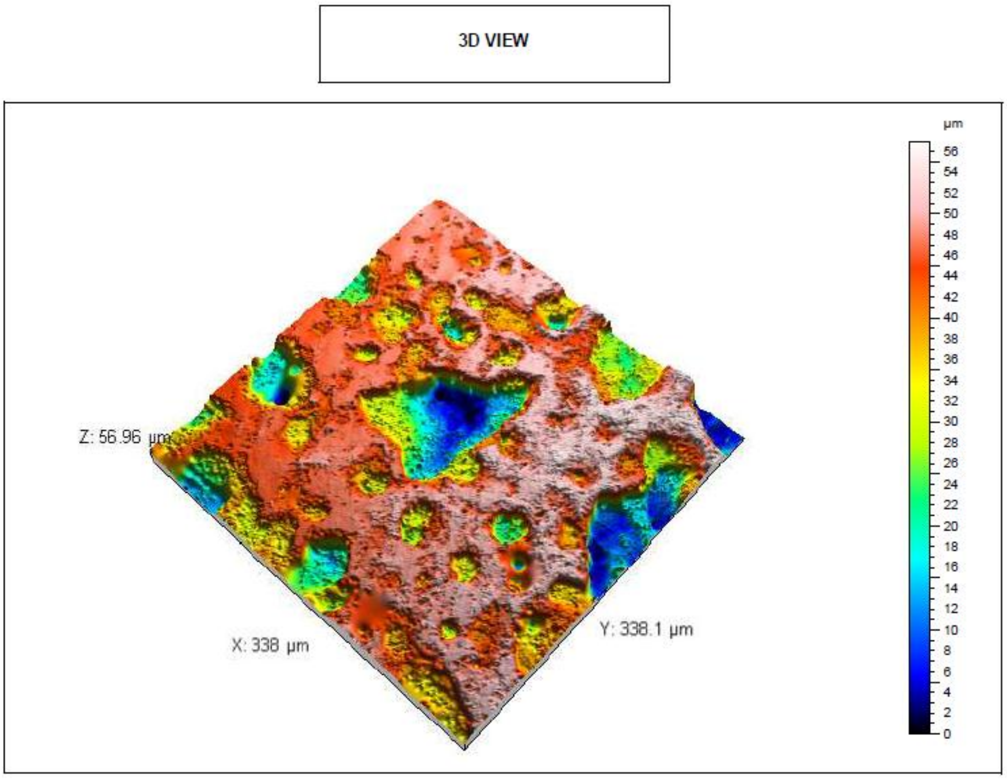


Figure 6.2.16 - 3D surface image of sample BH

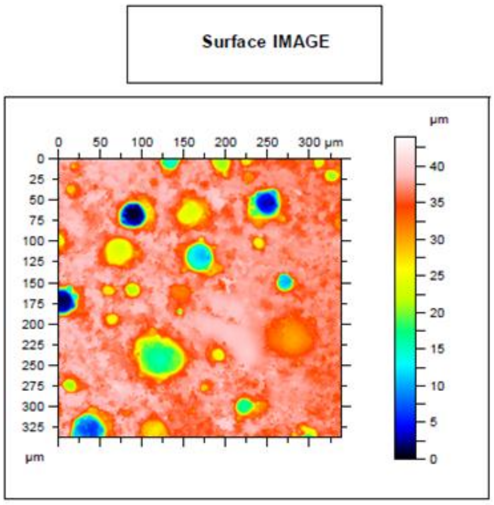


Figure 6.2.17 - 2D surface image of sintered SLG

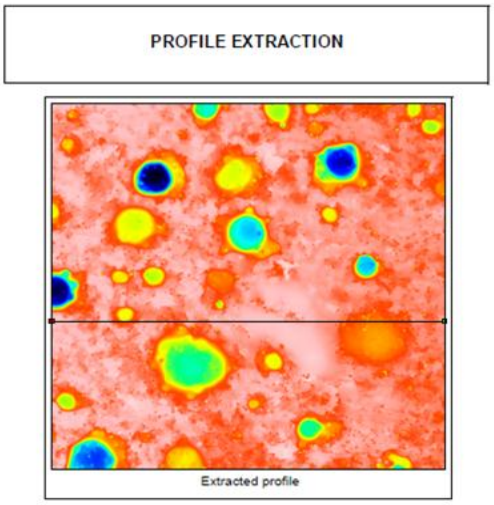
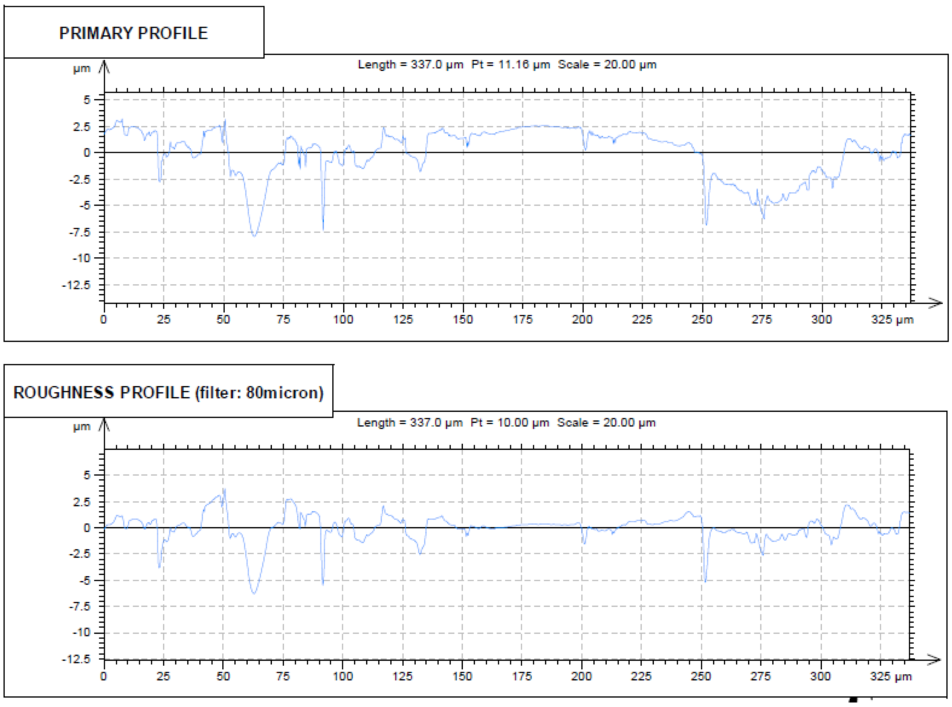


Figure 6.2.18 Extracted 2D profile of sintered SLG



6.2.19 - Primary profile and roughness profile (with 80 mm filter) of the sintered SLG

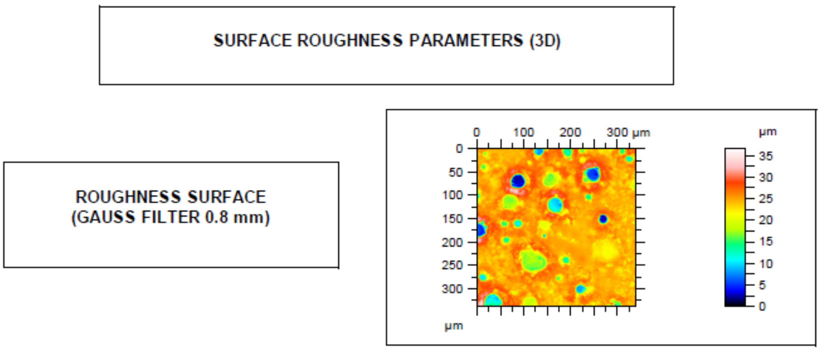


Figure 6.2.20 - 3D surface roughness parameters of sintered SLG with gauss filter

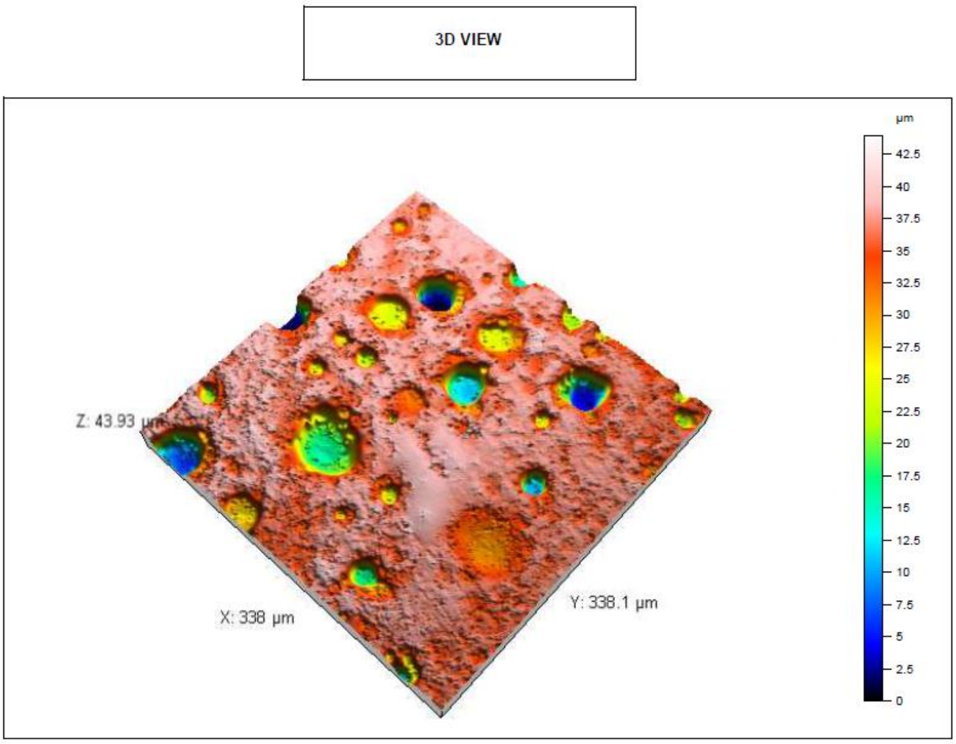


Figure 6.2.21 - 3D surface image of sample SLG

Cell proliferation & cell viability

In Figure 6.2.22 cell proliferation of MEF cells after 24 hours on SLG, BH and REF materials is shown. On both tested materials significant less cells are gown, compared to the REF. Furthermore, cell viability of MEF cells is reduced though the SLG material and cells attached on BH surface got no vitality. While the SLG materials caused any major cytotoxic effect, BH can be classified as a cytotoxic material.

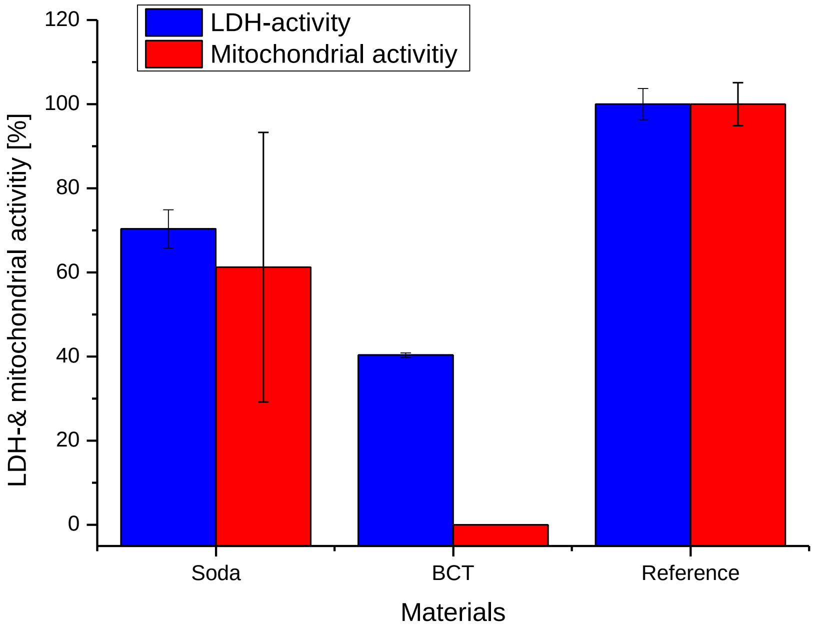
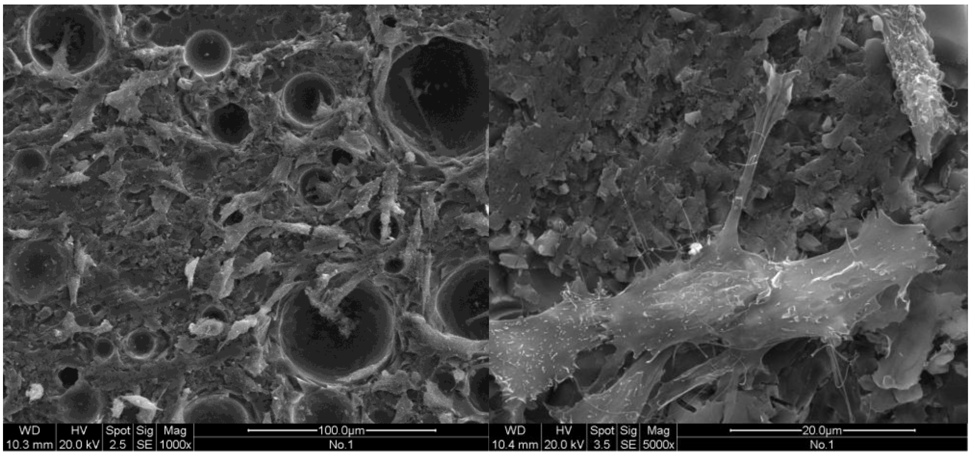


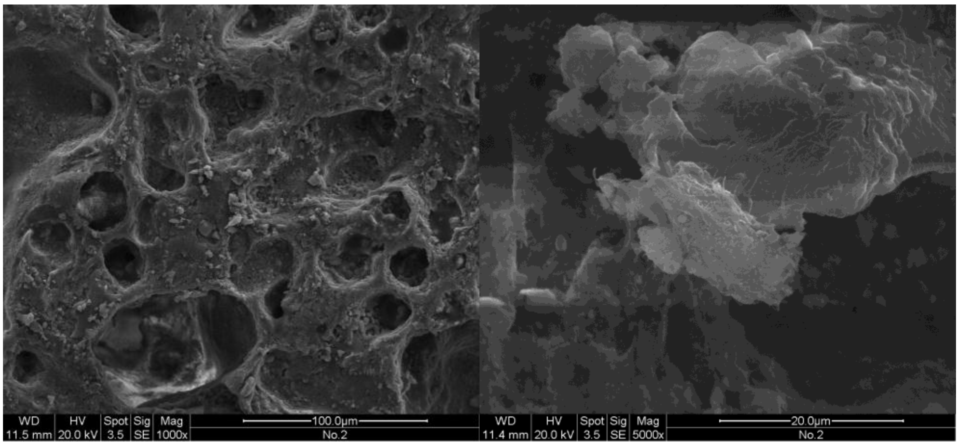
Figure 6.2.22: Results of cell proliferation analysis: LDH- and mitochondrial activity of MEF cells cultured on SLG, BH and REF materials over 24 hours.

Analysis of the cell morphologies (Fig. 6.2.23-26) support the measurements shown in related SEM images. MEF cells are homogenous distributed on the SLG surface. Nevertheless, MEFs grown on the reference showed a more structured cell membrane than the cells on SLG. Cells are well attached and got a fibroblastic phenotype. On BH only few cells attached, the cell morphology is mostly a globular form with no membrane structures (SEM-image Fig. 6.2.26), which indicated the highly toxic effect of this material.



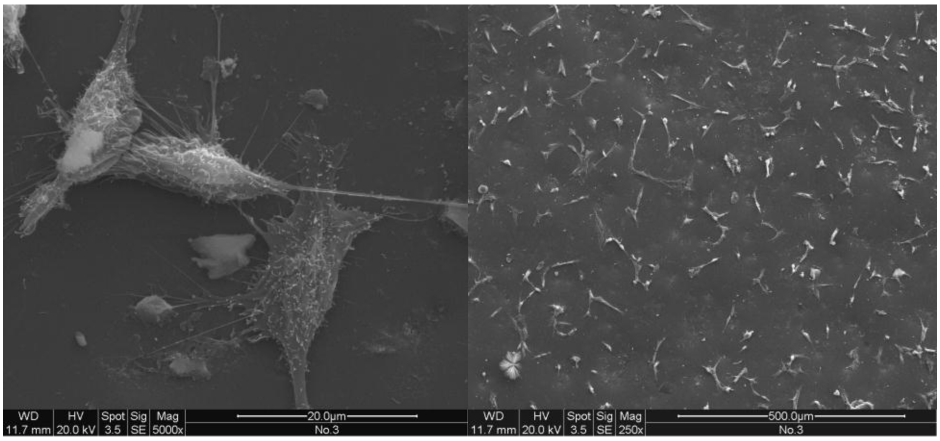
(a) (b)

Fig. 6.2.23: SEM-images of MEF cells grown on SLG after 24 hours, a) low magnification, b) high magnification



(a) (b)

Figure 6.2.24 SEM-images of MEF cells grown on sample BH after 24 hours, a) low magnification, b) high magnification



(a) (b)

Figure 6.2.25 SEM-images of MEF cells grown on reference sample (REF) after 24 hours, a) low magnification, b) high magnification

Figure 6.2.26 Cell morphology on sample BH

6.3. Wollastonite glass-ceramics from fly ash borate wastes

The samples prepared with composition B without holding time are named FB, with 1 hour of holding time were FBH, same coding applied also for composition B2

The sample FB95 sintered up to 950°C with a heating rate of 19°C/min in order to observe its microstructural characteristics at a relatively lower temperature.

In heating microscopy analyses it has seen the earliest reacting material was SLS with a 30% change in volume between 650 and 850°C, where borate waste began to melt around 880°C. As being a residue from power plants FA did not give any reaction till 1250°C except 1-2% volume change. The heating microscopy results of the raw materials and the prepared compositions are reported in figure 6.3.1.

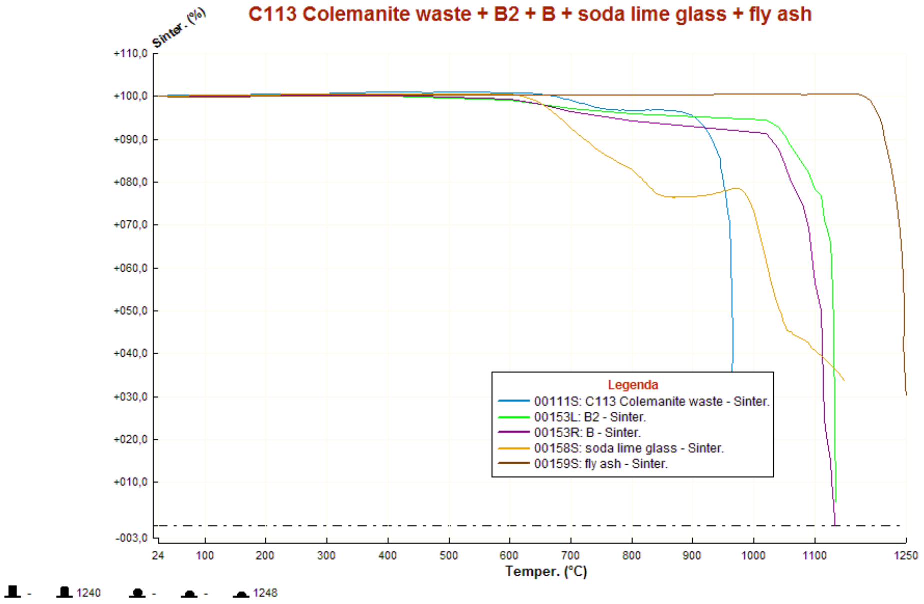


Figure 6.3.1 The heating microscopy results of the raw materials and the prepared compositions

XRD results of all examined samples exhibited similar results which wollastonite (PDF#43-1460) and diopside (PDF#41- 1370 were main phases. In sample FB95 due to the low temperature sintering process, formation between 950-1050°C causing sintering in liquid phase did not take place as in the other samples, therefore traces of Albite (PDF#9-466)and Crystoballite (PDF#39-1425) came forward to low intensities of the main phases.

Figure 6.3.2 shows low magnification SEM image of sample FB95, a homogenous porosity can be seen easily. Colemanite and SLG existing in compositions begin to melt around 920°C, the short sintering time applied to sample FB95, sintering ended up with a liquid phase together with occurrence of little crystals attributed to wollastanite and diopside. As an aim of the study, in order to promote size of the crystals in a positive way and provide a glass phase with the existed silicates, samples sintered up to 1050°C.

The low magnification images of sample FB (Figure 6.3.3) is similar to the sample FB95,in addition pore sşze on the surface of the sample are larger than the pore sizes of FB95. The FB2 sample (Fig. 6.3.4) with 50 wt % of SLG exhibited higher porosity due to the gas release in its softening point and higher amount of crystallization supported by Xrd results report in Figure 6.3.12.

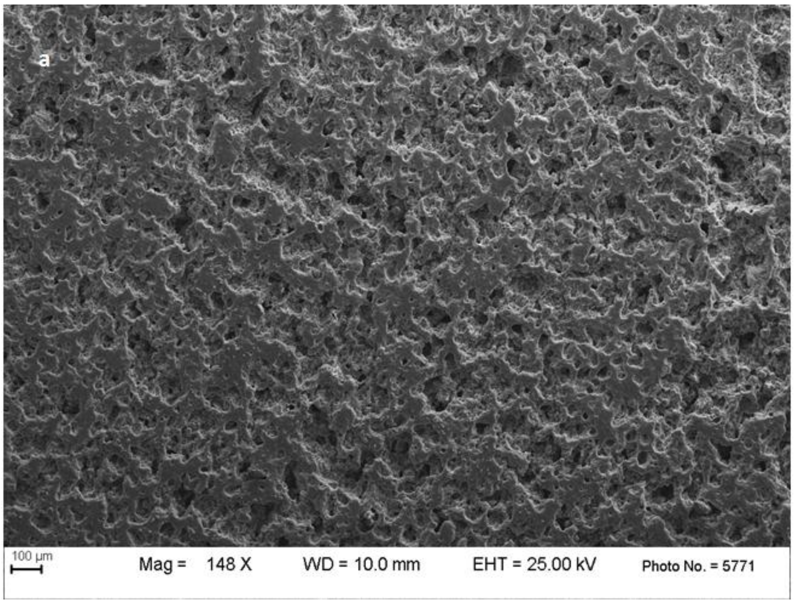


Figure 6.3.2 – Low magnification SEM image of FB95

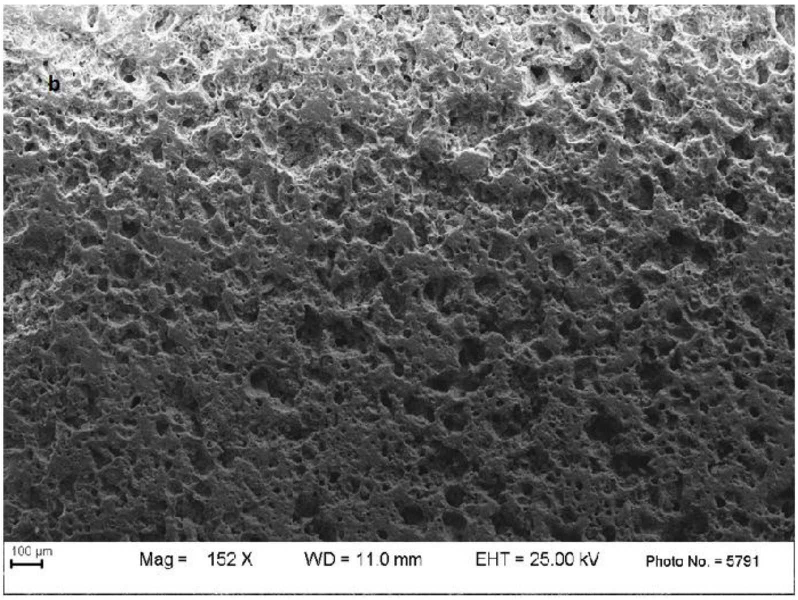


Figure 6.3.3 – Low magnification SEM image of FB

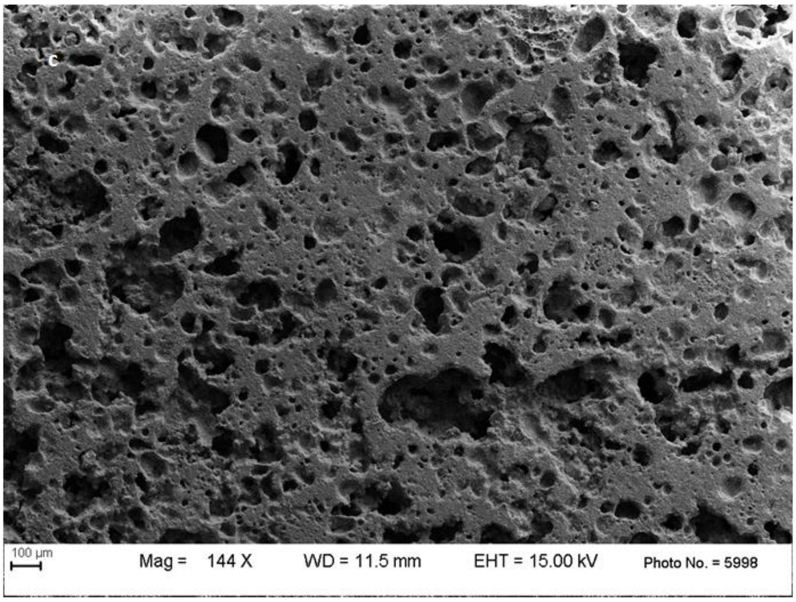


Figure 6.3.4 – Low magnification SEM image of FB2

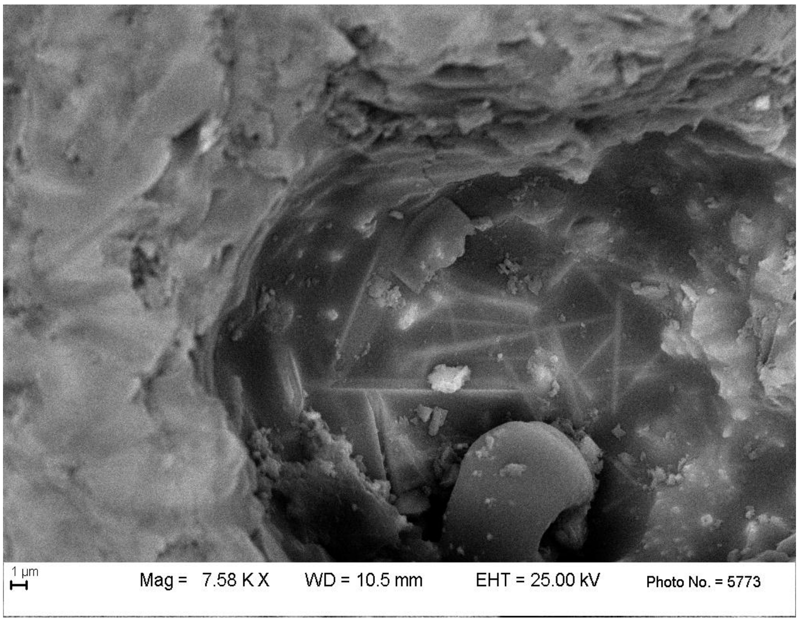


Figure 6.3.5 High magnification SEM image of FB95

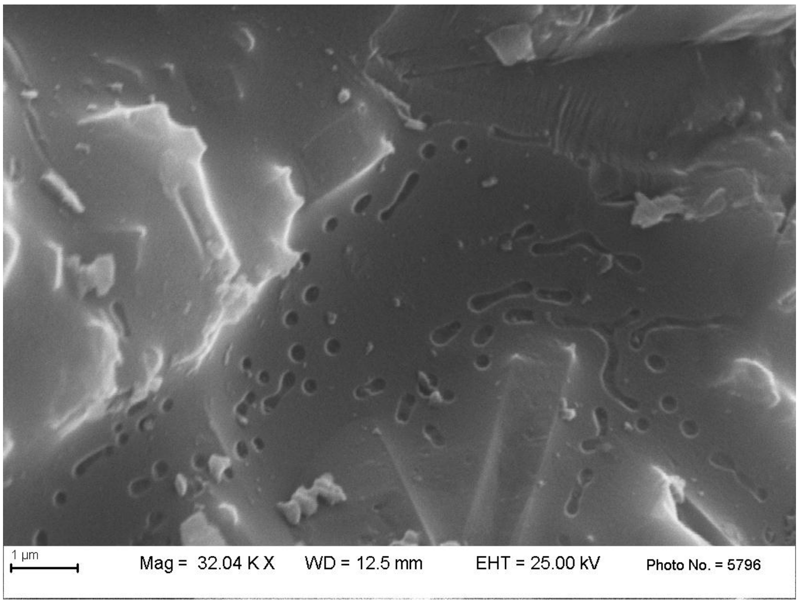


Figure 6.3.6 High magnification SEM image of FB

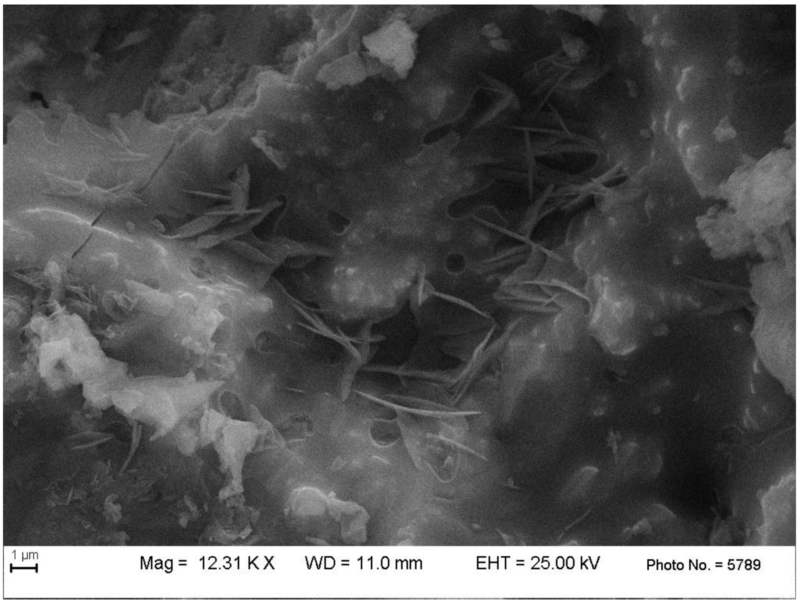


Figure 6.3.7 High magnification SEM image of FB

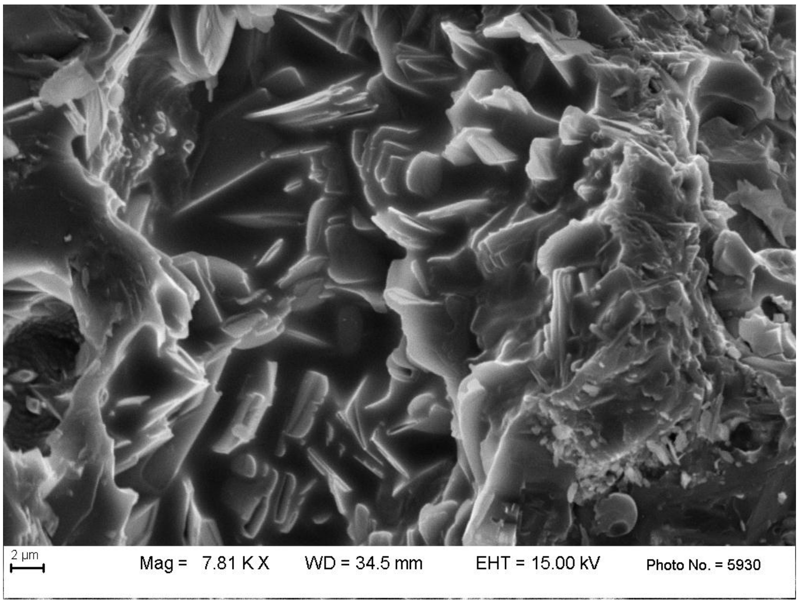
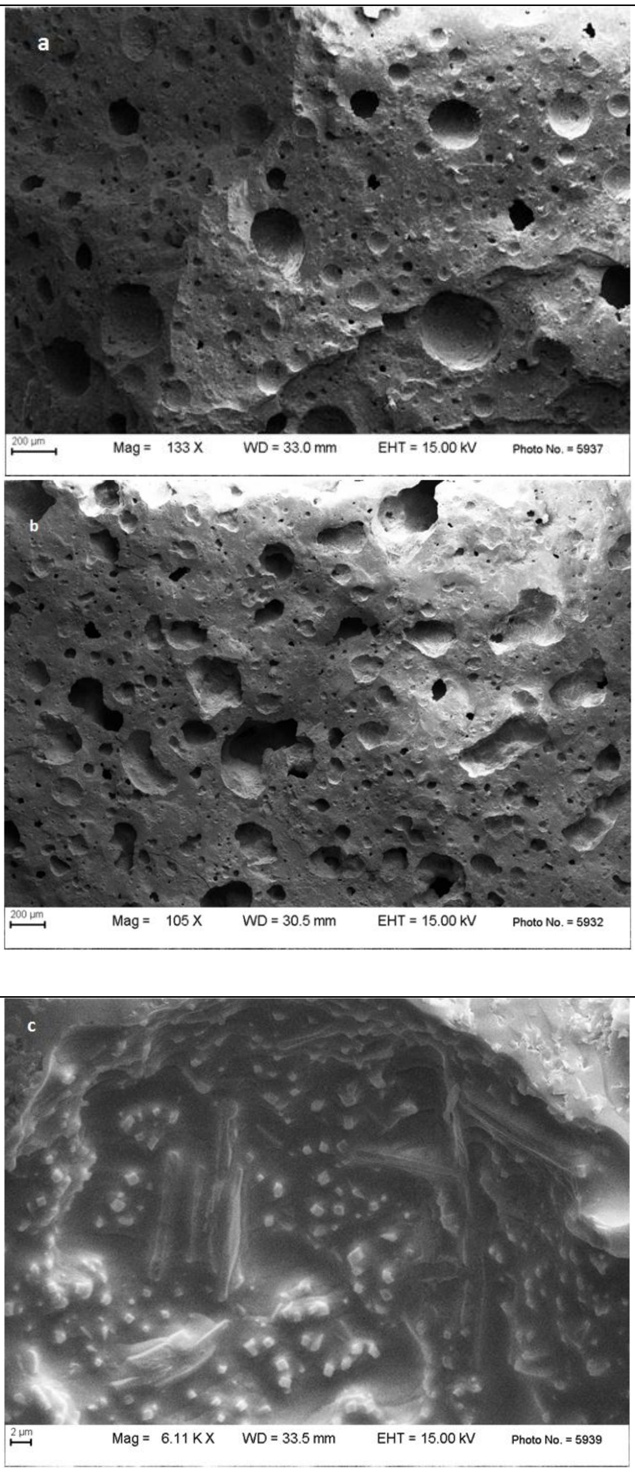


Figure 6.3.8 High magnification SEM image of FB2 (calcium aliminium silicate)

In low magnification images of sample FB95 (Fig. 6.3.5) relatively small crystals can be seen easily. In sample FB (Fig. 6.3.6) glass phase with presence of diopside crystals (supported with EDS) and high amount of related crystals

(Fig. 6.3.7) expected to be wollastonite 2M exhibits an expected glass ceramic structure.



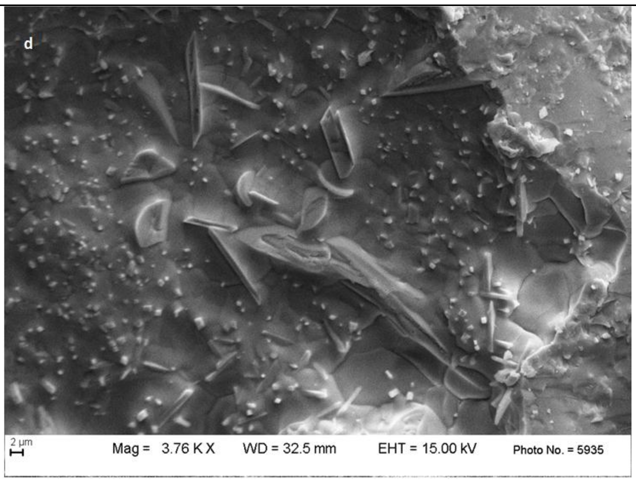


Figure 6.3.9 High and low Magnification SEM image of a)FBH b)FBH2 c)FBH d)FBH2

The samples sintered with a holding time exhibits crystals merged into glass structure with a porosity caused by primarily investigated reactions which can be seen in figure 6.3.9.

The Xrd patterns of the sintered waste compositions, in different heating rates are reported in figures 6.3.10 to 6.3.14.

The sintered samples exhibit very similar results. The main reason for these results is; the similarly prepared compositions containing amounts close in each other in order to meet the required proportion of the wollastonite glass-ceramic ternary system. Due to the many overlapping in the patterns, manual identification applied. The silicate phases; Wollastonite ($CaSiO_3$ PDF#43-1460) and Diopside ($CaMgSi_2O_6$ PDF#43-1370) are the main phases followed by quartz (SiO2 PDF# 461045) traces. In shown figures wollastonite and diopside phases are represented as their capital letters “W” and “D”. In some cases both phases are appearing in the same peak.

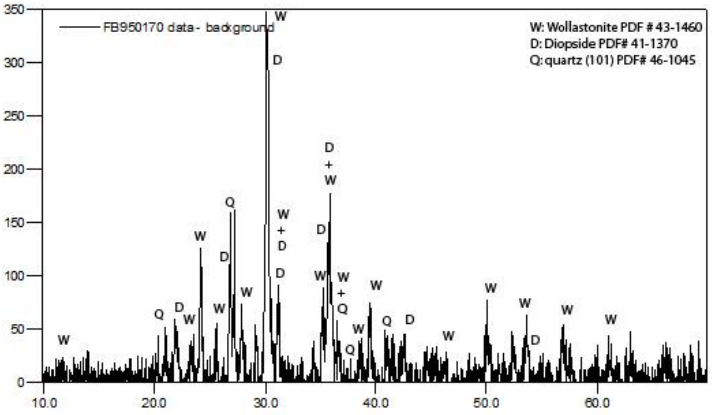


Figure 6.3.10 X-ray diffraction patterns of the Sample FB95

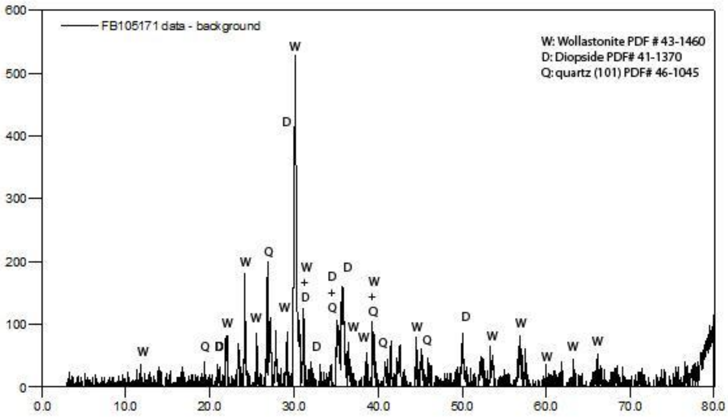


Figure 6.3.11 X-ray diffraction patterns of the Sample FB

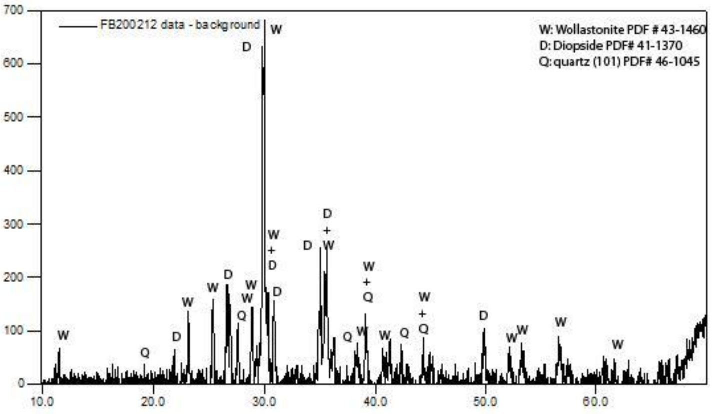


Figure 6.3.12 X-ray diffraction patterns of the Sample FB2

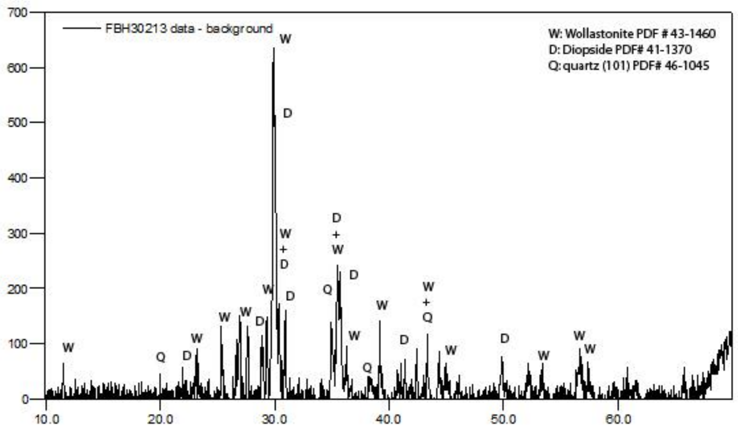


Figure 6.3.13 X-ray diffraction patterns of the Sample FBH

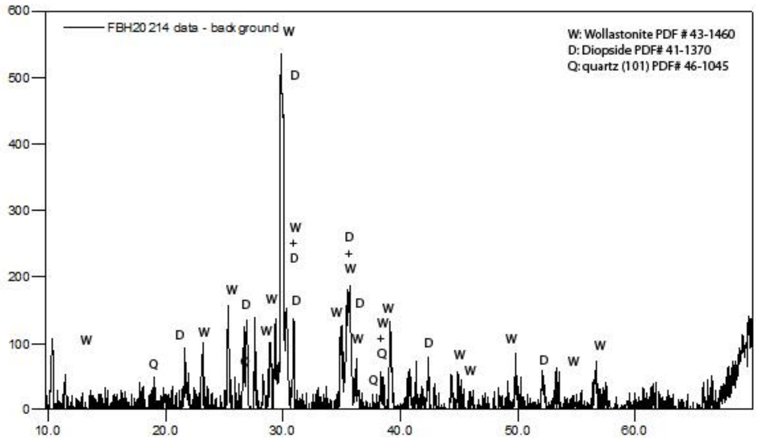


Figure 6.3.14 X-ray diffraction patterns of the Sample FBH2

The most crystalline phases can be seen in samples FB2 (figure 6.3.12)and FBH (figure 6.3.13) .

Figure 6.3.10 represents sample FB95. Due to low sintering temperature, the peaks are lower than the samples sintered up to 1050ºC, exhibiting less crystallization. The sample FB, (figure 6.3.11), sintered up to 1050º C represents higher amount of crystallization with wollastonite as main peak. The sample FBH sintered up to 1050º C with a holding time of 1 hour acts similar to the sample FB but as a result of 1 hour of holding time. In sample FB2 (figure 6.3.12) as a result of containing high amount of SLG, in rapid sintering, higher amount of crystallization can be observed where the sample FBH2 (figure 6.3.14), same composition sintered up to 1050º C with a holding time of 1 hour ended up with a lower crystallization, due to the dissolution of the Silicates (mainly in SLG) operated by the secondary components of BW .

References

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[1] S. Piskin: Thermal properties of hydrated boron minerals, *Doctoral Dissertation, Istanbul Technical University,* 1983.

[2] Ö. Yildiz, The effect of heat treatment on colemanite processing: a ceramics application Powder Technol., 142 (2004) 7-12.

[3] M.S. Celik, F. Suner: *A thermodynamic analysis of the decrepitation process*, Thermochim Acta, 245 (1995) 167174

[4] E. Bernardo, L. Esposito, E. Rambaldi, A. Tucci and S. Hreglich, *Recycle of Waste Glass into “Glass-ceramic Stoneware*, J Am Ceram Soc 91, (2008) 2156-2162.

[5] W. Höland, G. Beall, *Glass Ceramic Technology*, The American Ceramic Society, Westerville OH, 2002.

[6] Foamed Concrete, Composition and Properties, *British Cement Association,* (1994), Ref. 46.042.

[7] S. Fotiadou, M.C. Limbachiya, A.N. Fried and J.J. Roberts: Proceedings of International Conference Thomas Telford, September, (2004) 305–312.

[8] T.W. Cheng, Y.S. Chen, *Characterisation of glass ceramics made from incinerator fly ash*, Ceram. Int., 30 (2004) 343–349

[9] E . Bernardo , M. Varrasso , F. Cadamuro , S. Hreglich, *Vitrification of wastes and preparation of chemically stable sintered glass-ceramic products,* J. Non. Cryst. Solids, 352 (2006) 4017–4023

[10] T.W. Cheng, T.H. Ueng, Y.S. Chen, J.P. Chiu, *Production of glass-ceramic from incinerator fly ash,* Ceram Int, 28 (2002) 779–783

[11] E. Bernardo, *Fast Sinter-crystallization of a glass from waste materials,* J. Non. Cryst. Solids, ,354 (2008) 3486–3490

Chapter 7

Conclusions

7.1 Micro porous glass ceramics from combination of borate, phosphate and silicate wastes

BW and MBM ash can be combined, together withinbexpensive kaolin clay, to produce glass ceramic articles, generally featuring anorthite and phosphate crystals. While the resulting phosphate phase corresponds to that already present in MBM ash, anorthite was formed by the reaction between clay residues and Ca rich compound. BW acts as a flux, allowing the formation of liquid phase even at the moderate temperature of 1050ºC.

In the studied mixtures, the water fraction included in the colemanite present in BW is less useful due to the low evolution temperatures, while CO2, escaping from the decomposition of calcite mineral fraction, constitutes a valid foaming agent. The liquid phase provided by BW is insufficient for a massive foaming operated by calcite decomposition, mainly for the remarkable precipitation of anorthite crystals. Even if the anorthite crystallisation may be controlled by adjusting the heating rate, extensive foaming is essentially associated with the addition of SLS glass waste. The optimised formulation led to highly porous and homogenous bodies that could be exploited for both thermal and acoustic insulations and even embedded in lightweight concrete.

7.2 Dense glass-ceramics from borate and silica wastes and for its cytotoxic characterization

Glass-ceramics were obtained for the first time from a combination of three wastes; i) boron waste, ii) meat bone and meal ash and iii) soda lime silica glass waste. The effects of rapid sintering, particle sizes of the selected wastes, additive amount of the glass-ceramic forming oxides and sintering cycle were found to be significant.

Boron within BW acts as a flux, providing a lower liquid phase forming temperature of 950°C. The reaction between, MgO and CaO together with the silicate phase forms mainly wollastonite and diopside phases.

The cell toxicity analyses showed the obtained materials were cytotoxic (toxic to cells). The properties of the obtained glass-ceramics show that the obtained material cannot be considered as waste delivered bioactive material but as in the case of building materials it can be employed as building structural blocks or as an additive in the cement and ceramic industries.

7.3 Wollastonite glass-ceramics from fly ash borate wastes

Wolastonite glass-ceramics from i) Boron Waste ii) Fly Ash iii) SLG was successfully obtained through rapid sintering process.

The wollastonite glass-ceramic structure was expected, but due to the little amount of MgO existing in the starting wastes, diopside phase was a critical goal of the study in order to achieve a strong material . The Xrd results showed the reactions during rapid sintering lead to wollastonite phase followed by Diopside ($MgCaSi_2O_6$) formation.

This structure can be called “diospide reinforced wollastonite glass-ceramic” which is a desirable structure in glass-ceramics. The crystallization process and crystal size are controlled with adjusting heating rates and compositions.

The literature research and the derived results show the obtained material can be used as an additive in ceramic, cement and brick industry.