

REPUBLIC OF TURKEY
YILDIZ TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**UTILIZATION OF BORON MINING AND ENRICHMENT
WASTES IN THE PRODUCTION OF CERAMICS AND FRITS**

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MASTER OF SCIENCE THESIS

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Emirhan Karadağlı





*Dedicated to my family
and to the one I love the dearest.*

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TABLE OF CONTENTS

LIST OF SYMBOLS.	xi
LIST OF ABBREVIATIONS.	xiii
LIST OF FIGURES.	xv
LIST OF TABLES.	xviii
ABSTRACT	xx
ÖZET	xxii
1 Introduction.	1
1.1 Literature Review.....	1
1.2 Objective of the Thesis	3
1.3 Hypothesis	3
2 Boron.	5
2.1 General Properties.....	5
2.2 Atomic Structure	5
2.3 Physical Properties.....	7
2.4 Chemical Properties	7
3 Boron Minerals/ Borates..	8
3.1 Sodium Borates	14
3.1.1 Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).....	14
3.1.2 Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)	14
3.1.3 Tincalconite ($\text{Na}_2(\text{B}_4\text{O}_7) \cdot 5\text{H}_2\text{O}$)	14
3.2 Sodium-calcium borates	16
3.2.1 Ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$).....	16
3.2.2 Probertite ($\text{NaCaB}_3\text{O}_9 \cdot 5\text{H}_2\text{O}$)	16

3.3 Calcium Borates	17
3.3.1 Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$)	17
3.3.2 Pandermite ($\text{CaB}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$)	17
3.3.3 Inyoite ($\text{Ca}(\text{H}_4\text{B}_3\text{O}_7) \cdot (\text{OH}) \cdot 4\text{H}_2\text{O}$)	17
3.4 Magnesium Borates.....	18
3.4.1 Hydroboracite ($\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$)	18
3.4.2 Boracite ($\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$)	18
4 Boron Deposits in Turkey, The World .	20
4.1 Boron Reserves	20
4.1.1 Boron Reserves in the World.....	20
4.1.2 Boron Reserves in Turkey	23
4.2 Boron Production.....	24
4.2.1 Boron Production in the World	24
4.2.2 Boron Production in Turkey	25
4.3 Import and Export Datas.....	28
5 Usage Areas of Boron.	30
5.1 General Applications	30
5.1.1 The Use in the Production of Borasilicate Glasses	30
5.1.2 Use in Ceramics.....	31
5.1.3 Frits and Enamels.....	32
5.1.4 Use in Hygiene and Whitening Industry	33
5.1.5 Uses in Agriculture	36
5.1.6 Use in Textile Fiberglass Production	36
5.2 Other Use of Areas	37
5.2.1 Construction-Cement Industry	37
5.2.2 Fiberglass Insulation.....	38

5.2.3 Nuclear Applications.....	39
5.2.4 Combustion-Preventive Matters	39
5.2.5 Metallurgy	40
5.2.6 Automobile Airbags and Antifreeze	41
5.2.7 Health.....	41
5.2.8 Electronics, Computer and Advanced Technology.....	42
5.2.9 Energy and Heat Storage.....	43
5.2.10 Others.....	44
6 Boron Concentration and Production of Boron Chemicals ..	49
6.1 Boron Concentration.....	49
6.2 ETI Kirka Boron Mining Management.....	49
6.2.1 History... ..	49
6.2.2 Products	50
6.2.3 Capacities	50
6.2.4 Borax Pentahydrate (Etibor 48 – $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)	50
6.2.5 Etibor-68 (Anhydrous Borax) ($\text{Na}_2\text{B}_4\text{O}_7$)	52
7 Boron Wastes.	56
7.1 Liquid Wastes	56
7.2 Solid Wastes	57
7.2.1 Mining SBW	57
7.2.2 Enrichment SBW.....	57
8 Experimental Section.	58
8.1 Materials	58
8.2 Preparation of Wall and Floor Tile Slurries	58
8.3 Preparation of Transparent and Matt Opaque Frits and Glazes	59
9 Characterization Studies..	62

9.1 Chemical Analysis (Compositional)	62
9.2 Minerological and Phase Analysis	62
9.3 Microstructural Analysis	62
9.4 Thermal Analysis	62
9.5 Optical and Color Analysis	63
9.6 Mechanical and Chemical Resistance Tests	63
10 Results and Discussion.	65
10.1 Characterization Results of the BWs	65
10.2 Methodology for the Development of Waste-containing Tile Compositions	69
10.2.1 Development of Waste-containing Floor Tile Compositions	70
10.2.2 Development of Waste-containing Wall Tiles	72
10.2.3 Development of Waste-containing Porcelain Tiles	74
10.3 Methodology For the Development of Waste-Containing Frit and Glaze Compositions	75
10.3.1 Development of Waste-Containing Transparent Frits	76
10.3.2 Development of Waste-Containing Matte Opaque Frits	77
10.4 Results of Rheology and Characterization Studies of Waste-Containing Tile Compositions	78
10.4.1 Rheological Study	78
10.4.2 Results of the Characterization Studies	81
10.5 Characterization Results of Waste-Containing Frits and Glazes	104
10.5.1 Transparent Frits	104
10.5.2 Matt Opaque Frits	110
11 Conclusion and Recommendation..	133
References.	135



LIST OF SYMBOLS

μm	Micrometer
$\text{\AA}$	Angstrom
Al	Aluminum
Al_2O_3	Alumina
B	Boron
B_2O_3	Boron Trioxide
BaO	Barium oxide
CaO	Calcium oxide
cm^3	centimeter cube
Cr_2O_3	Chromium oxide
eV	Electron volt
Fe_2O_3	Iron oxide
g	Gram
H_2O	Water
H_3BO_3	Boric Acid
He	Helium
J	Joule
K	Kelvin
K_2O	Potassium oxide
kJ	Kilojoule
km	Kilometer
kV	Kilovolt
Li	Lithium

lt	Liter
m	Meter
m ²	Meter square
mg	Milligram
MgO	Magnesium oxide
MJ	Mega Joule
mm	Millimeter
mm ²	Millimeter square
N	Newton
Na	Sodium
Na ₂ O	Sodium oxide
nm	nanometer
P ₂ O ₅	Phosphorus penta-oxide
ph	Potential hydrogen
ppm	Parts per million
rpm	Revolutions per minute
Si	Silicon
SiO ₂	Silica
SnO ₂	Tin oxide
wt. %	Weight percent
ZrCMS	Zirconia-calcia-magnesia-silica

LIST OF ABBREVIATIONS

BNCT	Boron Neutron Capture Therapy
BOG	Bright Opaque Glaze
BPA	Bisphenol A
Bt	Billion Tons
BW	Boron Waste
CD	Compact Disc
CMC	Carboxymethyl Cellulose
DTA	Differential Thermal Analysis
DVD	Digital Versatile Disc
EDX	Energy-Dispersive X-Ray Spectroscopy
EN	Europeane Norm
ESBW	Enrichment Solid Boron Waste
FT	Floor Tile
HK	Hardness Knoop
HV	Hardness Vickers
ISO	International Standardization Organization
LBW	Liquid Boron Waste
LCD	Liquid-Crystal Display
MOF	Matt Opaque Frit
MSBW	Mining Solid Boron Waste
Mt	Million Tons
NATO	North Atlantic Treaty Organization
OPEC	Organization of the Petroleum Exporting Countries

PT	Porcelain Tile
PVA	Polyvinyl Alcohol
SBW	Solid Boron Waste
SEM	Scanning Electron Microscopy
TEAD	Tetraacetyl Ethylene Daimine
TF	Transparent Frit
TS	Turkish Standards
Tt	Thousand Tons
USA	United States of America
WT	Wall Tile
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

LIST OF FIGURES

Figure 2.1	Boron crystal structure (α -rhombohedral).....	6
Figure 3.1	Borate (B_2O_3)	8
Figure 3.2	Sodium-calcium borates, a. ulexite, b. probertite	15
Figure 3.3	Sodium-calcium borates, a. ulexite, b. probertite	16
Figure 3.5	Magnesium borates, a. hydroboracite, b. boracite	19
Figure 4.1	Boron reserves in the world 2013, leading countries (1000 metric tones)	22
Figure 4.2	Distribution of the boron reserves in the world	23
Figure 4.3	Distribution of the boron reserves in the Turkey 2012, on the basis of mineral	24
Figure 5.1	Boron in borasilicate glasses	31
Figure 5.2	Firing ranges of wall and floor tiles which includes B_2O_3	32
Figure 5.3	Process flow sheet of the production of laundry soap.....	35
Figure 5.4	Cement production from recycling of industrial and urban wastes	38
Figure 5.5	Nuclear characteristics of elements.....	39
Figure 5.6	Schematic of explanation of BNCT reaction.....	42
Figure 5.7	Crystal structures of different compounds.....	43
Figure 5.8	The usage areas of boron	46
Figure 6.3	The flow-sheet of Kirka solubilization plant	55
Figure 8.1	Flow chart of the experimental procedure applied to the FT and WT bodies.....	59
Figure 8.2	Flow of fabrication of opaque frits	60
Figure 8.2	Flow of process for producing glazes	61
Figure 10.1	XRD patterns of the boron wastes A1 (a), A2 (b), A3 (c), A4 (d), A5 (e), A6 (f).....	68
Figure 10.2	Sintering behaviour graph of FT-STD under continuous firing condition.....	83
Figure 10.3	Sintering behaviour graph of FT-STD with a peak temperature and holding time.....	84
Figure 10.4	Sintering behaviour graph of FT3-A6 under continuous firing condition.....	85
Figure 10.5	Sintering behaviour graph of FT3-A6 with a peak temperature and holding time.....	86
Figure 10.6	XRD patterns of fired FT3-A6 and FT-STD bodies.....	87
Figure 10.7	(a) SEM image of fired FT-STD body. (b) EDX analysis results of pointed regions in SEM image.....	88
Figure 10.8	(a) SEM image of fired FT3-A6 body (10 μm). (b) SEM image of fired FT3-A6 body (2 μm). (c) EDX analysis results of pointed regions in SEM images.....	90
Figure 10.9	XRD patterns of fired WT-STD and WT3-A6 bodies.....	92

Figure 10.10	(a) SEM image of fired WT-STD body. (b) EDX analysis results of pointed regions in SEM image.....	93
Figure 10.11	(a) SEM image of fired WT3-A6 body. (b) EDX analysis results of pointed regions in SEM image.....	94
Figure 10.12	Sintering behavior of PT-STD under continuous firing conditions	96
Figure 10.13	Sintering behaviour of PT-STD as a function of the peak temperature and holding time	97
Figure 10.14	Sintering behaviour of PT3-A6 under continuous sintering conditions.....	97
Figure 10.15	Sintering behaviour of PT3-A6 as a function of the peak temperature and holding time (1210-1220 °C)	98
Figure 10.16	XRD patterns of fired PT-STD and PT3-A6 bodies	99
Figure 10.17	SEM image of fired PT-STD body and EDX analysis results of pointed regions in SEM image.....	101
Figure 10.18	SEM image of fired PT3-A6 body and EDX analysis results of pointed regions in SEM image.....	102
Figure 10.19	SEM images from the cross-sections of the sintered PT-STD and PT3-A6 bodies	103
Figure 10.20	Result of thermal analysis applied to frits by using heat microscope.....	105
Figure 10.21	XRD patterns of TF1, TF1-A5, TF1-A6, TF1-A6-2	106
Figure 10.22	SEM images taken from the surface of TF1 (a), TF1-A5 (b), TF1-A6 (c), TF1-A6-2 (d).	107
Figure 10.23	SEM images taken from the cross-section of TF1 (a), TF1-A5 (b), TF1-A6 (c), TF1-A6-2 (d).....	108
Figure 10.24	Digital photos of the glazes TF1, TF1-A5, TF1-A6, TF1-A6-2 applied on the tile surface.....	109
Figure 10.26	Results of thermal analysis of frits using heat microscope.....	111
Figure 10.27	Results of DTA analysis of frits	112
Figure 10.28	Results of DTA analysis of frits	112
Figure 10.29	Results of thermal analysis of bright opaque glazes using heat microscope.....	114
Figure 10.30	Results of DTA analysis of bright opaque frits.....	114
Figure 10.31	XRD patterns of MOF1, MOF1-A1, MOF1-A2, MOF1-A3 and MOF1-A4.....	116
Figure 10.32	XRD patterns of MOF1, MOF1-A5, and MOF1-A6	116
Figure 10.33	XRD patterns of BOG, BOG-A3 and BOG-A5 glazes.....	117
Figure 10.34	SEM images of surfaces of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4.....	118
Figure 10.35	SEM images of surfaces of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6.....	119
Figure 10.36	SEM images of surfaces of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4.....	120
Figure 10.37	SEM images of surfaces of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6.....	121

Figure 10.38	SEM images of cross-sections of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4	122
Figure 10.39	SEM images of cross-sections of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6	123
Figure 10.40	SEM images of cross-sections of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4	124
Figure 10.41	SEM images of cross-sections of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6	125
Figure 10.42	(a), (d), (g) SEM (backscattered electron) images of surfaces of BOG, BOG-A3, and BOG-A5. (b), (e), (h) SEM (backscattered electron) images of marked areas in (a), (d), and (g) at higher magnification. (c), (f), (i) EDX analysis of dotted crystals in (b), (e), and (h)	126
Figure 10.43	(a), (d), (g) SEM (backscattered electron) images of cross-sections of BOG, BOG-A3 and BOG-A5. (b), (e), (h) SEM (backscattered electron) images of the marked areas in (a), (d) and (g) in higher magnification. (c), (f), (i) EDX analysis of dotted crystals in (b), (e) and (h)	127
Figure 10.44	Digital photographs of MOF1, MOF1-A5, and MOF1-A6 glazes, applied to tile surfaces.	128

LIST OF TABLES

Table 2.1	Main atomic properties of boron	6
Table 2.2	Main physical properties of boron	7
Table 2.3	Main chemical properties of boron	7
Table 3.1	Industrially significant borates	8
Table 3.2	Boron minerals (continuation)	10
Table 3.3	Boron minerals (continuation)	11
Table 3.4	Most common boron minerals and their properties	12
Table 3.5	Most common boron minerals and their properties (continuation)	13
Table 4.1	Principal boron producers in the world (1000 tones / year B_2O_3)	24
Table 4.2	The capacities of the concentrated and refined boron products (1000 tons/year)	27
Table 4.3	Export datas	28
Table 4.4	Import datas	29
Table 5.1	Energy source and energy values	44
Table 5.2	The usage areas of boron	45
Table 5.3	Areas of some important concentrated and refined boron compounds	46
Table 5.4	The usage areas of some special boron chemicals	47
Table 10.1	Chemical compositions of employed boron mining and enrichment wastes	66
Table 10.2	Chemical compositions of standard floor, wall and porcelain tile ...	69
Table 10.3	Seeger formulations of FT-STD composition	70
Table 10.4	Seeger formulations of waste-containing FT compositions in comparison with FT-STD	71
Table 10.5	Seeger formulations of WT-STD	72
Table 10.6	Seeger formulations of waste-containing WT compositions in comparison with WT-STD	73
Table 10.7	Seeger formulations for the PT-STD composition	74
Table 10.8	Seeger formulations for the waste-containing PT compositions in comparison with that of PT-STD	75
Table 10.9	Seeger tables for TF1, TF1-A5, TF1-A6 and TF1-A6-2 frits	76
Table 10.10	Seeger tables for MOF1, MOF1-A1, MOF1-A2, MOF1-A3, MOF1-A4, MOF1-A5 and MOF1-A6 frits	78
Table 10.11	Critical temperatures in sintering stage of the BW-containing floor tiles	81
Table 10.12	Optical, mechanical and thermal properties of FT-STD and FT3- A6	91

Table 10.13	Optical, mechanical and thermal properties of FT-STD and FT3-A6.....	95
Table 10.14	Sintering behaviour of waste-containing PT compositions in comparison with PT-STD	95
Table 10.15	Optical, mechanical and thermal properties of FT-STD and FT3-A6.....	104
Table 10.16	Results of the thermal analysis applied to developed frits.....	105
Table 10.17	Color, brightnes and roughness values of developed glazes.	109
Table 10.18	Results of thermal analysis of developed frits.	111
Table 10.19	Color, brightness, and roughness values of developed glazes	129
Table 10.20	Color and brightness values of bright opaque glazes.....	129
Table 10.21	ISO 10545 test results of the BOG, BOG-A3 and BOG-A5	130



Utilization of Boron Mining and Enrichment Wastes in the Production of Ceramics and Frits

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Department of Metallurgical and Materials Engineering

Master of Science Thesis

Advisor: Assist. Prof. Dr. Buğra Çiçek

Boron which is shown with symbol B in periodic table is just a member of non-metal in group IIIA. Compounds made with many metal and non-metal boron is used in many different areas of industry because of its different features.

Largest boron deposits are lying under the borders of Turkey, Russia and USA. The amount of boron present in the reserves is predicted to be 1.2 Bt. Turkey holds the largest of shares with 72.5%, followed by Russia and USA with 7.7% and 6.2% respectively.

Excessive amounts boron wastes are formed during the mining and enrichment activities of the producer countries, causing both economical and environmental issues, entailing to come up with a sustainable utilization method immediately. In this study, their suitability for becoming a raw material for the production of ceramic tiles to reduce energy consumption via affecting sintering temperature, owing to the fluxing abilities of its valuable constituent boron trioxide (B_2O_3) has been inspected. New waste-containing tile compositions were designed, produced and characterized. Together with the tile compositions, addition of boron wastes as

a potential B_2O_3 source into the frit compositions has also been experimented and characterized.

Owing to the fluxing ability of B_2O_3 added only around 5-6%wt into the compositions affected the sintering mechanism, decreasing the needed temperature for the developed wall tiles down to 1050 °C which is 70 °C lower aligned to base commercial ceramic composition. Sintering temperatures of both floor and porcelain tiles were also decreased. For floor tiles, 65 °C decrease was measured and sintering temperature was recorded 1130 °C. For porcelain tiles, sintering temperature was 1195 °C, recording a 38 °C decrease.

Mechanical, chemical and physical properties of the waste-containing tiles were similar to the commercial tiles. They provided the desired properties to meet the TS EN ISO 10545 standards in the means of water absorption and strength.

Utilization potential of boron wastes in frits was to reduce boric acid (H_3BO_3) consumption and if possible, substitute them for H_3BO_3 used for frit production. During the laboratory and pilot-scale production, recently used industrial methods were applied. The produced frits were then used to yield glazes. Applied glazes successfully met the necessities of EN ISO 10545 standards showcasing optimum properties.

Bor Maden ve Zenginleştirme Atıklarının Seramik ve Frit Üretiminde Değerlendirilmesi

Emirhan Karadağı

Metalurji ve Malzeme Mühendisliği Bölümü

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Bor periyodik tabloda “B” sembolü ile gösterilen, IIIA grubunun metal olmayan tek üyesidir. Bor, metal ve metal olmayan elementlerle yaptığı bileşikler ve bu bileşiklerin göstermiş olduğu farklı özellikler nedeniyle sanayinin pek çok farklı alanında kullanılmaktadır.

Dünya’da ki bor rezervlerin başlıcaları Türkiye, Amerika Birleşik Devletleri ve Rusya’da bulunmaktadır. Bu rezervlerin toplam miktarı 1.2 milyar ton olup, bu miktarın %72,5’i Türkiye’de, %7,7’si Rusya’da ve %6,2’side Amerika’da bulunmaktadır.

Bor üreticisi olan tüm ülkelerde her yıl çok büyük miktarlarda bor maden atıkları oluşmakta ve bu durum acilen bir değerlendirme sonucu bulunmasını zorunlu tutmaktadır. Atıkların seramik karo üretiminde enerji tasarrufu sağlaması amacıyla kullanılması, frit üretiminde ise borik asit (H_3BO_3) yerine bor trioksit (B_2O_3) kaynağı olarak kullanılması ihtimalleri incelenmiştir.

İçeriğinde % 5-6 B_2O_3 atığı içeren seramik karo kompozisyonlarında atıklardan, %1-33 oranında yararlanılmıştır. B_2O_3 ’ün sahip olduğu flaks özelliğinden kaynaklı

olarak, endüstriyel olarak üretimi sağlanan karolara göre, duvar karolarında 1050 °C ile 70 °C'lık, yer karolarında 1130 °C ile 65 °C'lık, porselen karolarda 1195 °C ile 38 °C'lık bir düşüş kaydedilmiştir.

Yeni geliştirilen kompozisyonların mekanik, kimyasal ve fiziksel özellikleri, endüstriyel karo özelliklerine yakındır. Geliştirilen karolar su emme ve pişmiş mukavemet değerleri açısından TS EN ISO standartlarını sağlamaktadır.

Kolemanit ($\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) maden ve zenginleştirme atıkları, borik asit'in (H_3BO_3) yerine B_2O_3 kaynağı olarak kullanılmak üzere frit üretiminde kullanılmıştır. Seramik endüstrisinde kullanılan metodlar ile laboratuvar ve pilot ölçekli üretimler yapılmıştır. Fritlerden üretilen sırlar TS EN ISO 10545 standardının gerekliliklerini, yüzey pürüzlülüğü, kimyasal dayanım, termal şok dayanımı ve lekelenme dayanımı açısından sağlamıştır.

1.1 Literature Review

It's known that the most essential boron reserves are lying under the borders of Turkey, Russia and USA. It's estimated that the total boron reserves on earth is 1.2 billion tones and 72,5% of the reserves are located in Turkey, 7,7% of them are located in Russia and 6,2% is located in USA[1]–[3].

Boron mining started in Turkey in 1861 by foreign companies. Later, mining exploitation rights were transferred to state sector, namely, Etibank. Turkey has 72% of the world reserves, but the figures are 35% in the production and trade.

Eti Mine is the largest producer of boron products around the world. Its facilities generate 400 Tt of boron waste per year[4], [5]. This huge amount of waste is formed the concentration and beneficiation processes. Caused by the B_2O_3 content and clayey structure of the wastes, different valorisation options are studied and tried out[6]–[15]. However, utilizing this waste at the industrial scale remains a challenge.

High B_2O_3 content (16 – 31%) and clayey structure of boron wastes, increases its chances to be utilized as a raw material in ceramic tile production. B_2O_3 is not only a glass-former for ceramic structures, it also takes the mission of becoming a fluxing agent which does not uplift the thermal expansion coefficient differentiating from other fluxes, which will end up as a decrease in the energy consumption in ceramic tile production[16], [17].

In 2016, 13,056 million m^2 of fired tiles were fabricated globally and Turkey has a 2.5% offer in this huge industrial activity[18]. Distinctive kinds of earthenware products are manufactured having different physical and concoction properties relying upon the application area. Thus, clay tiles are mostly used in structural and constructional applications where endurance and appearance (particularly for porcelain tiles) are of real significance. Be that as it may, the expanding development

rate of the earthenware tile advertise brings an ecological obligation regarding the business, pushing scientists and industrial partners to come up with supportable methodologies with the end goal to change the procedures more cost-effective.

Sintering is the most power-devouring phase of the tile production process which occurs at raised temperatures running from 900 °C to 1450 °C relying upon the usage area and employed raw materials[19], [20]. There have been various investigations distributed on the issue of energy in tile production, however the majority of them concentrated on the productivity as opposed to focusing on the sintering procedure itself.

Frits are a basic clay segment comprising of different non-crystalline materials. Frit production includes three essential stages, to be specific, the mixing and blending of the raw materials, their heating at a lifted temperature (1400 °C), and resulting shock-cooling in water down to room temperature. Quenching is the main mechanism behind the forming of amorphous phases. The manufactured frits showcase a non-crystalline structure that comprises of crystalline nucleuses. The frit is the most critical constituent of glazes and enamels, included between 80– 90% in the compositions.

The employment of B_2O_3 in the fabrication of frits and by implication in the making of glazes has various constructive outcomes from both a specialized and a visual perspective. B_2O_3 is a glass-former and a fluxing agent which does not raise the thermal expansion coefficient, as opposed to different fluxes (earth metals). Thermal expansion attributes of coatings are critical on the grounds that a coating is connected as the last layer on a tile's surface. Along these lines, if the warm extension coefficient of the coating isn't inside the coveted range, the coveted surface inclusion won't be accomplished. Further, B_2O_3 is exceedingly successful for network alignment, enhancing the chemical and mechanical strength. It has likewise been accounted for that B_2O_3 expands the scratch resistance of glazes[21], [22].

Because of the way that boric acid can provide exceptionally pure B_2O_3 in expansive sums, it is regularly adopted as the B_2O_3 source for frit fabrication and in addition in other B_2O_3 -related businesses. Considering the large amounts of boron waste generation by the producers and the high amounts of B_2O_3 present in this wastes

(16– 31%), it is predicted to consider valorizing this waste as a B_2O_3 source and an option in contrast to boric acid for frit fabrication.

1.2 Objective of the Thesis

The first objective of the present study is to modify ceramic tile compositions by adding boron wastes in order benefit by the glass-forming effect of B_2O_3 , resulting in a decrease in firing temperatures. Employment of the wastes was done respecting the Seger formations of the standard composition in order to minimize the possible differences in both rheological and mechanical properties. Finally, waste-containing porcelain tiles were characterized and investigated in order to see the effects on the microstructure, phase evolution and distribution, physical, thermal and mechanical properties.

The second objective of this study is to use colemanite enrichment wastes from Bigadiç and Bandırma as a source of B_2O_3 to produce opaque frits which are produced in a ZrCMS glass-ceramic system. The waste was added to the starting composition based on the Seger formula for the standard composition, to ensure that there were no rheological irregularities. The waste-based frits were then used to produce glaze slips, and the resulting glazes were applied to the tile surfaces, which were then characterized.

1.3 Hypothesis

It is determined that B_2O_3 encourages the formation of amorphous phases, concluding in fast devitrification. It is proposed that, owing to high B_2O_3 content of the BWs, they can be used as a fluxing agent to decrease the sintering temperature of the ceramic tiles.

Likewise, concerning the amount of B_2O_3 present in the BWs, they can be used as a source for B_2O_3 instead of H_3BO_3 in the production of frits. Owing to other earthy-soil based components of the BWs, addition of them into the compositions did not cause severe impurities.

In this study, it is predicted and assumed that by the employment of BWs, sintering temperature of ceramic tiles can be decreased. By this reduction, an industrial retrenchment can be achieved along with a sustainable solution.

As a second prediction, BWs can also be used as a B_2O_3 source in the fabrication of frits, indirectly in glazes. This can priorly provide a decrease in raw material costs and also a slight decrease in firing temperature as an extra outcome.



2.1 General Properties

Boron is the only non-metallic member of the IIIA group and it's represented by the letter "B". It has two stable isotopes with an atomic number of 5 and mass numbers of 10 and 11[23].

Boron doesn't exist free in nature but it's bounded to the structure of over 150 minerals. Crystalline boron is black, ductile, hard and solid but amorphous boron shaped as a powder and its brown to black[24].

Boron is used in the different areas of the industry because most of its compounds with metals or ametals are showing lots of different properties. Boron doesn't showcase metallic behaviour in a compound but pure boron is conductive. Boron in crystalline state is like diamond, concerning the appearance and optical properties and it's almost as hard as diamond.

For the first time, pure boron element was synthesized by French chemists J. L. Gay-Lusaac and Baron L. J. Thenard and British chemist H. Davy in 1808 [25].

2.2 Atomic Structure

Boron element can make 3 bonds through its 3 valance electrons. Boron crystal has 12 boron atoms in per unit cell and it has 3 different crystal structures. These three different crystal structures are;

1. Alfa-rhombohedral
2. Tetragonal
3. Beta-rhombohedral[26].

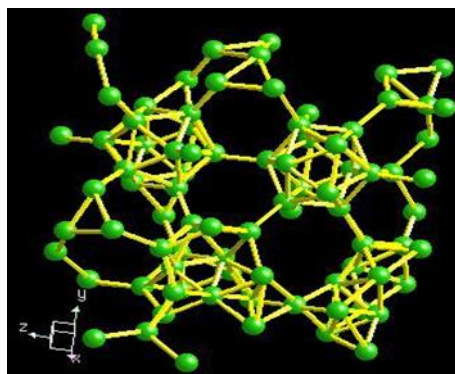


Figure 2.1 Boron crystal structure (α -rhombohedral)

Table 2.1 Main atomic properties of boron [25]

Properties	Value
Atomic radius, Å	1,17
Atomic volume, cm ³ /mol	4,6
Electron configuration	1s ² 2s ² p ¹
Ionic radius, Å	0,23
Number of electrons (neutral)	5
Number of neutrons	6
Number of protons	5

2.3 Physical Properties

Table 2.2 Main physical properties of boron [25]

Properties	Value
Atomic mass, g/mol	93,13
Density, g/cm ³	2,34
Boiling point, °C	4002
Melting point, °C	2300
Heat of vaporization, kJ/mol	480
Heat capacity, J/(mol·K)	11,087
Knoop hardness, HK	2100 - 2580
Mohs hardness (diamond-15)	11
Vicker's hardness, HV	5000

2.4 Chemical Properties

Table 2.3 Main chemical properties of boron [25]

Properties	Value
Electrochemical equivalent, g/A.h	0,1344
Electronegativity (pauling)	2,04
Fusion heat, kJ/mol	50,2
Valance electron potential (-eV)	190

Borates are a group of minerals which includes B_2O_3 in its structure. Most common borates are tincal, colemanite and ulexite. All of the minerals, except sodium perborate, can be used instead of each other because the main substance in act is B_2O_3 . Sodium perborate is used as an active oxygen carrier[27].



Figure 3.1 Borate (B_2O_3)

Borates can be mainly categorized as hydrogen borates, sodium borates, sodium-calcium borates, calcium borosilicates, magnesium borates and other borates. Subgroups and members are given in Table 3.1 in detail.

The most commonly used borates and their properties are also given in the Table 3.2.

Table 3.1 Industrially significant borates [28]

Type	Mineral	Formula	B_2O_3 (%)	Notes
Hydrogen Borates	Sassolite	H_3BO_3	56,3	Natural boric acid, it was produced in Italy.

Sodium Borates	Tincal (Borax)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	36,5	Kırka, USA, Argentina, Bolivia, India
	Tincalconite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$	48,8	It's mostly used as an acceseoire.
	Kernite (Rasorite)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$	51,0	Kernite deposits are located in the Blanca district of Argentina. Also there are deposits located in Turkey, USA and China.
Sodium-Calcium Borates	Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$	43,0	Ulexite deposits are located in Chile, USA, Peru, Serbia, Bolivia,
	Probertite	$\text{NaCaB}_3\text{O}_9 \cdot 5\text{H}_2\text{O}$	49,6	Their deposits are located in USA, Death
Calcium Borates	Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$	50,8	The biggest reserves are located in Turkey.
	Pandermite (Priceite)	$\text{CaB}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$	49,8	Deposits are located in Peru, Kırka and Bigadiç reserves. (Got it's name from Bandırma Province.)
	Nobleite	$\text{CaB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$	62,0	Their deposits are located in USA, Death Valley boron deposits.
	Inyoite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$	37,6	
	Meyerhofferite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$	46,7	

Table 3.2 Borates

Type	Mineral	Formula	B ₂ O ₃ (%)	Notes
Calcium Borosilicates	Datolite	CaBSiO ₄ OH	24,9	Datolite deposits are especially located in the east of the Russia and Kazakhstan.
	Danburite	CaB ₂ Si ₂ O ₈	28,3	Danbury, Connecticut, USA
	Havlite	Ca ₄ Si ₂ B ₁₀ O ₂₃ ·5H ₂ O	44,5	Bigadiç, Susurluk
Magnesium Borates	Hydroboracite	CaMgB ₆ O ₁₁ ·6H ₂ O	50,5	In Argentina, there are also hydroboracite deposits along with the colemanite deposits. Also there are deposits in Turkey and Kazakhstan.
	Inderborite	CaMgB ₆ O ₁₁ ·11H ₂ O	41,5	Inder, Kazakhstan
	Szaibelite	MgBO ₂ OH	41,4	This mineral mostly appears in Kazakhstan and China.
	Boracite	Mg ₃ B ₇ O ₁₃ Cl	62,2	In Turkey, this mineral appears too often in Emet, Kırka, Bigadiç borate deposits. Sometimes it appears along with ulexite, colemanite and tunelite.

	Kurnakovite	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$	37,3	Inder, Kazakhstan
	Inderite	$\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot 5\text{H}_2\text{O}$	37,3	Inder, Kazakhstan
	Suanite	$\text{Mg}_2\text{B}_2\text{O}_5$	46,3	Suan, North Korea
	Kotoite	$\text{Mg}_3\text{B}_2\text{O}_6$	36,5	BundjiroKoto (1856-1935)

Table 3.3 Borates

Type	Mineral	Formula	B_2O_3 (%)	Notes
Other Borates	Kahnite	$\text{CaAsBO}_6 \cdot 2\text{H}_2\text{O}$	11,7	Emet, Kütahya
	Vonsenite	$(\text{Fe},\text{Mg})_2\text{FeBO}_5$	10,3	Magnus Vonsen (1879-1954), Riverside, California
	Ludvigite	$(\text{Fe},\text{Mg})_4\text{Fe}_2\text{B}_2\text{O}_7$	17,8	Ernst Ludwig (1842-1915)
	Tunelite	$\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$	52,9	George Tunnel (1900-1996)
	Bakerite	$\text{Ca}_4\text{B}_4(\text{BO}_4)(\text{SiO}_4)_3(\text{OH})_3 \cdot \text{H}_2\text{O}$	27,9	Death Valley, California

	Searlesite	$\text{NaBSi}_2\text{O}_5(\text{OH})_2$	17	Searles, California
	Teepleite	$\text{Na}_2\text{B}(\text{OH})_4\text{Cl}$	21,7	John Edgar Teeple (1874-1931), Searles, California

Table 3.4 Most common borates and their properties [29]

Mineral Name	Formula	B_2O_3 (%)	H_2O (%)	Crystal Structure	Hardness (Mohs)
Borax (Tincal)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ $\text{Na}_2\text{O}_2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	36,51	47,24	Monoclinic	2,0–2,5
Colemanite (Borocal사이트))	$2\text{CaO}_3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ $\text{Ca}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$	50,80	21,92	Monoclinic	4,0-5,0
Ulexite (Boronatrocalsite)	$\text{Na}_2\text{O}_2\text{CaO}_5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$	42,95	35,57	Triclinic	2,5
Kernite (Razorite)	$\text{Na}_2\text{O}_2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ $\text{Na}_2[\text{B}_4\text{O}_6(\text{OH})_2] \cdot 3\text{H}_2\text{O}$	50,95	26,37	Monoclinic	2,5-3,0

Probertite (Kramelite)	$\text{Na}_2\text{O}_2\text{CaO}_5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ $\text{NaCaB}_5\text{O}_9 \cdot 5\text{H}_2\text{O}$ $\text{CaNa}[\text{B}_5\text{O}_7(\text{OH})_4] \cdot 3\text{H}_2\text{O}$	49,59	26,65	Monoclinic	3,0-3,5
Datolite (Gadolinite)	$4\text{CaO}_2\text{B}_2\text{O}_3 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ O $\text{Ca}_2\text{B}_2\text{Si}_2\text{O}_9\text{H}_2\text{O}$ $\text{Ca}_4[\text{B}_4(\text{SiO}_4)_4(\text{OH})_4]$	21,76	5,63	Monoclinic	5,0-6,0

Table 3.5 Most common borates and their properties

Mineral Name	Formula	B ₂ O ₃ (%)	H ₂ O (%)	Cyrstal Structure	Hardness (Mohs)
Sassolit(Natural Boric Acid)	$\text{B}(\text{OH})_3$, $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ H_3BO_3	59,26	43,71	Triclinic	1,0
Hydroboracite	$\text{CaOMgO}_3\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ $\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$ $\text{CaMg}[\text{B}_3\text{O}_4(\text{OH})_3] \cdot 23\text{H}_2\text{O}$	50,53	26,16	Monoclinic	2,0-3,0

Szaibelyite (Ascherite)	$2\text{MgOB}_2\text{O}_3 \cdot \text{H}_2\text{O}$ $\text{Mg}_2\text{B}_2\text{O}_5 \cdot \text{H}_2\text{O}$ $\text{Mg}_2(\text{OH})[\text{B}_2\text{O}_4(\text{OH})]$	41,38	10,71	Monoclinic	3,0-3,5
Boracite	$5\text{MgOMgCl}_{17}\text{B}_2\text{O}_3$, $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$ $\text{Mg}_3[\text{B}_3\text{O}_5]_2[\text{BO}_3]\text{Cl}$	62,15	-	Orthorombic >265°C	7,0-7,5

3.1 Sodium Borates

3.1.1 Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)

Also known as sodium tetraborate, or disodium tetraborate, is an important borate and is the salt of boric acid. In nature, it's transparent and colourless but due to impurities they might be pink, yellow-ish and gray. Borax dissolves in water and forms tincalconite quite easily. Largest reserves are located at Turkey, Eskisehir-Kirka[30].

3.1.2 Kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)

Kernite was first discovered in 1926 in the Kramer District in Boron, California, in an enormous underground deposit. Almost immediately, its commercial importance was recognized and it became the most significant source of the chemical borax, becoming an even more profitable ore than the mineral borax itself (kernite contains less water than borax). It has a monoclinic crystal system and it forms in thick, solid veins[30].

3.1.3 Tincalconite ($\text{Na}_2(\text{B}_4\text{O}_7) \cdot 5\text{H}_2\text{O}$)

Tincalconite has a trigonal crystal system and it's shiny, glassy. Tincalconite is also used as a source of chemical borax. It has hexagonal crystal structure and it showcases same crystal forms with borax[30].

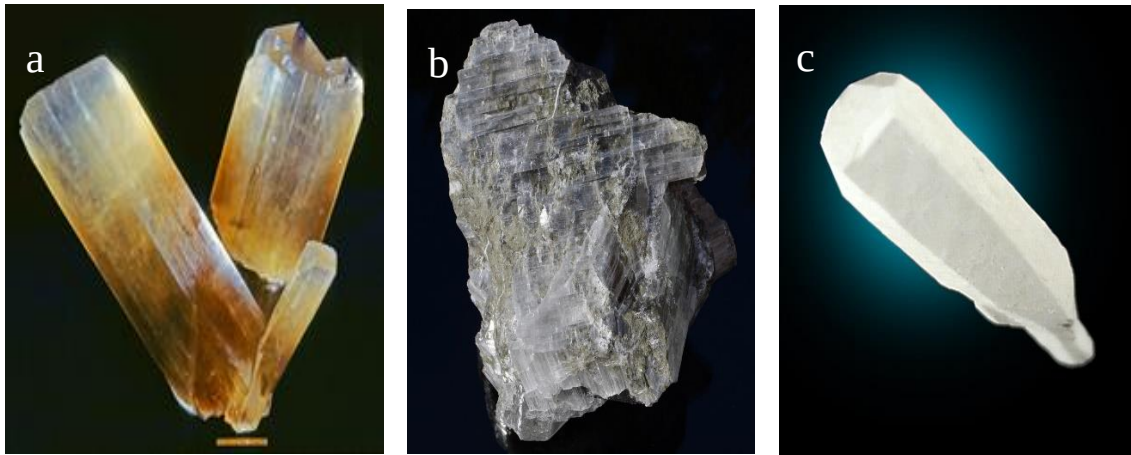


Figure 3.2 Sodium-calcium borates, a. ulexite, b. probertite [31]

3.2 Sodium-calcium borates

3.2.1 Ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$)

Ulexite has triclinic crystal structure. Its crystals can be found in many different shapes but mostly, it elongates straight along then forms as fibrous cottonball-like masses. In compact, it contains parallel fibrous veins and compact nodular groups. Ulexite is highly soluble in water. It's naturally colorless but white in aggregates and gray if mixed with clays[30].

3.2.2 Probertite ($\text{NaCaB}_3\text{O}_9 \cdot 5\text{H}_2\text{O}$)

Crystal structure of probertite is monoclinic. It's a brittle mineral and its hardness is 3.5. Its transparent to translucent. It can be found in the nature colorless, white, gray or pale yellow colors. It's generated in the Turkey-Kestelek mineral deposits as the secondary mineral[30].

Pictures of the members of sodium-calcium borates; ulexite, probertite minerals are given in Figure 3.3.

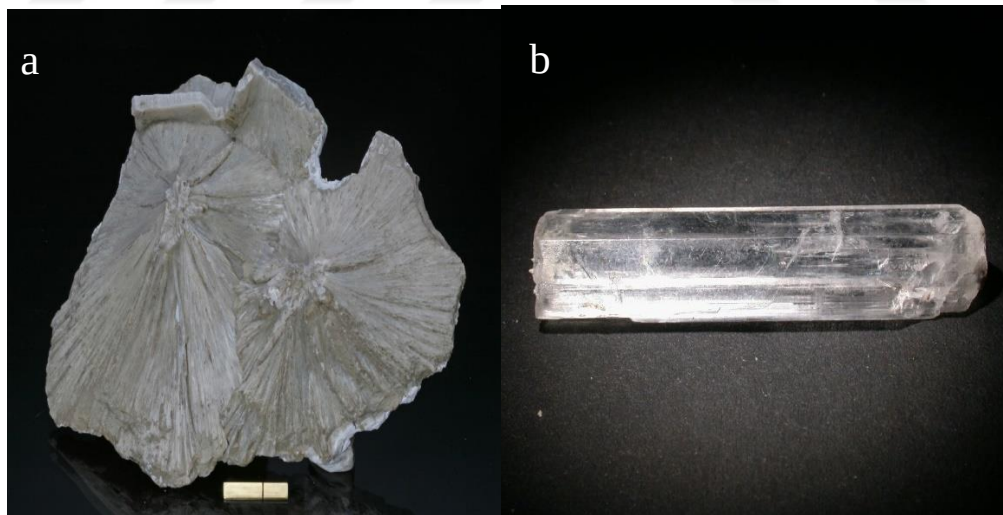


Figure 3.3 Sodium-calcium borates, a. ulexite, b. probertite [31]

3.3 Calcium Borates

3.3.1 Colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$)

Colemanite is the most common borate. The crystal structure of colemanite is monoclinic. Its optical properties are from transparent to translucent. It's mostly milky white and pale yellow. At very low temperatures, colemanite show pyroelectric and piezoelectric properties. Extensive deposits about one billion tones are located in Turkey, as in the Bigadiç borate district, Balıkesir Province, large crystals; from the Kestelek borax deposit, Eskişehir Province; at the Emet borate deposits, Kütahya Province, large crystals; from Mustafakemalpaşa deposits. Also there are deposits in USA, California[30].

3.3.2 Pandermite ($\text{CaB}_{10}\text{O}_{19} \cdot 7\text{H}_2\text{O}$)

The other name used for pandermite is priceite. It has a monoclinic crystal structure. It's a semitransparent mineral. It can be found in the nature in white color or colorless in transmitted light. In Turkey, the deposits are located at Sultançayır, Bursa and in Bigadiç borate district[30].

3.3.3 Inyoite ($\text{Ca}(\text{H}_4\text{B}_3\text{O}_7) \cdot (\text{OH}) \cdot 4\text{H}_2\text{O}$)

Inyoite has a monoclinic crystal structure. It's brittle and soluble in water. It's transparent but translucent when dehydrated. It's normally colorless but white when dehydrated. It's distributed from many deposits in the Bigadiç borate district, Turkey. Also there are large amounts of inyoite in the Inder boron deposit, Kazakhstan[30].

Pictures of the members of calcium borates; colemanite, pandermite and inyoite minerals are given in Figure 3.4.

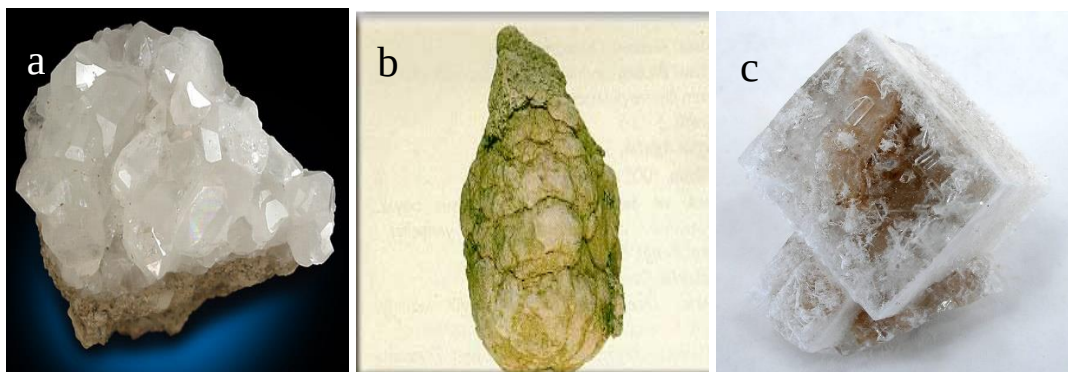


Figure 3.4 Calcium borates, a. colemanite, b. pandermite, c.inyoite [31]

3.4 Magnesium Borates

3.4.1 Hydroboracite ($\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$)

Hydroboracite has a monoclinic crystal structure. The hardness of this mineral varies from 2-3 to 5-6 mohs. It's partially soluble in boiling water. It's vitreous, but silky if fibrous. If grain is fibrous, the color is white but mostly it appears in colors as yellow or red-ish caused by the impurities. It's distributed in Turkey, from several deposits in the Bigadiç borate district, Kilik, Hisarcık and Espey borate mines[30].

3.4.2 Boracite ($\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$)

Boracite has a Orthorhombic, pseudocubic crystal structure. The hardness of the mineral is 7 - 7.5 mohs and its density is 2.91 - 3.10 gr/cm³. It's soluble in water and also it's strongly pyroelectric and piezoelectric. It can be seen in different colors, such as; white, gray, yellow, bluish green and green to dark green if ferrous. Its deposits are located in Germany, Canada, England, Kazakhstan, China and Australia[30].

Pictures of the members of magnesium borates; hydroboracite, boracite minerals are given in Figure 3.5.

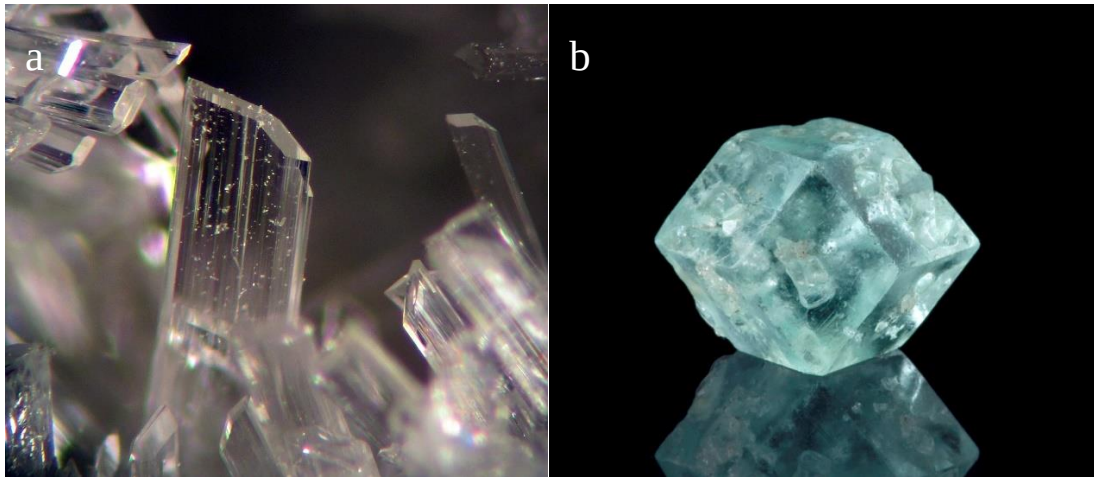


Figure 3.5 Magnesium borates, a. hdyroboracite, b. boracite [31]

Boron Deposits in Turkey, The World

4.1 Boron Reserves

Boron is an element that is commonly found in ground, rocks and water. The content of boron in the ground is around 10-20 ppm and boron reserves are located in the western areas of US, extending from Mediterranean to Kazakhstan. Boron content in sea water is between 0.5-9.6 ppm and boron content in fresh water is around 0.01-1.5 ppm. High concentration of oxide components of boron are obtained in droughty, volcanic, hidrothermally active regions of Turkey and US [25].

4.1.1 Boron Reserves in the World

Largest boron deposits are located in Turkey, Russia and US. Total amount of boron reserves are predicted to be 1.2 Bt. Also, world commerical boron reserves come together in four Regions which are;

- “Mojave Desert”, South of California, State of the USA.
- “And Region”, South America
- “South-Middle Asia Orojenic Region”, Turkey
- “East Russia”, Russia

Distribution of other important boron reserves are;

- **Boron Deposits, North America:** According to Rio Tinto’s report in 2010, total reserve of B_2O_3 is 24 Mt. It is ran via open-furnace system by Rio Tinto Company.
- **Serbia:** In 2005, Rio Tinto has purchased Jadar Boron Basin which contains Li_2O 1,8%, B_2O_3 13,1%. According to Rio Tinto’s activity report in 2010, reserve of basin is 16.2 Mt. The deposit consists of colemanite and Jadar minerals. Also, it is estimated that 2,9 Mt B_2O_3 reserved in Piskanja, the South of Serbia.

- **Fort Cady Calcium Boron Deposit Mojave Desert, California:**

It is hard and expensive via solution mining to process low-grade deposit which is located in the depth of 410 meters by Fort Cady Minerals.

- **Billie Mine:** Deposits contain colemanite, ulexite, probertite and ores are processed via underground furnaces operated by American Borate Company. However, production in those deposits aren't available now.

- **South America Boron Reserves:** The most important drawback of South America boron reserves is that its wide distribution in the area. Reserves are majorly located at And Mountain around 4.000 meter altitude, so the location can be counted as a major drawback too. Moreover, the grade of these mines are generally low. Majority of South America reserves are consisted of ulexite.

- **Tincalayu, Argentina:** Deposits include 300 Tt B_2O_3 by the borates tincal and kernite.

- **Salar de Surire Boron Deposits, Chile:** Deposit which is processed by Qui Borax Company, basically produces boric acid. It is one of the largest reserves around the world that has 1.5 Bt ulexite (B_2O_3 30 Mt) in Arica at altitude 4.050m.

- **Salar de Carcote ve Salar de Ascotan, North Chile:** In that source, 7 Mt B_2O_3 based ulexite are processed by SQM Salar Company.

- **Asian Boron Deposits:** Generally, Asian countries' boron reserves are constituted by magnesium borate (ascarite), limited tincal and boron silicate. Ores are generally low-grade so it causes many technological obstacles throughout production processes. Majority of ascarite ores, averagely contain 8-10% B_2O_3 , are located in China and Kazakhstan. Despite the amount of boron under the borders of China, 90% of their mine grades are under 12% (in the means of B_2O_3). Boron production is substantially carried out by employing the ascarite ores in the Northeast China but it is expected that these deposits will be consumed away soon. Qinghai boron sources have

similar mineral groups at an altitude of 4.000 meters as same as in South America.

Russian Boron Mines: Dalnegorsk is the most prominent boron deposit in Russia which has a grade of 9-12% B_2O_3 [25].

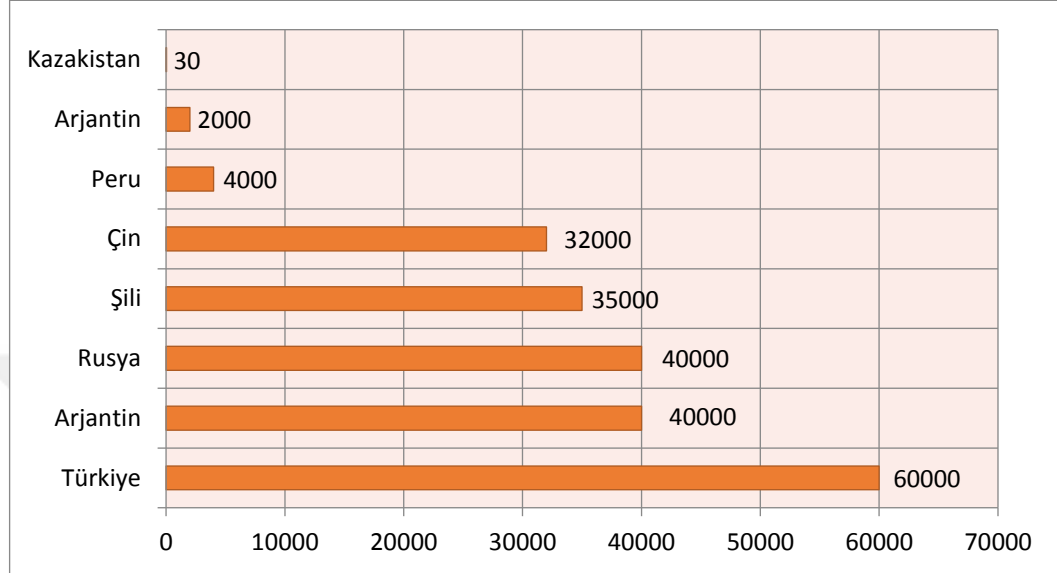


Figure 4.1 Boron reserves in the world 2013, leading countries (1000 metric tonnes)[28]

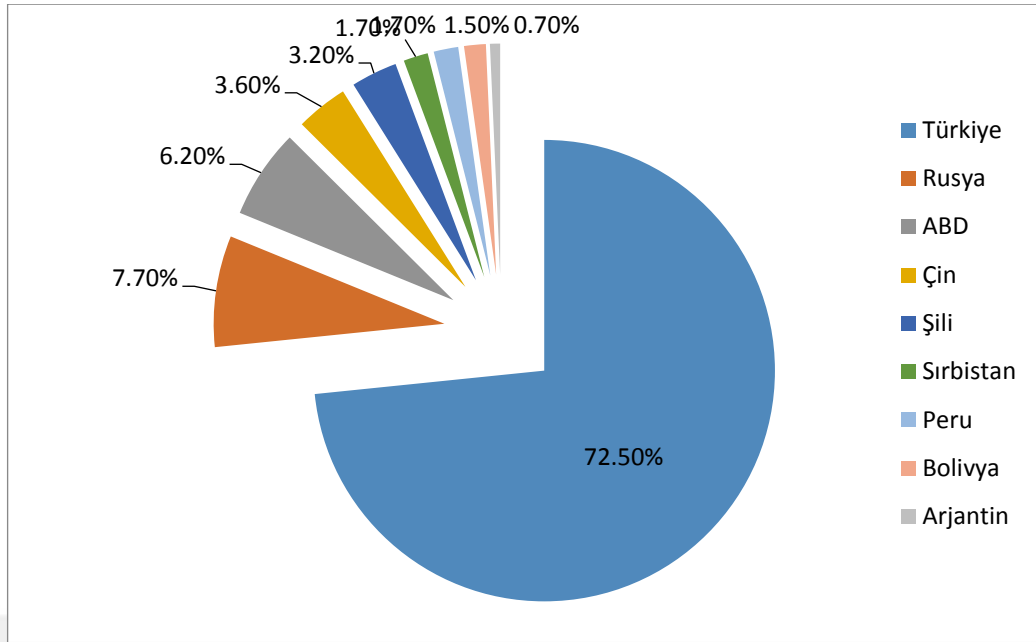


Figure 4.2 Distribution of the boron reserves in the world [28]

4.1.2 Boron Reserves in Turkey

By means of 2172 numbered law in Turkey, all activities related to boron mines were totally left to state-owned EtiMine which controls Kırka, Emet, Bandırma, Bigadiç and Kestelek operators in order to produce, process and market the resource for the state. The reupon, researches for boron ores have been widely concentrating since 1978.

Known borate deposits in Turkey are located in Kırka/Eskişehir, Bigadiç/Balıkesir, Kestelek/Bursa and in Emet/Kütahya. It is observed in the content of Boron Master Resarch Project which is carried on by Eti Mining Company in 2001 that the gross amount of deposits raised from 2.071.853.997 tons to 3.063.635.210 tons and the amount of B_2O_3 based minerals increase from 562.577.259 tons to 850.938.893 tons. It showed that the total amount of B_2O_3 based boron reserves in Turkey was increased from 64% to 72% in the World[32].

Tincal and colemanite are the most common ores in Turkey. Tincal reserves are located in Kırka and colemanite reserves are located in and around Emet and Bigadiç. Small amounts of ulexite ore appear in Bigadiç and it is produced as semi-finished products in Keselek from time to time[28].

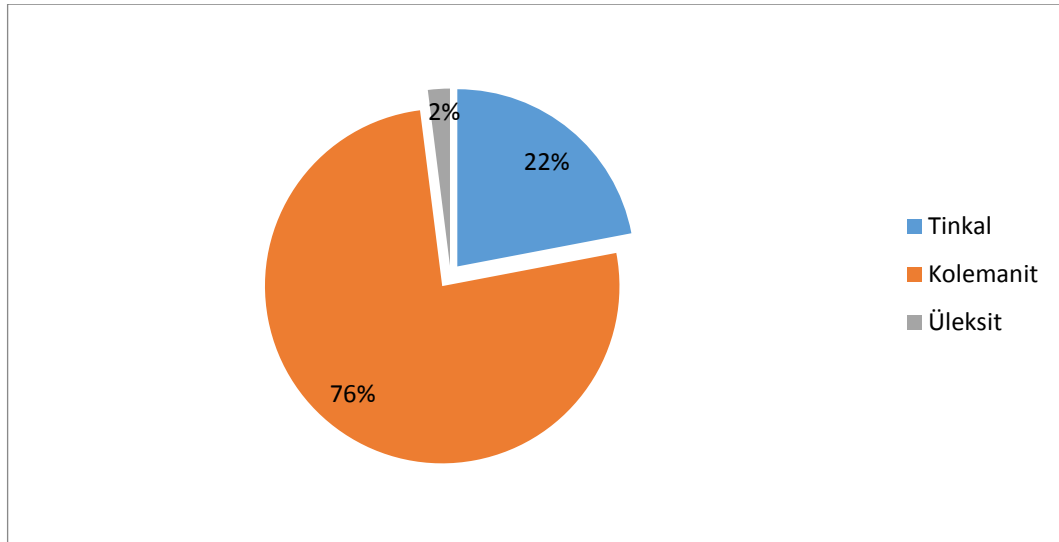


Figure 4.3 Distribution of the boron reserves in the Turkey 2012, on the basis of mineral [28]

4.2 Boron Production

4.2.1 Boron Production in the World

Leading boron-producer countries are Turkey, USA, Argentina, Russia, China and Chile. Turkey and USA take 72% of the whole pie just by themselves. While total B_2O_3 production was 768 Tt in 1970 in the world, it increased to 2.7 Mt in 2016. As one of the most important producer, Turkey has accelerated its B_2O_3 production from 122 Tt in 1970 to 1 Mt in 2012. In 2002, worldwide B_2O_3 production allocated 35% to Turkey and 34% to USA. However, Turkey has accelerated its portion from 35% to 40% in 2004 so the portion of USA drop behinded 33% in 2004[32].

Table 4.1 Principal boron producers in the world (1000 tones / year B_2O_3)[28]

Establishment	Country	Production (1998)	%	Production (2004)	%
Rio Tinto US Borax Co. (Borax Argentina included)	USA	587	41	565	33
Eti Maden Management	Turkey	434	30	671	40

Government Organizations	China	140	9	-	-
JSC Boron	Russia	73	5	-	-
Sucersal Argentina	Argentina	50	3	-	-
Quiborax	Chile	44	3	-	-
Searles Lake Valley Co. (IMC Global)	USA	27	2	-	-
SQM Salar	Chile	16	1	-	-
Inka Boron	Peru	13	1	-	-
Others		67	5	460	27
Total		1438	100	1696	100

4.2.2 Boron Production in Turkey

Eti Mining is a state foundation and the single producer and supplier of boron products in Turkey. Concentrated and refined boron production are handled by Eti Mining by means of running Kırka, Emet, Bigadiç and Kestelek mines.

Bigadiç Boron Mining Management production facility is settled in Osmanca village which is located in northeast Turkey, 12 km away from Bigadiç. The facility produces concentrated colemanite and ulexite. Three furnaces named as Tülü, Acep and Simav are operational to this day since 2005. Extracted boron ores are beneficiated in concentrator and some part of are sold as concentrated product and other of that are used to produce grinded colemanite and refined boron products.

Emet Boron Mining Management production facility is located at Espey (4 km to North of Emet) and Hisarcık (12 km to South Emet) regions which are 100 km away from Kütahya. Colemanite is produced in both regions. Extracted boron ores are beneficiated in concentrator and some part of are sold as concentrated product and other of that are used to produce boric acid.

Kırka Boron Mining Management production facility is located in Kırka which is 74 km away from Eskişehir. It's the largest tincal deposit around the world. Tincal ores are processed by open-running system. After they are converted to concentrated tincal, most of them are used to produce borax pentahydrate.

Kestelek Boron Mining Management production facility is located in Kestelek which is 83 km away from Bandırma. Only colemanite is produced in this open-pit mine. Produced colemanite ores are beneficiated in concentrator and processed to produce concentrated colemanite.

Bandırma Boron and Acid Factories Mining Management production facility is established on 667,350 m² area which is 4 km away from city center on the road between Bandırma and Balıkesir. In these facilities, Borax decahydrate, borax pentahydrate, boric acid, sodiumperborate monohydrate and sodiumperborate tetrahydrate. Also, It is started to produce Boron oxide by putting into operation with a new plant in December in 2005[32].

Table 4.2 The capacities of the concentrated and refined boron products (1000 tons/year)[33]

Establishment	Product	Consantrated Boron	Refined Boron
		Situated Capacity	Situated Capacity
Kırka Boron Management	Tincal Concentrate	800	-
	Borax Pentahidrate	-	480
Bandırma Boron and Acid Factories Management	Borax (Deka+Penta) Hidrate	-	55
	Boric Acid	-	85
	Boron Oxide	-	1
	Sodium Perborate	-	20
Bigadiç Boron Management	Concentrate Colemanite+Ulexite	650	-
	Grain Colemanite	-	90
Emet Boron Management	Consantrated Colemanite	900	-
	Boric Acid	-	100
Kestelek Boron Management	Consantrated Colemanite	100	-
Total		2450	831

4.3 Import and Export Datas

The import and export datas of the leading countries are given in Table 4.3 and Table 4.4 respectively.

Table 4.3 Export datas [34]

Country	Value (\$)	Percent (%)
USA	187.709.397,2	30
TURKEY	164.280.132,8	27
CHILE	74.041.525,4	2
RUSSIA	57.372.963,8	9,3
ARGENTINA	26.316.482,3	4,3
PERU	25.658.857,6	4,2
BELGIUM	13.732.065,8	2,2
CHINA	11.280.878,5	1,8
BOLIVIA	11.187.632,9	1,8

Table 4.4 Import datas [34]

Country	Value (\$)	Percent (%)
CHINA	124.168.766,8	19
JAPAN	72.542.212,9	11
SOUTH KOREA	38.038.502,8	5,8
BRASIL	36.642.251,3	5,6
HOLLAND	36.058.713,7	5,5
USA	36.058.713,7	5,5
TAIWAN	33.689.000	5,2
GERMANY	28.588.897	4,4
OTHER ASIA	26.919.851	4,1

5.1 General Applications

- Glass
- Ceramic
- Detergent
- Agriculture
- Other Applications [35]

5.1.1 The Use in the Production of Borasilicate Glasses

The main use of borates is glass industry. Boron oxide is an essential compound of borasilicate glasses, textile glass emanels and insulation glass emanels. These three well-known products are the main consumption of boron compounds in Glass industry. Boron also can be rarely found in the content of plate and container glasses. B_2O_3 can be added as anhydrous borax or boric acid into glass composition. B_2O_3 is a strong glass-former which means it devitrification (crystalization). It decreases expansion rate, causes resistance against thermal shocks[36].

Boron supplies heat resistance, quick melting, devitrification protection for glasses. Moreover, it gains many properities such as: Reflection, breakage, shining etc. Also, Boron protects glasses against acids and scratching. Melted glass occurs with a percentage of Boron oxide between 0.5% and 0.23% that depends on glass type. Generally, borax, colemanite, boric acid are mixed and used as additional to glass[35].

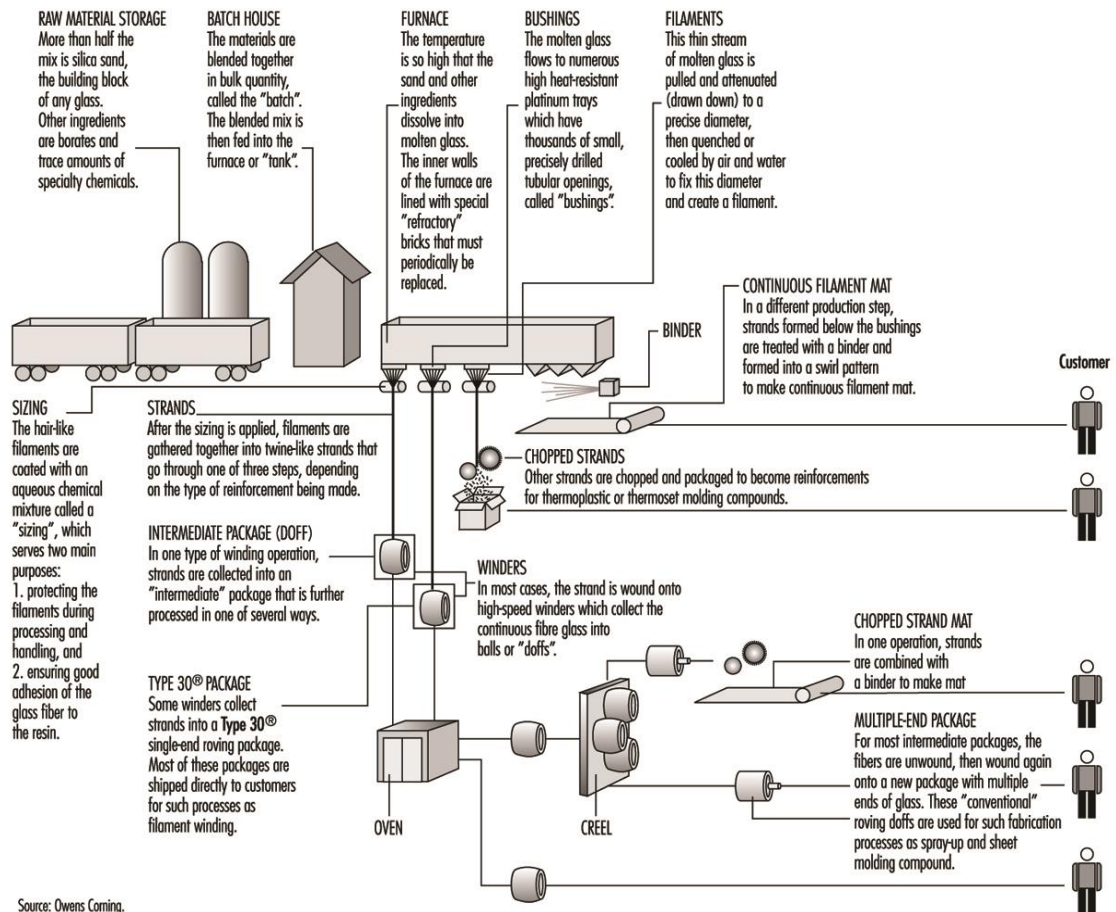


Figure 5.1 Boron in borasilicate glasses [25]

5.1.2 Use in Ceramics

Boron oxide, borax, colemanite and other sodium borates are used to produce ceramic glazes. These components are formed the mass percentage between 8-24% in production of ceramic glazes.

Effective role of boron in glazes is that it provides heat coherence between glass and material. Another role is that boron supplies glass occurrence in first steps of melting. Also, adding boron to glaze increase mechanical strength and stratching resistance.

Boron oxide can be used to until 20% for enamels to decrease viscosity and saturation heat additional raws in enamels are between 17 and 32% boric acids but preferably used aqueous boraxes. In some cases, boric acid or anhydrous borax also could be used. Enamels protect metals from oxidation and give them better appearance. Steel, aluminium, copper and silver can be covered by enamels. Also,

enamels raise up resistance against acids. they are generally used to cover kitchen tools, baths, chemistry equipments, water tanks, guns etc.[37].

Process	B ₂ O ₃ content in the frits (% by weight)	Firing conditions (Temperature/time)
Wall tiles - traditional double firing	8 - 20	(980-1000)°C / (360-720) min.
Wall tiles - fast double firing	4 - 10	(1060-1080)°C / (30-55) min.
Wall tiles - fast single firing	3 - 6	(1100-1120)°C / (35-55) min.
Stoneware floor tiles - fast single firing	0 - 3	(1140-1180)°C / (35-55) min.

Figure 5.2 Firing ranges of wall and floor tiles which includes B₂O₃ [38]

5.1.3 Frits and Enamels

Use of borates for glazes depends on resolution in water. Borax, boric acid and borax pentahydrate are highly decomposed in water. Resolved borate minerals need to be fritted to use as glazes. Fritting is a process, described that raw materials of glazes are melted and turn into glasses which are not resolved in water. Especially for floor and wall tiles, frit is commonly used. Borates which does not dissolve in water, and oxides are preferred for high temperature glazes because of their neglectable resolution rate in water. Colemanite is such a mineral that does not decompose in water but also it is a source of B₂O₃ so it becomes very useful for production of many glazes. Borates increases refractive index of glazes and provides brightness leading to decrease viscosity and surface tension of glazes. Also, it accelerates development of glazes and occurs smooth surface. Additional borates raises mechanical and scratching strength. Last but not least, it gains resistance against chemicals and hydro-shocks.

Enamels are used to cover metals. Covering metals with enamels serves the purpose to have chemical and heat resistance, supplies decorative appearance. Enamel frits are obtained by using borax, silica and soda. Contemporary frits could contain 25% boron oxide. Adding boric acid provides adhesion and covering for glazes at low temperatures. Enamel frits are different type of covering applications. They supply corrosion resistance and decorative appearance for metallic surface of under furnaces and washing machines by covering enamels. Enamel frits are produced by melting mixture of raw materials. In this process, obtained raw materials from glass are quartz, feldspar and borax. Enamel frit can be applied by blasting, dipping or

electrostatic blasting. Boron oxide supplement into existing raw materials between 17 and 32% of B_2O_3 as borax, borax decahydrate or borax pentahydrate. In some cases, boron oxide is added as anhydrous borax or boric acid[36].

5.1.4 Use in Hygiene and Whitening Industry

Modern detergents comprised of various materials. Surface active materials (sulfonate) decreases the surface tension of water so it wets fabric, supports the removal of oils and other stains. Detergent formatives (zeolite) get calcium and magnesium ions away from water if they are used in tough water. Therefore, efficiency of surface active materials increase. Bleaches (perborate and hypochlorite) remove stains by means of oxidation. Bleaching activator TEAD (tetraacetyl ethylene daimine) and sodium salts are used to gain bleach efficiency at low temperatures. Borax decahydrate is used less than 10% in soaps and detergents to kill microps and make water softer. On the other hand, sodium perborate is added around 10-20% in order to gain whitening effect [37].

Oxygen based sodium perborate and sodium hypochlorite are two main bleaches in detergent industry. Sodium perborate-including bleaches are used in Europe but, sodium hypochlorite based detergents are used in the United States. Hypochlorite is effective at 40°C. Perborates are more effective at 60°C. However, they are not sufficient at 40°C. To develop activity of sodium perborate at low temperature, washing time or bleach amount should be improved. Nowadays, TEAD, such an activator has used for increasing efficiency of perborate bleaches.

Bleaching sodium perborate is a white, solid and stable boron compound, obtained by reacting between hydrogen peroxide and borax. Sodium perborate contains 10,5% active oxygen. It also includes 15,5% active oxygen if it is produced with dehydration of tetrahydrate. Bleaches are not used for powder and liquid detergents. Conventional powder detergents comprise of 15-25% sodium perborate tetrahydrate. Sodium perborate is present as monohydrate up to 20% in its compact formulation. The most important reason of decreasing washing temperature of sodium perborate from 60° C to 40° C by last researchers is increasing use of polyester and synthetic fibers in its content because these materials need to be

washed at low temperatures. Perborate bleaches are less effective at low temperatures so high concentration is needed to have same performance [36].

Perborates carries active oxygens. Perborate monohydrates take place instead of perborate tetrahydrate for production of detergent because monohydrate is more resolvable than tetrahydrate in cold water [39].



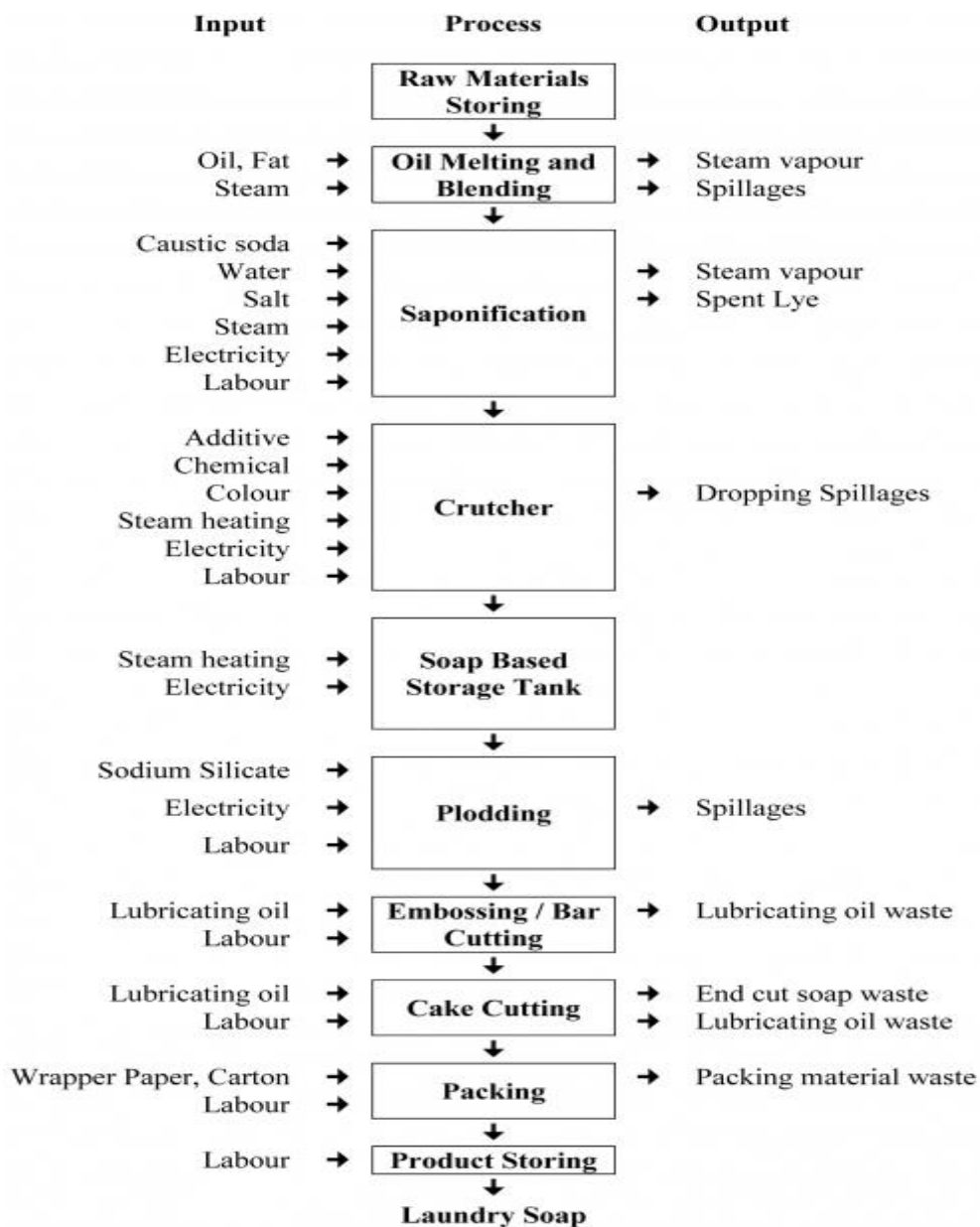


Figure 5.3 Process flow sheet of the production of laundry soap [21]

Bleaching activators also lead perborate to be solved at low temperatures. Low temperature determines type of used perborate. Sodium perborate tetrahydrate is less resolvable than monohydrate so its bleaching efficiency is not rapid enough. For that reason, detergent-producers use monohydrate even it is more expensive than tetrahydrate. Use of chlorade based bleaches cause harm to environment so it is started to stop using in the U.S.A a result, perborate based bleaches are requested day by day in most countries.

5.1.5 Uses in Agriculture

Boron is used in agriculture as fertilizer because use of fertilizer gains efficiency. Only 1,5 kilogram boron based fertilizer can obtain 18% more efficiency of tomato planting for each hectare. Boron fertilizer provides averagely 17% more efficiency for both suger beet and nut. Boron oxide is used for two purposes by applying low and high concentration: micronutrient, plant killer. Boron, copper, manganese, iron, molybden, zinc and cobalt are added to top dressing as micronutrient. Boron is added as granuls into top dressing compound and liquid fertilizer before blasting. Lack of boron causes short trunk, formless leaves, fragility in plants. Micronutrient fertilizers contains at least 200 ppm of boron. In agriculture, boric acid, sodium oktaborate, borax pentahydrate and boraxe are commonly used.

Even though little amount of boron is necessary for plants, high amount of it is poisonous. For that reason, borate can be used plant killer by means of its toxicity. However, it is limited in agriculture applications since it is not selective. Therefore, it is used to kill weed. Boric acid or borax pentahydrate or similar formulations are boron-containing compounds. Borax protects lumber from bugs. Boron components are especially posionous for flying insects. These insects damage structure of lumbers [36].

Boron minerals are also used in order to boost or decline development of endemic. Boron is a nutrient for many plants. Tuber crops (especially sugar beet), clovers, fruit trees, pear, olive, coffee, tobacco and cotton have lack of boron minerals. In these cases, fertilizers which are mixed with anhydrous borax and borax pentahydrate are used. Also easy-solutable sodium perborate and disodium oktaborine are used by spraying onto agricultural products. Boron minerals take asisstant roles to develop plant roots, leaves, bloom, polen production, shoots, seeds and fruits [35].

5.1.6 Use in Textile Fiberglass Production

The most important properities of textile fiberglas are that tension strength, toughness, chemical resistance and lightness. Becase of these characteristics, textile fiberglasses are used in order to supply strength for plastic fiberglasses and

composites. Colemanite does not include alkali so it is preferred to utilize for production of low-alkali borosilicate (E-glass). Boron is added to textile fiberglass as colemanite mineral or boric acid. Modern E-glass contains 6-10% B_2O_3 . Boron oxide contributes stability to glass. Colemanite which does not contain sodium is used for applications instead of expensive boric acid. Low alkali rate decreases melting of glass conversely boron oxide increases. Colemanite also contributes Calcium oxide to blend so it causes decline for use of lime. E-glass is used in boat, aircraft and automobile industries. E-glass is also an calcium aluminosilicate glass that has determinate mechanical, chemical and electronic properties. Therefore, it is utilized for composites. High tension glass materials which have low dielectric properties are significant for confidentiality because these materials can not be detected by radars [36].

5.2 Other Use of Areas

5.2.1 Construction-Cement Industry

Boron is used in order to increase strength, isolation for constructions (harder, lighter and durable constructions against earthquakes). Expanded perlite can be used for walls and floors in order to have insulation of sound and heat. In these applications, Expanded perlite is filled between double walled facade. As an inorganic material, perlite's pH is around 6-7. Therefore It is chemically passive and does not degrade. Also, it is not affected from bacteria and bugs. The use of boron gains strength to cement. Boron mixed cement are especially used for concrete roads and dam constructions. A thousand meters road are builded in North of Turkey to search road performance effect and utility of boron based cements for boron road building. In worked searches, potential use of boron cements are determined:

- i. For tunnels because of high strength
- ii. Dams and concrete roads
- iii. Tubular passage
- iv. Construction of nuclear energy station
- v. High buildings [35]

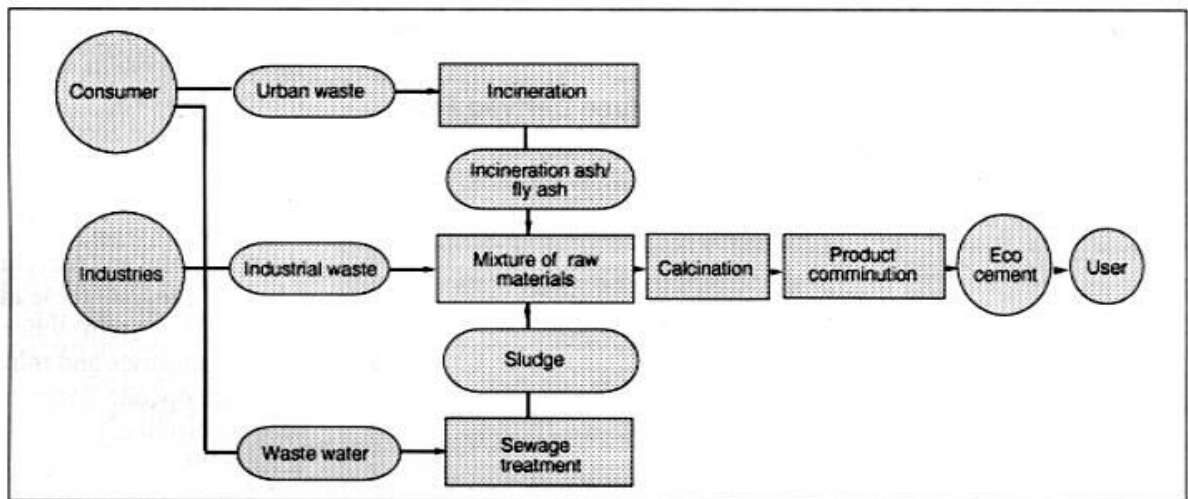


Figure 5.4 Cement production from recycling of industrial and urban wastes [40]

5.2.2 Fiberglass Insulation

Fiberglass contributes hardness and durability to materials. It is pretty cheap light material and has good tensile strength and resistance against chemical effects. For these properties, it takes a part in plastic, rubber and paper sectors. Sclerotic plastics are used in automotive and aviation industries and also used for steel and other metals [35].

Production of insulation type of fibreglasses comprises process of expanding surface area of glass to produce fibrous and wooly products. Raw materials which are used for glasses are similar to used materials for insulation type of glasses. After raw materials mixture is melted at 1450°C , it is poured on stainless steel spinner or twister. Fibers, produced by these processes, are plastered with binding chemicals before it goes to furnace. These kind of fibreglasses are able to be utilized 6-9 mm diameters and up to 60 m in length. Felts are obtained by getting together fibers to provide heat and sound insulation [5].

Boric acid is a mineral that makes glass and decreases viscosity of melt to help becoming fibrous. Borax pentahydrate is commonly used to utilize insulation type of fibreglasses. Insulation type of fibreglasses are used as rolls to apply insulation on walls and ceiling in construction industry [36].

5.2.3 Nuclear Applications

Boron steels, boron carbides and titanium-boron alloys are used in atom reactors. Stainless boron steel is used as neutron absorbent rather than others. Approximately, each boron atom can absorb one neutron atom. Boron acts a part in reactor control systems, cooling pools and to shut reactors down by alarming system. Also, colemanite is used to stock nuclear wastes [37].

	B-10	B-11	Ag-105	Ag-107	Cd-113 †	In-115	Hf-174	Hf-176	Hf-177	Hf-178	Hf-179	Hf-180
σ_a (barns)	3835	0.006	38	91	20600	202	561	24	373	84	41	13
Natural Abundance (%)	20	80	52	48	12	96	0.2	5	19	27	14	35

Figure 5.5 Nuclear characteristics of elements

5.2.4 Combustion-Preventitive Matters

Boric acid and borate supply fire resistance to cellulose matters. They get hydric oxide away from cellulose before combustion temperature and cover surfaces of formed coals to prevent more advanced combustion. Usage of Boron components are dramatically increase because of their preventitive property against combustion. The primary boron compounds which avoid combustion are zinc borate, barium metaborate and amonium fluoborate [35].

Poliethylenic polymers are used in a wide range of applications like transportation and electricity. Concerning their chemical composition, these polymers can easily flamed. For this reason, flame retardants are crucial for these polymers. There are lots of different flame retardant materials. Recently, halogen compounds are widely used in this area but concerning their disadvantages (toxic smoke, corrosive), the world has turned to other materials for these applications. As a result, flame retardants like zinc borate, aluminum hydroxide and magnesium hydroxide get all the attention in this industry. Zinc borates are a group of flame retardants which are used with PVA (polyvinil asetate) [41].

Borates are used in textile industry in the form of glass fibre, through their flame retardant property. By the addition of flame retardants, the combustion and the spread of the flame are prevented.

Zinc borate is the product of the reaction between boric acid and zinc oxide. The use of zinc borate along with the alumina hydrates is developing day by day. Because these two materials do not create halogen coal during the production and they do not create toxic smoke in the case of burning. Borates avoid the combustion by melting and covering the materials surface, this way it cuts the contact between the flame and oxygen. Zinc borates are used with plastics.

The consume of the zinc borates per year is about couple thousand tons. They are mostly used with vinyl plastics. They are used only by themselves or along with other flame retardants like antimon oxide [42].

5.2.5 Metallurgy

Borates are used in the industry of non-ferrous alloys due to their stability, stickiness, the protectiveness and ability to create a burr-free slag in high temperatures. Borates are important supplies in electrolyte covering industry. Boric acid is used for the covering of nickel, fluoborates and fluoboric acids are used as an electrolyte for non-ferrous alloys. In steels, they are mostly used as a hardness increasing agent. They are also used as property boosters in friction-wear resistant materials, welding electrodes, refractories, brick materials, soldering, casting supplies, composite materials etc. Boron is normally used in steel production in the form of ferrous-boron. Ferrous-boron is produced by carbothermic reaction; reduction of boron oxide with carbon in high temperatures. Ferrous-boron can also be produced by aluminothermic reactions. Boron carbide is used as emery grains or powders. Boron carbide is also used for the surface hardening of steels and other ferrous-alloys. This process is sorted out by the diffusion of boron into the metals surface. This way, a ferrous-boron layer which has a thickness of 10 - 1000 μm , occurs. This layer is resistant to wear due to its high hardness. Commercial EKabor is used for this application [43].

Borate is utilized to have properties for liquids at high temperatures which are smooth sticky clear and without burs to be formed protective slag and to accelerate melting in non-ferrous industry. Fluborate, floboric acids, tin, lead, copper and nickel are used as electrolyte for non-ferrous metals and also boric acid is used for nickel plating. In addition to these, it is applied to increase hardener affect of steel for alloys. Especially ferrous boron takes an important part in that area. 50 ppm additional boron develop hardening property of steel in steel production [37].

5.2.6 Automobile Airbags and Antifreeze

Boron is used in order to swell up airbags as soon as possible at the moment of crash. In that second, powder mixture of elemental boron and potassium nitrate is activated by means of electronic sensor. It needs only 40 msec. to activate both system and airbags. Boron is used also as an antifreeze-agent in automobiles and its hydrolic systems [35].

5.2.7 Health

BNCT (Boron Neutron Capture Therapy) is used for cancer treatment. Especially in brain cancer, it is so preferable because it acts a vital part to choose and demolish injurious cells and also does not harm healthy cells. Furthermore, boron products are utilized in the treatment of other cancer types such as: lung and prostate cancers. Besides, it balances boron, calcium, magnesium and phosphorous amounts in metabolism. Last but not least, it helps to develop healthy bones, muscles and brain functions [37]. Boron components, used for BNCT applications are that Mercaptoundecahydrododecaborate , ($\text{Na}_2\text{B}_{12}\text{H}_{11}\text{SH}$, sodium borocaptate or BSH), bisphenol (BPA) and their derivatives.

The physical base of BNCT is simple. It is a dual compound system based on nuclear reactions. Helium (^4He) (α particles) and Lithium (^7Li) nuclei occur when low-energy or thermal neutrons are beamed up a stable isotope of Boron (^{10}B). These high energy particules cannot move further so they load their energies to tumor cells. In this way, they prevent breeding of tumor cells by directly damage DNA.

Basic reaction of BNCT is shown below:

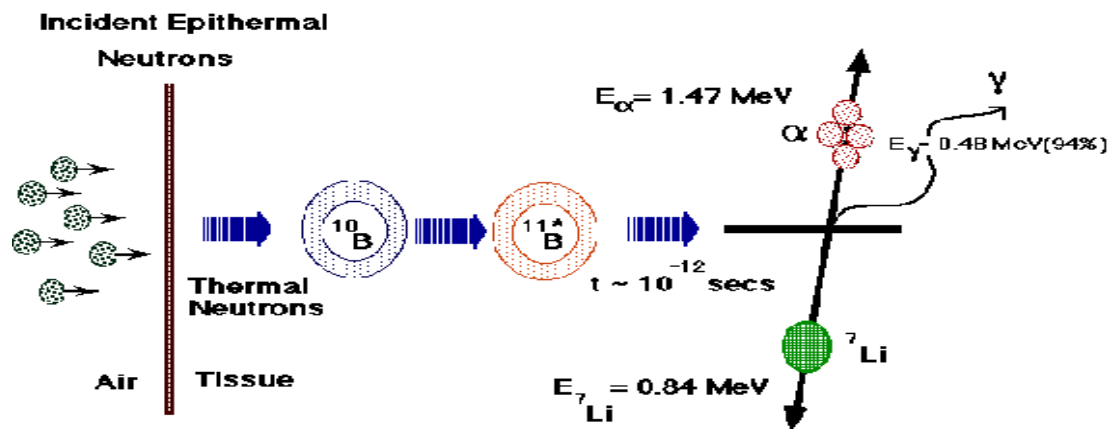
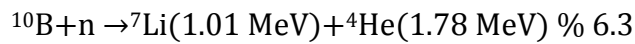
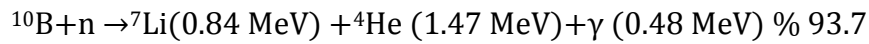


Figure 5.6 Schematic of explanation of BNCT reaction [40]

5.2.8 Electronics, Computer and Advanced Technology

Obtained fiberoptic glasses from boron and its derivatives effectively transmits light photons. Fiberoptic cables are an advanced technology that have wide application, especially for phones and computers. Recent years, new developed fiberoptic cables able to get high speed data conduction. Boric acid is extremely important for production of LCD screens. Turkish colemanite is raw material for current plate technology productions. These technology procuments are used for mobile communication devices such as: notebooks, computers, mobile phones. Also it is used for Information technologies boron is utulized also to produce capacitors. Capacitor is an electric device that stores and distribute energy in computers, automobiles, televisions, mobile phones, stereo equipments, CD players etc.

Known as METGLAS (Boron type) can save over 70% energy by means of combination of iron and rare earth elements. This strong magnetic production is used various applications such as: CD/DVD roms, direct current motors, household goods, portable power tools etc. Usage of Boron compounds in batteries and accumulators prodives decreasing cost loss and protection of environment [35].

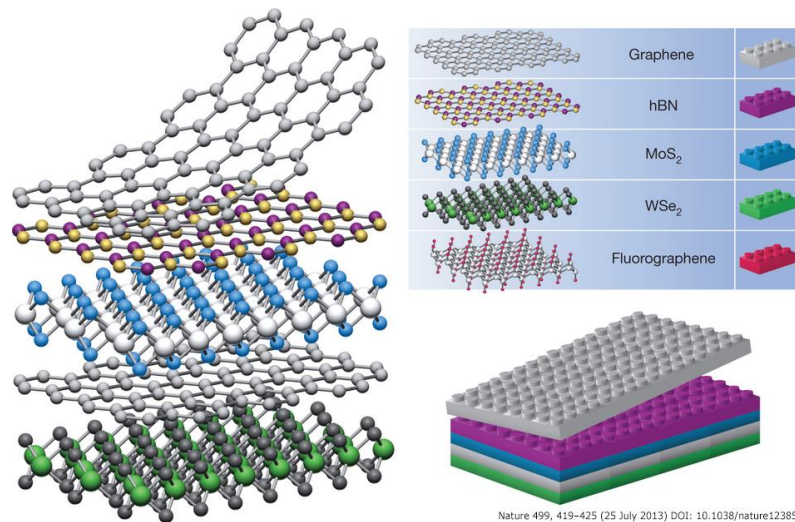


Figure 5.7 Crystal structures of different compounds [44]

5.2.9 Energy and Heat Storage

85% of total energy in the world, means almost whole amount of fossil fuel ruled by OPEC which is an organization that consist of 12 industrialised countries think the source will run out in next 50 years and this will cause that the organization will lost its dominance. It is known that The United states have been seaching for alternative energy sources since the beginning of 1950s. From this time to until end of 1963s, it is thought by U.S.A army that especially boron has strategic importance and as known that after Turkey become a member of NATO, it exported Boron minerals to Poland but it was prevented by USA navy in the dardanelles.

Today, Boron is used such a mineral for hydrogen fuel system that produces hydrogen during vechile motion and also supply 69% of fuel cell's energy for electrical motor-operated systems. Although it is technically developed an efficient alternative fuel system, costs of these system need to be decreased. For that purpose, researches work for it [45].

Combustion properties of boron directs researches to train it as alternative fuels and different type of technologies. A new system is developed that boron can be directly used as fuel and proved that it is better energy conveyor than hydrogen. Also boron compared with other alternative fuel systems such as: benzine, hydrogen, aluminium, magnesium, and determined its advantages [46].

Boron is on the top of elements which can produce energy themselves. Hydrogen is also upcoming alternative energy source because of its high energy intense. Scientists claim that hydrogen can be used in all use areas of fossil fuels [47].

Table 5.1 Energy source and energy values [46]

Energy Source	Energy(MJ/Lt.)
Hydrogen	8,03
Lithium	15,69
Beryllium	86,15
Carbon	54,01
Magnesium	29,52
Aluminum	57,42
Silicon	51,55
Phosphor	43,01
Boron	92,77

5.2.10 Others

- Cosmetics
- Explosives (firework etc.)
- Antifreeze
- Hydrolic Oils
- Petroleum Paints
- Nonflammable and Insoluble Paints
- Textile Paints
- Emery and abrasives
- Composite Materials
- Magnetic Tools

- Mummification [35]

Table 5.2 The usage areas of boron

Use Type	Distribution	
	Amount (Thousand Tones B ₂ O ₃)	Percent %
Type of Fiberglass Insulation	440	24,4
Type of Fiberglass Textile	370	20,6
Borosilicate Glasses	165	9,2
Enamel	350	19,4
Agriculture	120	6,7
Detergent	95	5,3
Other Areas	260	14,4
Total	1800	100

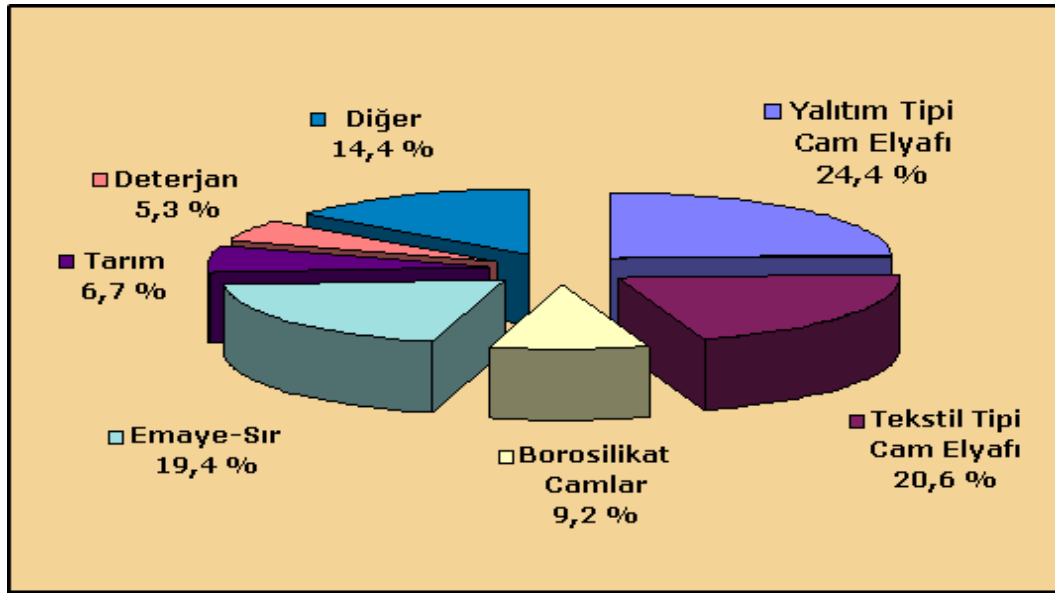


Figure 5.8 The usage areas of boron [3]

Table 5.3 Areas of some important concentrated and refined boron compounds [3]

Product	Use
Calcium Borate (Colemanite)	Type of fiberglass textile, boron alloys, metallurgical slag maker, nuclear waste storage
Sodium Borate (Ulexite ve Probertite)	Type of fiberglass insulation, borosilicate glasses, fertilizer
Tincal	Refined borons production (deka-penta), sodium perborate, boraks without water, disodiumoktaborate, pentaborate, metaborate,
Boric Acid	Antiseptics, boron alloys, nuclear applications, flame retardant, nylon, photography, textile, fertilizer, catalysts, glass, glass, enamel, cosmetics
Dehydrated Borax	Fertilizers, glasses, metallurgical slag maker, enamel, flame retardant, welding

Sodium Perborate	Detergent and bleach, textile, disinfectants and some of dental materials
Disodium Metaborate	Glue, detergents, agricultural, photography, textile
Sodium Pentaborate	Flame retardants, fertilizers
Refined Borax Dekahydrate	Adhesives
Refined Borax Pentahydrate	Cement, drugs and cosmetics, corrosion blocker, insect and fungus poisons, electrolytic refining, flame retardants, glass, fibre-glass, leather and textile
Disodium Oktaborate Tetrahydrate	Flame retardants, tree protectors

Table 5.4 The usage areas of some special boron chemicals [3]

Product	Use
Amorphous Boron	Military pyrotechnics
Crystalline Boron	Storage material for nuclear weapons and nuclear reactors
Bor Filaments	Composites for aviation and sports materials
Bor Halides (salts)	Drug Industry, Catalysts, Electronical Devices, Boron Filaments and Fibre Optics
Special Sodium Borates	Chemicals for photography, adhesives, textile, "finishing" compounds, materials of detergency and

	cleaning, fire retarder, fertilizer and agricultural medicines
Fluoboric Acid	Lamination suspensions, fluoborate salts, sodium boron hydrates
Trimethyl Borate	Sodium boron hydrates
Sodium Boron Hydrides (Sodium Borohydride)	Cleaning of metal surfaces, paper whitener and special chemical refining
Boron Esters	Catalysts for polymerization reactions, fire retardants

Boron Concentration and Production of Boron Chemicals

6.1 Boron Concentration

Main borates present in Turkey are tincal (sodium borate) and colemanite (calcium borate). Main gang minerals in the ore deposits are determined as clay minerals, quartz, volcanic tuff, calcite, gypsum, biotite, chlorite and limonite.

In colemanite ores, concentration is carried out by disintegration, washing and classification in the size fractions. In large sizes, colemanite concentrate is acquired through attrition tumbling and hand sorting. While in fines sizes (-6 mm), attrition scrubbing and classification in the size fractions are carried out. At Emet colemanite concentration plant at a capacity of 600,000 tons per year a colemanite ore of 27% B_2O_3 content is treated to produce a concentrate having 43% B_2O_3 at 300,000 tons per year. Flow sheet of the concentration plant is given Figure 6.1. In tincal ores, two different flow sheets are applied. The flow sheet in Figure 6.1, attrition scrubbing to the ore is followed by classification by the use of screens and cyclone. Then concentrate is produced in $-6\text{mm} + 0.1\text{mm}$ fraction. As sodium borate is soluble in water so that all the water is kept at close saturation with boron. At Kırka Concentration Plant, 1.2 million tons of tincal ore, having 26% B_2O_3 is treated to produce a concentrate of 34.5% B_2O_3 content with a total of 800,000 tons per year. In another process, where the effect of environmental impact is minimized, tincal ore is solubilized and solution is sent directly to produce boron salts. Solid waste is stored in a suitable area as indicated in Figure 6. In solubilization plant, the tincal ore having 26% B_2O_3 is treated at 200,000 tons per year [48].

6.2 ETI Kırka Boron Mining Management

6.2.1 History

Located in Kırka Town of the county of Seyitgazi/Eskisehir, Kırka Boron Works was established in 1970. The enterprise which was taken into operation through

organization of the Construction Site in 1970, acquired the "plant" status with the groundbreaking of the concentrator, and started to operate in "enterprise status" in 1975 with the commissioning of the concentrator.

The Enterprise Directorate was changed into Kırka Boron Works Enterprise Directorate as of 01/04/1979 and then, through its restructuring, into Enterprise Directorate as of 01/05/1998. As of 31/01/2004, the enterprise continues its activities as "Kırka Boron Works" affiliated to Eti Mine Works General Directorate. Today, Etibor-48 (borax pentahydrate) is produced in a total of 4 operating plants. The fifth Boron Derivatives Plant is currently in the phase of construction and will be commissioned in 2015. In addition, Etimatik Boron-based Cleaning Product has been taken into production within 2014. The investment on 30.000-ton capacity compacted calcined tincal production plant is still in progress and will be commissioned in 2015 [49].

6.2.2 Products

Etibor-48 (Borax Pentahydrate) ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)

Etibor-68 (Anhydrous Borax) ($\text{Na}_2\text{B}_4\text{O}_7$)

Calcined Tincal (Compressed)

Etimatik Boron-based Cleaning Product

6.2.3 Capacities

Borax Pentahydrate 840.000 tons per year

Borax Decahydrate 80.000 tons per year

Anhydrous Borax 10.000 tons per year.

6.2.4 Borax Pentahydrate (Etibor 48 – $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)

Ore (tincal) is provided from the open mine by exploding, than the homogenization processes will be done until the tincal concentration reaches 25-27%. The transportation to the factory is carried out by the trucks. Firstly, crushing and elimination processes are carried out in the factory. During the elimination process, undersize grains (<75 mm) will go straight to the silos. The ore which is deposited

inside the silos, is feeded to solubilisation gutter through the bands. Inside the solubilisation gutter, water is feeded (98 °C). The clay inside ore remains solid, the other constituents pass to liquid phase. The borax is separated from clay by helical system. The liquid phase will pass to decanter centrifuge, in this level, separation of the liquid and solid phase will continue.

In the thickener (the conical tank which includes a comb like part which achieves the separation of solid and liquid matter) precipitation process continues, flocculants are also added. The liquid acquired at the end of this process is yellow.

The following processes are carried out under saturated density (1.25 gr/cm³). The solution which is acquired at the end of the thickener process should not be cooled down. Because of this situation, there are liquid depositing tanks at the end of each station in order to keep the temperature stable.

The liquid acquired from the thickener passes through the filters in order to get purified from the microscale impurities. Purified liquid passes to the liquid deposit tank.

The liquid comes from the deposit tank, is subjected to crystallization process. During this crystallization process, the liquid super-cooled from 98 °C to 66 °C in vacuumed atmosphere. Bonded with the effects of temperature and pressure, a slop is acquired (5 or 10 mols H₂O). The slop passes to swan neck.

Inside the swan neck, the weak solution (consisting 10 moles H₂O) is separated from the main solution (consisting 5 moles H₂O). The main solution pass to pushing type centrifuge. After that, the main solution is forwarded to dryer.

Dryer is a horizontal fluid dryer. The delivery of the material is carried out by the vibration effect. The moisture percent is decreased from 5% to 1% in the dryer. The product acquired is elevated to the griddles. Oversize products are the ending product and they are deposited inside the silos. (Na₂B₄O_{7.5}H₂O). Undersize powder products are delivered to the anhydrous borax factory.

6.2.5 Etibor-68 (Anhydrous Borax) ($\text{Na}_2\text{B}_4\text{O}_7$)

The raw material of Etibor – 68 is powder formed Etibor – 48. The raw material is feeded in to furnace (1.5 tons/hour).

Natural gas is used as a fuel and it is applied inside the furnace from 4 different places. The temperature inside the furnace is 1000 °C. Feeded raw material transform from solid phase to liquid phase inside the furnace. The process occurring inside the furnace is dehydration.

5 mols H_2O is removed from the raw material. The liquid material which reached to the end of the furnace will fall to the cooling mill.

The liquid material will form a solid sheet after passing through the mill. The sheet material transported with steel bands to primary and secondary crushers.

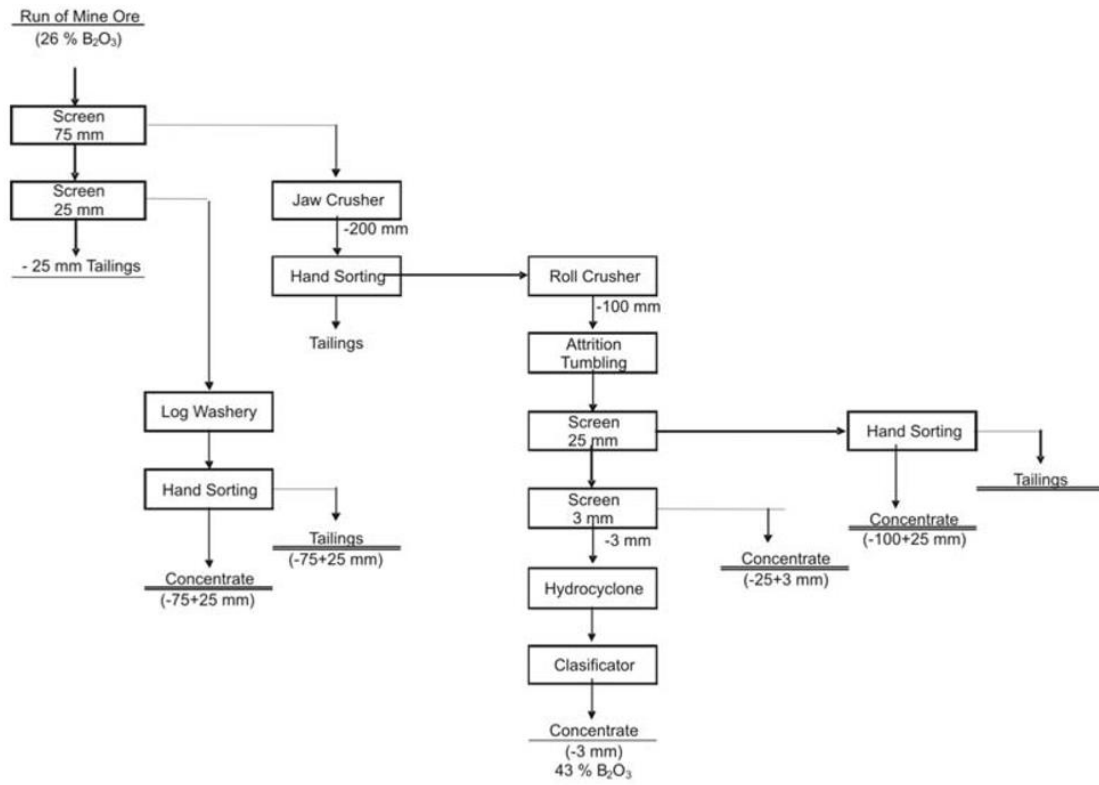


Figure 6.1 The flow-sheet of Emet colemanite concentration plant [48]

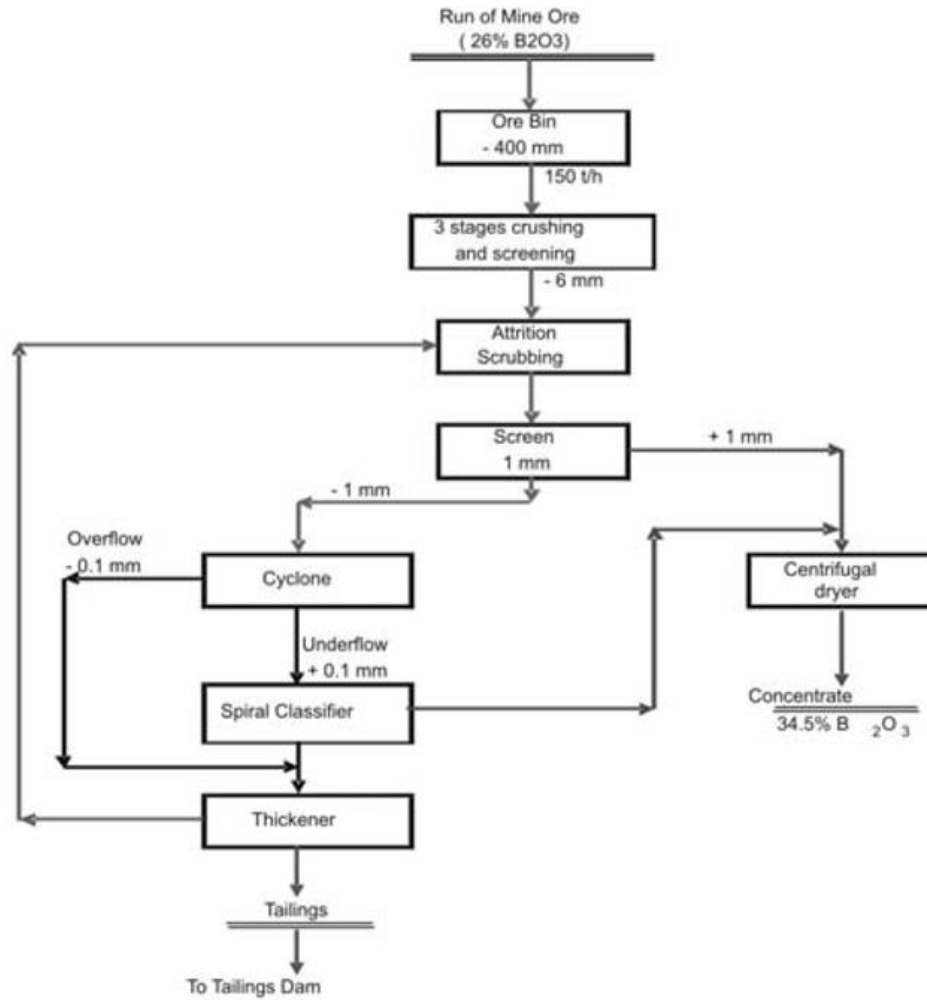


Figure 6.2 Flow-sheet of Kırka tincal concentration plant [48]

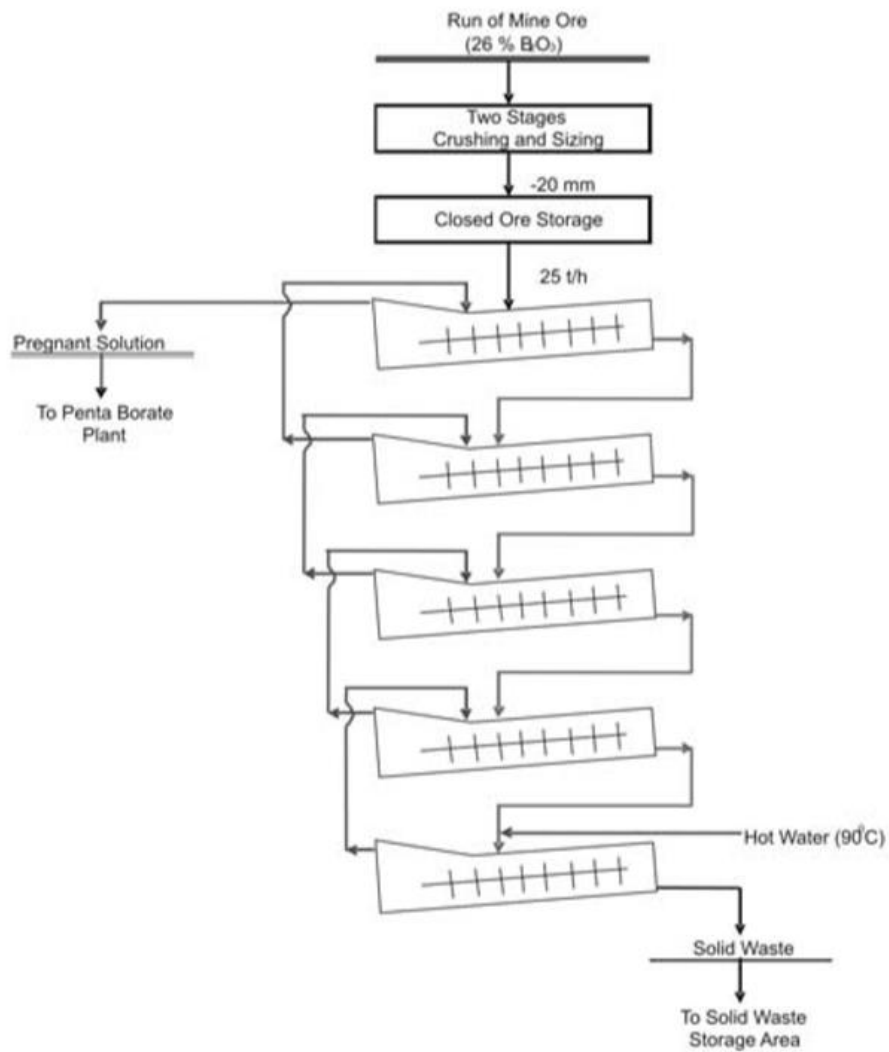


Figure 6.3 The flow-sheet of Kirka solubilization plant [48]

Increase in both production and consumption of boron based products year by year, affected the amount of wastes generated by the mining and enrichment processes in the same direction. In Turkey alone, owing to high production capacity of the mines, approximately 400 Tt of various boron-containing wastes are produced every year.

Discharge of the boron wastes causes soil pollution as well as economical loss due to dissolution of boron containing minerals with rain waters. Even boron is an essential element for plants, high concentrations can cause toxication. Therefore, numerous studies were carried out to understand the structure of boron wastes and utilize them in the appropriate industrial applications.

Boron wastes can be generated as both solid and liquid forms. Both forms have different characteristics due to differences in their content. Boron wastes used in this study only consisted of colemanite mining and enrichment wastes, so the following sections will only give details on colemanite wastes.

7.1 Liquid Wastes

Liquid boron wastes (LBW) are generated throughout the production of both refined and concentrated boron products. Amount of B_2O_3 in LBW are lower than most of the solid wastes and the included B_2O_3 is in aqueous form. LBW also include precious metals such as Li and Rb. Studies related to LBW mainly focused on the extraction of precious metals, not the B_2O_3 . The reason for that can be the low economical value of B_2O_3 when compared to Li or Rb. Because if the B_2O_3 present in the LBW were to be utilized, there should be an extra process for the precipitation.

In Turkey, LBW are stored as waste-lakes next to the mines. Dissoluted minerals present in the waste-lakes create risks for both economy and environment.

7.2 Solid Wastes

Solid boron wastes (SBW) are produced as side products in both mining and enrichment processes of borates. Amount of B_2O_3 in the SBW composition depends on the process it is formed in. SBW can be divided into 2 subgroups as mining and enrichment wastes.

7.2.1 Mining SBW

Mining SBW (MSBW) are generated during the mining processes which involves concentration of the mined borates. The amount of B_2O_3 present in the MSBW structures varies between 15-20%. 2 groups can be counted under MSBW, 1st group includes the wastes generated during the physical-manual extraction of the product from the clay structures and 2nd group includes the wastes generated during the enrichment via physical processes (watering, crystallization etc.). 1st group would likely to have lower B_2O_3 content when compared to 2nd group. MSBW include high amounts of CaO, SiO_2 and MgO in addition to B_2O_3 .

7.2.2 Enrichment SBW

Enrichment SBW (ESBW) are generated during the last stage of enrichment process which includes chemical treatment. Most of the clay structures present in MSBWs are removed from the structure of ESBWs. Therefore, the amount of B_2O_3 is significantly higher in ESBW ranging around 29-32%. Concerning the amount of B_2O_3 , enrichment wastes can be promising candidates to become a sustainable B_2O_3 sources. Only compound accompanying B_2O_3 in the structure of ESBW is CaO.

8.1 Materials

Starting the study, 6 different BWs (4 MSBW, 2 ESBW) were provided by Eti Maden. Necessary raw materials (clay, feldspar, calcite, etc.), deflocculants (Homopolymer sodium salt and sodium silicate), binders (CMC, etc.) for the production of wall, floor, porcelain tiles and opaque, transparent frits and glazes were provided by Eczacıbaşı-Vitra Yapı Gereçleri A.Ş..

8.2 Preparation of Wall and Floor Tile Slurries

To prepare the slurries, all the raw materials were dried in a Nüve FN 400 drying oven at 100 °C for 24 h in order to prevent humidity. Then, dried mixtures weighing 500 g were blended and grinded (Ceramic Instruments Rapid Mills-Moduler System SD Series) along with the addition of water and deflocculants to obtain a slurry. Compositions were grinded until a suspension with a particle size of 45 µm was acquired. Density of the slurry was measured by a TQC VF2097 pyknometer and was compared with the standard value range set for ceramic tiles (1648-1782 gr/lt). Asprepared slurry then subjected to a rheological study which included the addition of deflocculants until the slurry matched the desired (industrially standard) viscosity value and thixotropic characteristics. After each addition (0.1, 0.2 mg) of deflocculants, slurry was mixed by a IKA RW 20 Digital mixer at 700 rpm for 3 minutes for dispersion. After each addition and mixing, viscosity and thixotrophy values were measured by Brookfield Dial Reading viscometer. This process was continued until a viscosity within a range of 4.5-6.0 for floor tiles, 2.0-4.0 for wall tiles and 3.0-5.0 Poise for porcelain tiles was reached. The percentage of optimum deflocculant should be added was calculated according to Eq. 8.1. Flow-chart of the ceramic slurry preparation is given in Fig. 8.1.

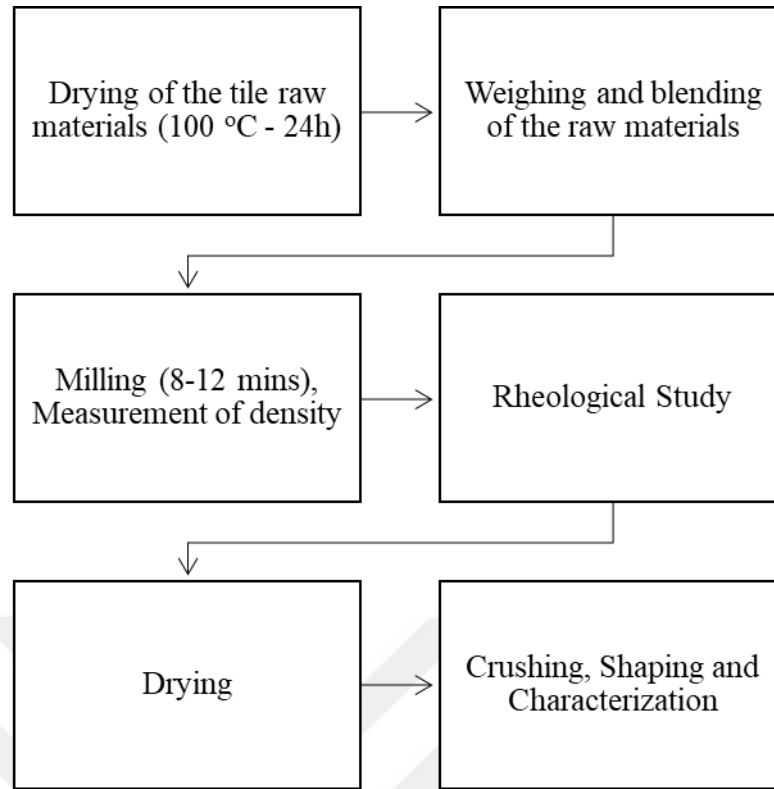


Figure 8.1 Flow chart of the experimental procedure applied to the FT and WT bodies

$$\frac{\text{Total Added Deflocculant Amount}}{\text{Total Solid Amount}} \times 100 = \text{Optimum Deflocculant Amount \%}$$

(Equation 8.1)

8.3 Preparation of Transparent and Matt Opaque Frits and Glazes

All the raw materials were first dried in a drying oven for 24 h at 100 °C to remove humidity. Then dried mixtures were weighed (500 g) and mixed. Prepared frit mixtures were put in porcelain crucibles and fired in Protherm PLF Series furnace for 1 h at a peak temperature of 1450 °C. Then fired frit mixtures were quenched in water down to room temperature to acquire frits. Acquired frits were dried at 100 °C for 24 h. Flow-chart of the frit preparation is given in Fig. 8.2.

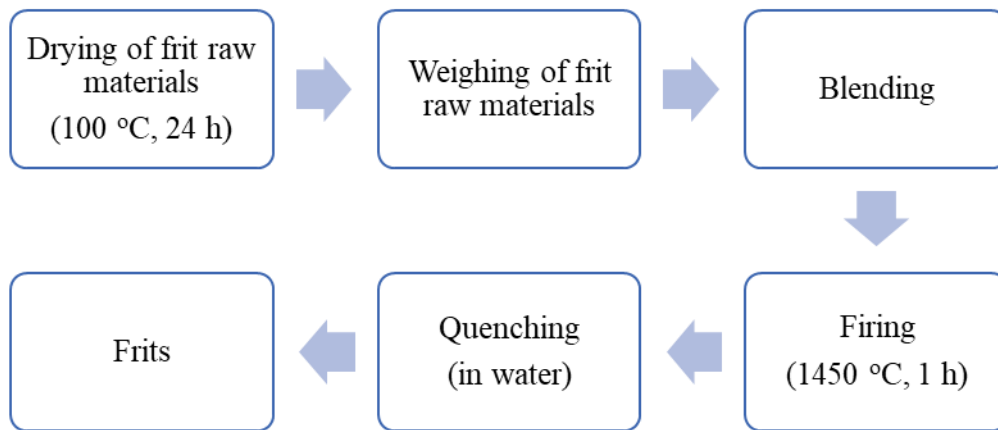


Figure 8.2 Flow of fabrication of opaque frits

Waste-containing frits were then weighed in 92 g and mixed with 8 g of kaolin, 0.1 g of carboxy-methyl cellulose, 0.4 g of sodium tripolyphosphate and 35 ml of water. Mixtures were ball milled to acquire a particle distribution under 45 μm . Acquired slips were named as “glaze suspensions” and applied on the sintered wall tiles. Glazed tiles were dried at 100 °C. Once dried, tiles were subjected to firing for 36 mins at 1145 °C in SACMI-FMS 2230 industrial roller furnace. Final layer on the tiles were termed as glaze. Flow-chart of the glaze preparation is given in Fig. 8.3.

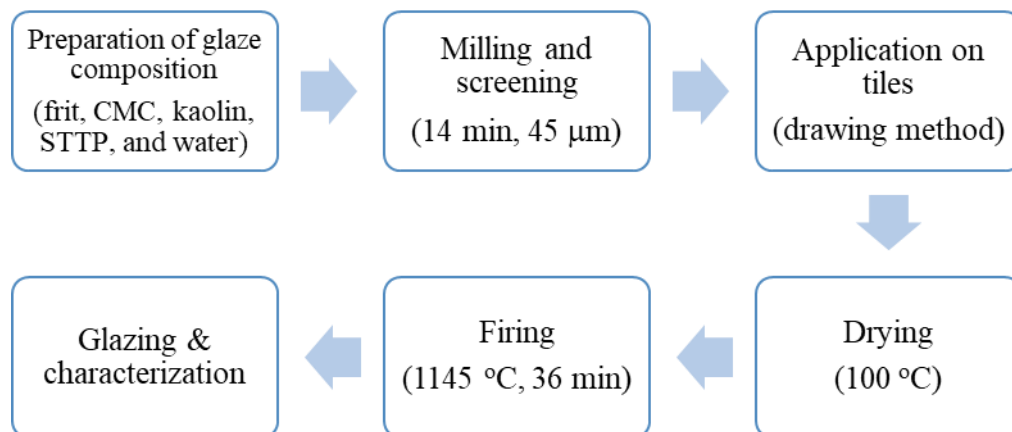


Figure 8.2 Flow of process for producing glazes

9.1 Chemical Analysis (Compositional)

Chemical compositions of the used BWs, standard wall, floor, porcelain tiles and frits were determined by XRF-Rigaku ZSX Primus analyzer. Exact amounts of the present compounds in all structures were characterized in order to assist the development of waste-containing compositions. Chemical analysis of the specific phases seen in the structure via SEM was carried out via SEM-Zeiss Evo 50 EP scanning electron microscope equipped with EDX.

9.2 Minerological and Phase Analysis

To identify the minerological content of the BWs, phase distributions of the fired tiles and developed frits, Rigaku Rint 2000 XRD analyzer was employed. Analyses were carried out with 40 kV acceleration voltage and 30 mA current by $\text{CuK}\alpha$ radiation. BWs were characterized between $10^\circ - 70^\circ$ while tiles and frits were characterized between $10^\circ - 90^\circ$.

9.3 Microstructural Analysis

Microstructures of the developed tiles and frits were characterized by SEM-Zeiss Evo 50 EP scanning electron microscope equipped with EDX. BWs, developed tiles and frits were first coated with a mix of Pd and Au.

9.4 Thermal Analysis

Sintering behaviour of the developed tiles and frits were determined by ODHT-HSM 1600/50, Misura 3.32 optical dilatometer. The sintering, softening, sphere, half-sphere, and melting temperatures of frits were determined by heating the frit samples to 400°C at a rate of $30^\circ\text{C}/\text{min}$ and to 1400°C at a rate of $10^\circ\text{C}/\text{min}$. For floor and wall tiles tests were carried out with a heating rate of $50^\circ\text{C}/\text{min}$ up to 1250°C and 1120°C respectively.

To determine the crystallization temperatures of the frits, differential thermal analysis (DTA) (Netzsch STA 409 PC) was performed; during the analyses, the frits were heated to 1200 °C with a rate of 10 °C/min.

9.5 Optical and Color Analysis

Color values (L^* , a , and b) of the developed tiles and frits were regulated using an X-rite color identifier and brightness values of the glazes derived from the developed frits were identified by using a Multi Gloss 268 Plus, Konica Minolta glass-meter.

9.6 Mechanical and Chemical Resistance Tests

Waste-containing tiles were shaped as discs ($D=5$) cm for water absorption and they were shaped as plates (10x5) cm for firing shrinkage tests and fired strength according to the TS EN ISO 10545 and tested [50]. Firing conditions of the developed tiles were determined earlier during the optical dilatometer tests, so mechanical tests were carried out on the fired tiles. Fired strength of the developed tiles were measured by Gabbrielli Flexi 100 three-point bending test device by the Eq. 9.1. Water absorption values of the developed tiles were determined by the vacuum method. Samples were held and vacuumed (600 mm Hg) in water absorption tank for 30 minutes, then the vacuum removed and samples were held in the water for another 15 minutes [51]. Water absorption of the samples were calculated by Eq. 9.2.

$$\sigma = \frac{3.P.L}{2.b.d^2} \quad (\text{Eq. 9.1})$$

σ : Strength (N/mm²)

P: Force (N)

L: Distance between supports (mm)

b: Length of the fractured plane (mm)

d: Width of the fractured zone (mm)

$$\% \text{ Water absorption} = \frac{100.(W-D)}{D} \quad (\text{Eq. 9.2})$$

D: Dry weight

W: Water absorbed weight

ISO 10545 standard defines the tests used on traditional ceramic tiles and glazes. According to this standard, chemical resistance, thermal shock resistance, staining resistance, Mohs (surface) hardness, surface abrasion resistance, and crazing resistance tests were carried out on the glazes derived from developed frits.



10.1 Characterization Results of the BWs

Beginning the research, received BWs were exposed to XRF and XRD tests to obtain their structure to consummately accomplish the implementation of them into tile compositions. 4 of the BWs were colemanite MSBW, 1 of them being a member of 1st group, coded as A4, 3 of them being a member of 2nd group, coded as A1, A2 and A3. Other 2 BWs were colemanite ESBWs and coded as A5 and A6. Chemical compositions and diffraction patterns of the BWs were given in Table 10.1 and Fig. 10.1 respectively.

As can be seen from Table 10.1, amount of B₂O₃ in the BW structures ranges between 16-32%. As earlier discussed, ESBWs have higher B₂O₃ concentration when compared with MSBW. CaO is present in every BWs content ranging between 23-53%. Such high CaO content in all structures is caused by the wastes being colemanite mining and enrichment wastes. Ca is the second most included element in colemanite structure. Also it can be seen that MSBW have higher amounts of MgO when compared to ESBWs. The reason for such difference is the chemical concentration process applied on the ESBWs.

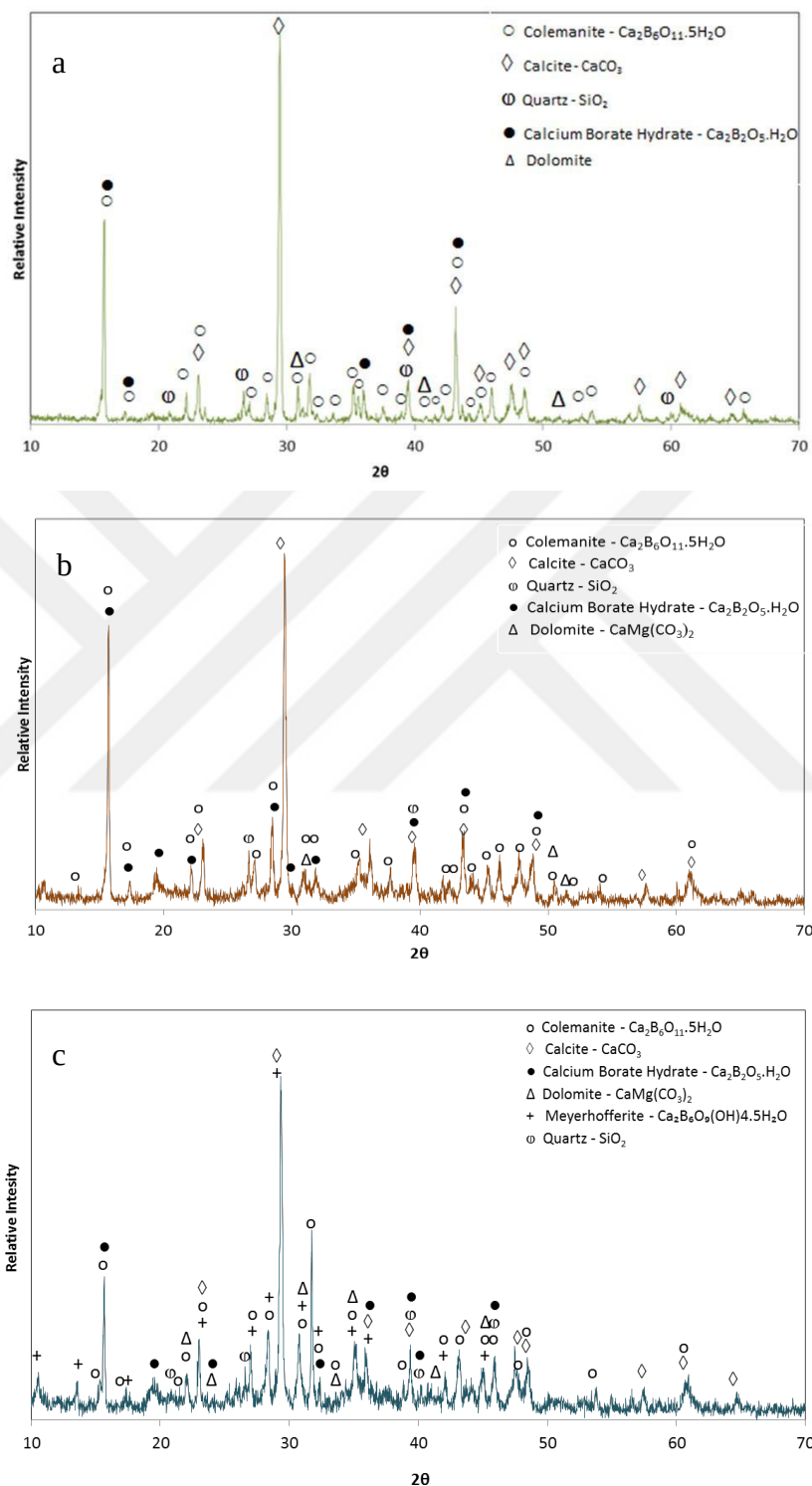
Table 10.1 Chemical compositions of employed boron mining and enrichment wastes

Oxides (wt.%)	A1	A2	A3	A4	A5	A6
SiO ₂	10.25	19.81	16.98	17.13	0.39	1.28
Al ₂ O ₃	0.34	0.72	0.57	0.31	0.11	0.63
Fe ₂ O ₃	0.19	0.33	0.24	0.31	0.13	0.13
B ₂ O ₃	20.41	18.41	21.20	16.37	29.52	31.11
CaO	34.18	25.34	23.31	31.28	52.75	33.41
MgO	3.70	8.96	8.82	7.32	0.80	0.60
K ₂ O	0.04	0.13	0.12	0.17	0	0.03
Na ₂ O	0.17	0.57	1.34	0	0.81	0.90
P ₂ O ₅	0	0.04	0.01	0.03	0.01	0.01
SnO ₂	0	0	0	0	0	0.338
Cr ₂ O ₃	0	0	0	0	0	0.03
BaO	0	0.23	0	0	0	0
*L.O.I.	30.17	24.11	24.97	25.43	14.68	30.74

*L.O.I.: Loss on ignition

As can be seen from the patterns in Fig. 10.1, BWs which are classified as MSBW_s included typical ceramic raw materials such as calcite, dolomite and quartz alongside with colemanite and calcium borate hydrate. Reason for the content of those soil elements is the BW_s being MSBW_s. This is also the reason for boron being included in the wastes as colemanite and calcium borate hydrate. For the ESBW_s

(A5 and A6), boron is no longer included as colemanite owing to the applied enrichment processes. Also typical soil phases are no longer present in A5 waste and the amount of those phases are decreased in A6 waste.



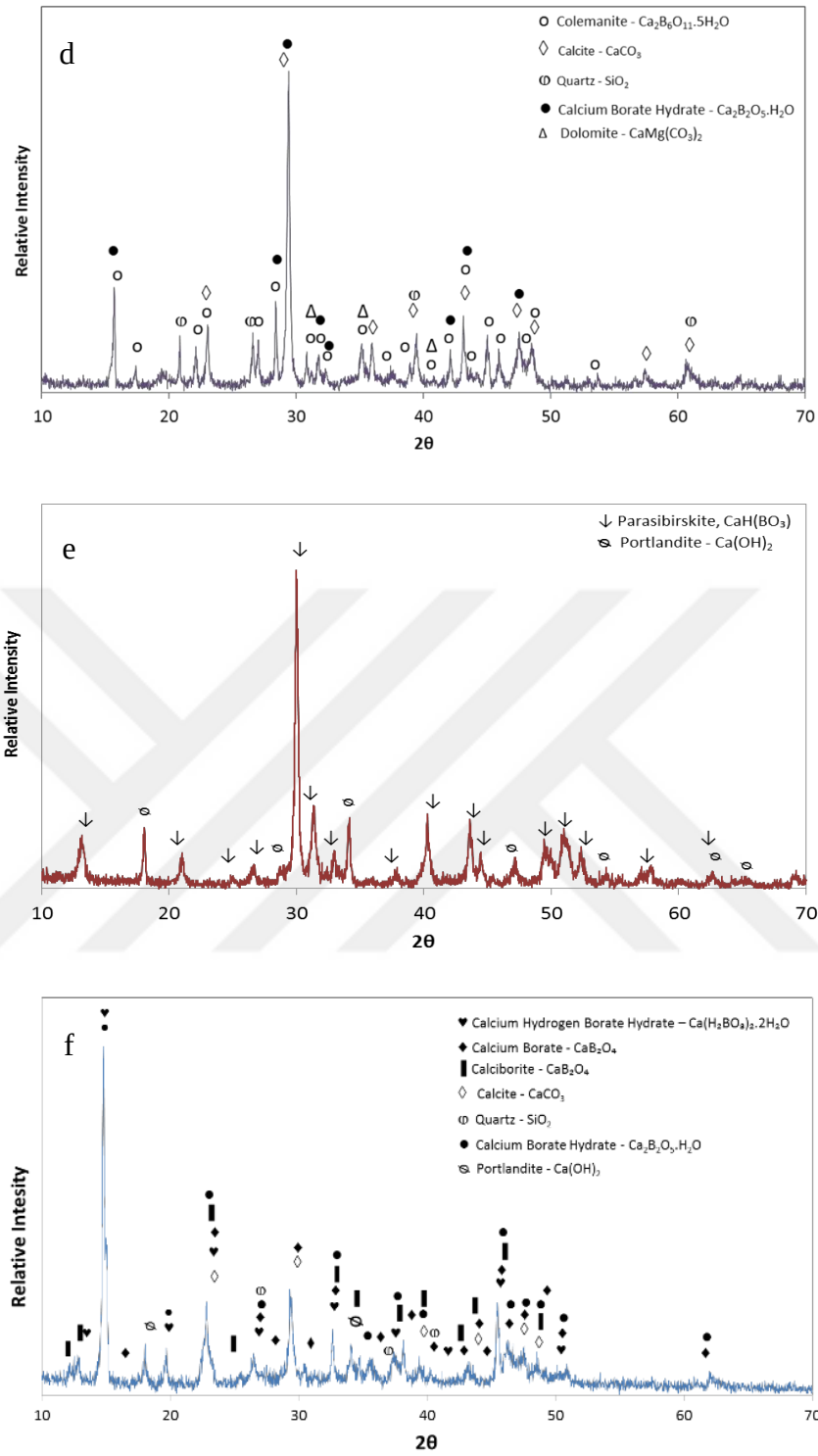


Figure 10.1 XRD patterns of the boron wastes A1 (a), A2 (b), A3 (c), A4 (d), A5 (e), A6 (f)

10.2 Methodology for the Development of Waste-containing Tile Compositions

As a start, industrially standardised wall, floor and porcelain tiles were subjected to XRF analysis to determine their exact oxide amounts and ratios, in other words Seger tables. Standard wall, floor and porcelain compositions were coded as WT-STD, FT-STD and PT-STD respectively. Chemical compositions of the standard tiles are given in Table 10.2.

Table 10.2 Chemical compositions of standard floor, wall and porcelain tile

	FT-STD	WT-STD	PT-STD
Oxides	Wt%	Wt%	Wt%
SiO ₂	63.58	56.42	67.11
Al ₂ O ₃	19.48	17.99	18.03
Fe ₂ O ₃	1.72	1.84	0.41
B ₂ O ₃	0.00	0.00	0.00
TiO ₂	0.60	0.75	0.41
CaO	1.60	8.57	2.48
MgO	2.14	0.42	0.88
Na ₂ O	0.00	0.74	2.36
K ₂ O	3.00	2.70	1.44
P ₂ O ₅	1.73	0.04	0.05
ZrO ₂	0.19	0.24	0.00
*L.O.I.	5.96	10.31	7.37
Total	100	100	100

*L.O.I.: Loss on ignition

The Seger tables were used to stabilize the entering amount of oxides in the new ceramic formulations identical to that of FT-STD, WT-STD and PT-STD compositions. Forming of the Seger tables was done by using the oxide ratios ($\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}/\text{K}_2\text{O}$, MgO/CaO), total amount of alkilines and total amount of R_2O_3 for FT-STD, WT-STD and PT-STD compositions. The rule of keeping these values constant was crucial for the experimental study, because changing amounts of oxides can encourage the formation of unwanted phases. Having different phases may result in showing different mechanical properties or having an unstable rheological behaviour. In order to prevent this obstacles, new compositions were developed under these circumstances.

10.2.1 Development of Waste-containing Floor Tile Compositions

Seger formulations corresponding to the FT-STD composition are given in Table 10.3. Depending on the XRF analysis, total alkaline concentration was 0.149%. For this reason, the new waste-containing compositions were modified to have the same value.

Table 10.3 Seger formulations of FT-STD composition

Seger Elements	Seger Ratios
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5.549
$\text{Na}_2\text{O}/\text{K}_2\text{O}$	2.629
MgO/CaO	1.867
B_2O_3	0.000
Total Alkaline (Li_2O , CaO , MgO , BaO , K_2O , Na_2O)	0.149

Total R ₂ O ₃	1.355
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The Seger tables of the waste-containing compositions are given in Table 10.4, and are compared to that for FT-STD. Waste-containing compositions were coded concerning their type, employed BW code and number. As seen from Table 10.4, total alkaline amount and ratios between oxides of the new FT compositions were similar to those of the FT-STD. However, the ratio of MgO/CaO was not controlled and maintained perfectly due to the high CaO content in the boron wastes used. Also it is known that increasing amounts of Ca⁺² cation provides excessive flocculation in the slurry. Ca⁺² cation has the highest flocculation coefficient among other cations. The reason for the efforts given to maintain the CaO/MgO ratio not only depends on the possible effects on mechanical properties, also on the rheological properties.

Table 10.4 Seger formulations of waste-containing FT compositions in comparison with FT-STD

	SiO ₂ / Al ₂ O ₃	Na ₂ O/ K ₂ O	MgO/ CaO	B ₂ O ₃	Total Alkaline	Total R ₂ O ₃	Waste Amount in Composition (wt.%)
FT-STD	5.549	2.629	1.867	0.000	0.149	0.202	0.00
FT1-A6	5.584	2.690	0.951	0.108	0.166	0.212	4.00
FT2-A6	5.547	2.642	1.326	0.055	0.160	0.207	1.96
FT3-A6	5.544	2.668	0.844	0.143	0.177	0.216	5.66
FT4-A6	5.636	2.682	0.268	0.199	0.149	0.222	6.62
FT1-A1	5.665	2.706	1.005	0.072	0.170	0.204	4.17
FT2-A1	5.564	2.631	1.355	0.036	0.160	0.204	1.96
FT3-A1	5.596	2.634	0.905	0.092	0.180	0.207	5.66
FT4-A1	5.688	2.642	0.358	0.113	0.149	0.211	5.76
FT1-A2	5.576	2.633	1.539	0.018	0.150	0.203	1.00
FT2-A2	5.813	2.607	0.532	0.196	0.200	0.217	1.80

FT3-A2	5.691	2.638	0.843	0.116	0.175	0.209	7.67
FT4-A2	5.733	2.655	0.563	0.104	0.149	0.209	5.85
FT1-A3	5.798	2.801	0.582	0.132	0.149	0.211	6.43
FT2-A3	5.825	2.779	0.571	0.154	0.160	0.212	8.05
FT3-A3	5.654	2.664	0.854	0.064	0.141	0.208	2.98
FT1-A4	5.711	2.622	0.471	0.085	0.149	0.208	5.34
FT2-A4	5.699	2.625	0.485	0.074	0.143	0.207	4.48
FT3-A4	5.589	2.625	1.297	0.031	0.156	0.203	2.04
FT1-A5	5.641	2.674	0.258	0.125	0.154	0.215	4.52
FT2-A5	5.641	2.668	0.281	0.111	0.149	0.214	3.90
FT3-A5	5.611	2.650	0.625	0.059	0.143	0.209	2.01

10.2.2 Development of Waste-containing Wall Tiles

Seeger ratios and chemical composition of the WT-STD are given in Table 10.5. Ca content of the WT-STD composition is higher than FT-STD, which opens up a bigger space for addition, especially A5 and A6. Total alkali amount of WT-STD is 0.206, new compositions were developed by the rule of keeping this value constant.

Table 10.5 Seeger formulations of WT-STD

Seeger Elements	Seeger Ratios
$\text{SiO}_2/\text{Al}_2\text{O}_3$	5.333
$\text{Na}_2\text{O}/\text{K}_2\text{O}$	0.413
MgO/CaO	0.069

B ₂ O ₃	0.000
Toplam Alkali (Li ₂ O, CaO, MgO, BaO, K ₂ O, Na ₂ O)	0.206
Total R ₂ O ₃	0.188

The Seger formulations of the waste-containing WT samples are given in Table 10.6 along with the WT-STD.

Table 10.6 Seger formulations of waste-containing WT compositions in comparison with WT-STD.

Composi tion	SiO ₂ / Al ₂ O ₃	Na ₂ O/ K ₂ O	MgO/ CaO	B ₂ O ₃	Total Alkaline	Total R ₂ O ₃	Waste Amount in Composition (wt%)
WT-STD	5.333	0.413	0.069	0.000	0.206	0.188	0.00
WT1-A1	5.376	0.418	0.099	0.070	0.206	0.199	4.90
WT2-A1	5.363	0.417	0.089	0.049	0.206	0.196	3.45
WT1-A2	5.401	0.426	0.135	0.053	0.206	0.196	4.10
WT2-A2	5.382	0.422	0.116	0.038	0.206	0.194	2.96
WT1-A3	5.390	0.443	0.130	0.058	0.206	0.197	3.93
WT2-A3	5.375	0.435	0.114	0.044	0.206	0.195	2.96
WT1-A4	5.388	0.412	0.120	0.045	0.206	0.195	3.95
WT2-A4	5.374	0.413	0.106	0.034	0.206	0.193	2.97

WT1-A5	5.332	0.435	0.073	0.086	0.206	0.205	4.19
WT2-A5	5.332	0.429	0.072	0.062	0.206	0.200	2.99
WT1-A6	5.314	0.526	0.080	0.486	0.206	0.269	2.42
WT2-A6	5.325	0.461	0.074	0.218	0.206	0.224	1.06
WT3-A6	5.328	0.439	0.072	0.122	0.206	0.208	5.64
WT4-A6	5.329	0.434	0.071	0.096	0.206	0.204	4.40
WT5-A6	5.330	0.429	0.071	0.075	0.206	0.201	3.48

10.2.3 Development of Waste-containing Porcelain Tiles

Sege formulations corresponding to the chemical composition of the PT-STD composition are given in Table 10.7. Depending on XRF analysis, total alkiline concentration was 0.120%. Therefore, new compositions were modified.

Table 10.7 Seger formulations for the PT-STD composition

Seger Elements	Seger
SiO ₂ /Al ₂ O ₃	6,327
Na ₂ O/K ₂ O	2,489
MgO/CaO	0,495
B ₂ O ₃	0,000
Total Alkiline	0,120
Total R ₂ O ₃	1,295

Sege formulations for the new waste-containing PT compositions are given in Table 10.8, in comparison with PT-STD composition. As can be seen from Table 10.8, oxide ratios and total alkiline amount of the new PT compositions are similar to those of

PT-STD composition. However, the ratio of MgO/CaO was not maintained perfectly, caused by the high CaO content of the BWs.

Table 10.8 Seger formulations for the waste-containing PT compositions in comparison with that of PT-STD

	SiO ₂ /Al ₂ O ₃	Na ₂ O/K ₂ O	MgO/CaO	B ₂ O ₃	Total Alkaline	Total R ₂ O ₃
PT STD	6,327	2,489	0,495	0,000	0,120	1,295
PT1-A6	6,326	2,497	0,547	0,039	0,116	1,296
PT2-A6	6,325	2,505	0,610	0,080	0,112	1,296
PT3-A6	6,322	2,446	1,252	0,120	0,112	1,294
PT4-A6	6,316	2,461	0,803	0,163	0,110	1,289
PT5-A6	6,320	2,369	0,682	0,196	0,114	1,276
PT1-A5	6,327	2,526	0,507	0,137	0,121	1,622
PT2-A5	6,311	2,511	0,283	0,210	0,154	1,338
PT3-A5	6,255	2,533	1,562	0,069	0,123	1,294
PT1-A1	6,377	2,496	0,620	0,140	0,123	1,577
PT1-A2	6,547	2,572	0,509	0,182	0,119	1,639
PT1-A3	6,500	2,600	0,540	0,219	0,119	1,673
PT1-A4	6,450	2,471	0,531	0,128	0,119	1,610

10.3 Methodology For the Development of Waste-Containing Frit and Glaze Compositions

In the beginning, XRF analysis was conducted on industrial transparent and opaque frits to determine the Seger formulations. Standard transparent frit and matt opaque frit compositions were coded as TF1 and MOF1 respectively. New

compositions were modified regarding the Seger tables of the initial compositions.

10.3.1 Development of Waste-Containing Transparent Frits

Composition and Seger tables of TF1 and BW added TF compositions are given in table 10.9. As can be seen, only A5 and A6 wastes were used in the development of new TF compositions. The reason for that is the complex composition of MSBW_s when compared to ESBW_s. The amount of B₂O₃ needed in the compositions was partially provided by the added wastes. In order to create space for the addition, calcite (CaO source) was totally removed from the compositions. But still, high CaO content of ESBW limited the full replacement of BW with H₃BO₃.

Table 10.9 Seger tables for TF1, TF1-A5, TF1-A6 and TF1-A6-2 frits

Oxides	TF1	TF1-A5	TF1-A6	TF1-A6-2
R ₂ O (Na ₂ O, K ₂ O)	6,230	6,500	5,000	6,320
RO (CaO, ZnO)	11,070	11,250	10,350	10,090
R ₂ O ₃ (B ₂ O ₃ , Al ₂ O ₃ , Fe ₂ O ₃)	21,240	20,920	22,290	21,750
RO ₂ (SiO ₂)	61,460	61,350	62,370	61,830
SiO ₂ /Al ₂ O ₃	11,611	11,550	11,210	11,380
Total B ₂ O ₃	0,918	0,877	1,090	0,991
*B ₂ O ₃ (BW)	0	0,120	0,470	0,420

*B₂O₃ (BW), boron trioxide derived from boron waste

10.3.2 Development of Waste-Containing Matte Opaque Frits

Composition and Seger tables of MOF1 and BW added MOF compositions are given in table 10.10. As can be seen, full substitution of BWs with H₃B₂O₄ as B₂O₃ source was achieved. The reason for that is the high CaO content of the MOF1 composition itself. In order to achieve the full replacement, dolomite (MgO and CaO source) was also removed from all compositions.



Table 10.10 Seger tables for MOF1, MOF1-A1, MOF1-A2, MOF1-A3, MOF1-A4, MOF1-A5 and MOF1-A6 frits

	OXIDE	MOF1	MOF1-A1	MOF1-A2	MOF1-A3	MOF1-A4	MOF1-A5	MOF1-A6
Seger oxide content (% mol)	R ₂ O (Na ₂ O, K ₂ O)	1.17	1.18	1.28	1.49	1.14	1.3	1.32
	RO (CaO, MgO,	35.5	35.80	36.23	35.69	35.44	35.75	35.4
	R ₂ O ₃ (B ₂ O ₃ , Al ₂ O ₃)	6.60	6.61	6.56	6.57	6.77	6.55	6.64
	RO ₂ (SiO ₂ , ZrO ₂)	56.73	56.44	55.93	56.26	56.65	56.4	56.7
	TOTAL	100	100	100	100	100	100	100
Seger oxide ratio	SiO ₂ /Al ₂ O ₃	45.587	44.066	42.101	43.243	39.88	44.725	42.987
	MgO/CaO	0.910	0.908	0.866	0.912	0.9	0.901	0.905
B2O3 Seger molar value	Total B ₂ O ₃	0.146	0.144	0.140	0.142	0.145	0.143	0.145
	*B ₂ O ₃ (BW)	0	0.144	0.140	0.142	0.145	0.143	0.145
BW content in compositions	BW (wt%)	0.00	24.40	27.05	23.50	16.00	17.50	31.00

*B₂O₃ (BW), boron trioxide derived from boron waste

10.4 Results of Rheology and Characterization Studies of Waste-Containing Tile Compositions

10.4.1 Rheological Study

Elements, in other words particles of an argillaceous material, when suspended in water, act in two distinct ways, since the electrostatic charges on their surface may generate both attraction and repulsion. Ordinarily, in an acidic environment, the particles of an argillaceous material are attracted, pulled by, each other, this state is

called "flocculation". But in an alkaline environment these particles repulse, pushed by, each other and this state is called "deflocculation".

In the state of deflocculation, electrostatic charges on the surface of particles have been neutralized, the particles remain in the suspension without grouping and forming structures, as a single unit, resulting in a reduction in viscosity. While in the state of flocculation, suspended particles form three-dimensional groups or structures, due to electrostatic charges still present on the surfaces, which cause attraction, resulting in an increase in viscosity.

Neither overly-flocculated nor overly-deflocculated slurries are preferable. Viscosity of a slurry should be in the desired range in order to face no problems in the following manufacturing procedures.

For ceramic tiles, if the viscosity is too low, surface quality of the products will be poor and there might be cracks on the surface. If the viscosity is too high, this will cause pinhole defects and difficulties for the transportation of the slurry (mobility).

Ceramic slurry is a non-newtonian fluid and it shows thixotropic properties which can be defined as the change in viscosity of a stable ceramic slurry with time.

Thixotropy is also as important as viscosity. If the thixotropy is too high, drying time of the product will be long and if the thixotropy is too low, this will cause the product to become fragile.

As mentioned above, rheological properties of a slurry is directly related to viscosity and thixotropy, but all is controlled by flocculation and deflocculation mechanisms. Further, these mechanisms are also directly related to the distribution of cations present in the slurry composition.

Clay particles are negatively charged and they normally repel one other. By the effects of the common soil cations (alkaline and alkaline earth cations), clay particles stick together, in other words flocculate. Ca^{2+} and Mg^{2+} are the strong flocculators, due to their ability to make two bonds, while Na^{+} and K^{+} are referred as poor flocculators.

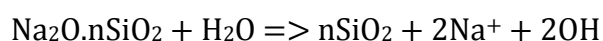
Used MSBW and especially ESBW include high amounts of CaO in their structure, which eventually pave the way for over-flocculation in the tile slurries. To overcome

the issue, methodology given under heading 10.2 was applied during the development of waste-containing tile compositions.

The term "deflocculant" stands for a compound which, when added to scattered particles in suspension, provides a reduction in apparent viscosity. Deflocculants avert flocculation by increasing zeta potential and therefore the opposite magnetic forces between particles. Different types of deflocculants act in various mechanisms such as shifting pH, substituting flocculant cations with alkilines, adding a protective colloid and increasing the negative electrical charges on agrillaceous particles. Deflocculants can be used as a mixture if more than one mechanism is needed to prevent flocculation[7].

For futher settings on the rheology, different types of deflocculants were employed in the studies. Typical tile compositions can easily be deflocculated by the kinds of polysilicates, polycarbonates and polyphosphates, while they are not adequate for the deflocculation of the developed tile compositions.

Sodium silicate is the main deflocculant used for the preparation of tile slurries. The ratio of SiO₂ to Na₂O can vary from 3.75:1 to 1:1 and is available in liquid or solid form. Sodium silicate increases the pH of the suspension, owing to hydrolisis, whereas the silicon separates out in the form of colloidal silica which also performs a role as protective colloid, according to the following reaction.



Liquid sodium silicate including 24.7% SiO₂ was firstly used to fluidify the BW-containing slurries. But the deflocculation mechanism ensured by sodium silicate was not adequate to provide enough fluidity to the BW-containing slurries. Concentration of flocculating cations were too high for the sodium silicate to act as an effective fluidifier. Therefore, a more complete and effective deflocculant defined as polyacrylate sodium salt was introduced to achieve the desired rheological characteristics. Polyacrylates reduce interactive forces between particles, attaching themselves to those areas of the particles whose charge is responsible for the formation of three-dimensional structures, another mechanism of flocculation. Polyacrylates act more strongly than polyphosphates and polysilicates in reducing

thixotrophy and yield point, and, like them, are strong absorber of polyvalent ions. Main reason for the introduction of sodium polyacrylate salt is to replace strong flocculating cations (Ca^{2+} and Mg^{2+}) with poor flocculating cation Na^+ .

10.4.2 Results of the Characterization Studies

10.4.2.1 Floor Tiles

- General Thermal Analysis

Critical temperatures in sintering stage of the BW-containing floor tiles are given in Table 10.11 in comparison with FT-STD. As can be seen, excluding few, most of the compositions showed a decrease in flex point. Reduction in the sintering temperature was assisted by the B_2O_3 provided by the added BWs. FT3-A6 composition showed the lowest flex point (1176°C). Therefore, the following characterizations included the comparison of FT-STD and FT3-A6.

Table 10.11 Critical temperatures in sintering stage of the BW-containing floor tiles

Composition	Flex Point Temperatures ($^\circ\text{C}$)	Firing Temperature Ranges ($^\circ\text{C}$)	Tried Furnace Regime Count
FT-STD	1225	1225	1
FT1-A1	1209	1140-1175	3
FT2-A1	1218	1140-1185	3
FT3-A1	1194	1120-1160	3
FT4-A1	1219	1140-1185	3
FT1-A2	1215	1140-1180	3
FT2-A2	1214	1140-1180	3

FT3-A2	1183	1120-1150	3
FT4-A2	1222	1140-1185	3
FT1-A3	1222	1140-1190	3
FT2-A3	1218	1140-1185	3
FT3-A3	1226	1140-1190	3
FT1-A4	1228	1140-1195	3
FT2-A4	1227	1140-1195	3
FT3-A4	1214	1140-1180	3
FT1-A5	1229	1140-1195	4
FT2-A5	1229	1160-1195	3
FT3-A5	1220	1170-1185	3
FT1-A6	1191	1140-1555	3
FT2-A6	1204	1140-1170	3
FT3-A6	1176	1120-1170	4
FT4-A6	1194	1145-1160	4

- **Benchmarking of FT-STD and FT3-A6 Compositions**

- ✓ *Sintering Behaviour*

First, sintering behaviour of the FT-STD body was obtained by a optical dilatometer under continuous firing condition with a heating rate of 50 °C/min up to 1250 °C. Flex point of the FT-STD was measured as 1225 °C (Fig. 10.2).

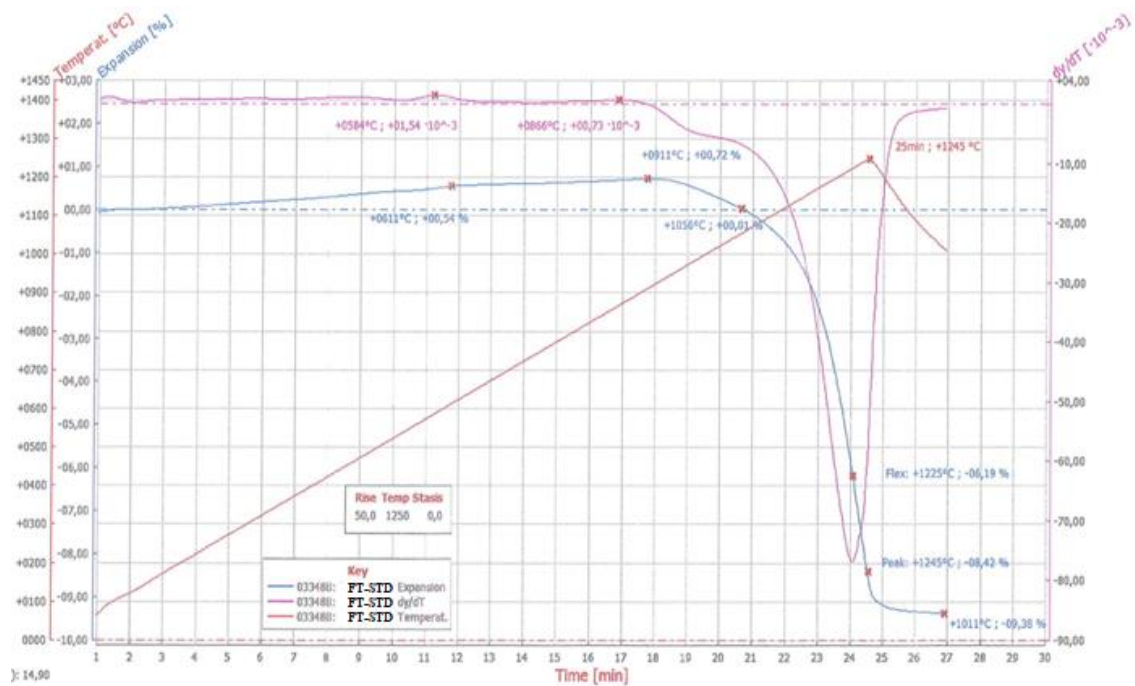


Figure 10.2 Sintering behaviour graph of FT-STD under continuous firing condition

To acquire the detailed thermal behaviour of the FT-STD, priorly measured flex point (1225 °C) was established as the peak value and FT-STD body was subjected that heat for 4 minutes. When we inspected the output graph (Fig. 10.3), we saw that the sintering of the FT-STD was finished. According to this information, the furnace regime was meant to set to a peak temperature of 1225 °C and 4 minutes holding time for the FT-STD body. But concerning the temperature difference between the optical dilatometer and the furnace (30 °C), peak temperature was set to 1195 °C.

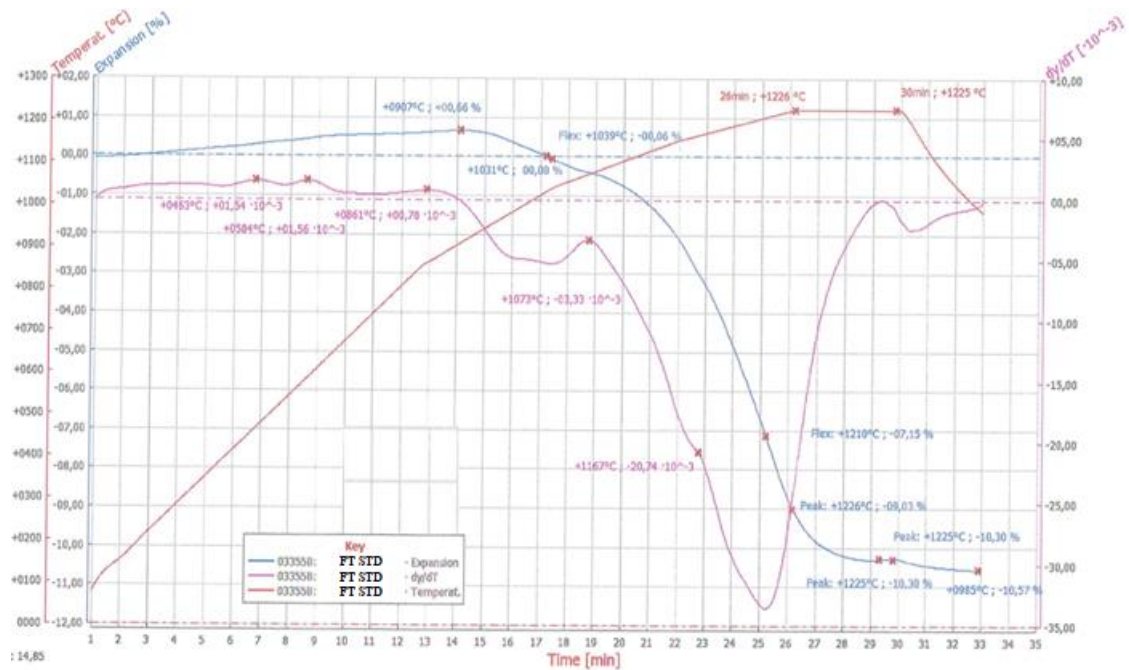


Figure 10.3 Sintering behaviour graph of FT-STD with a peak temperature and holding time.

Thermal characteristics of the FT3-A6 body was also acquired under continuous firing condition under the same conditions with the FT-STD. Flex temperature of FT3-A6 measured as 1176 °C, which exhibit 49 °C drop benchmarked to the FT-STD body (Fig. 10.4).

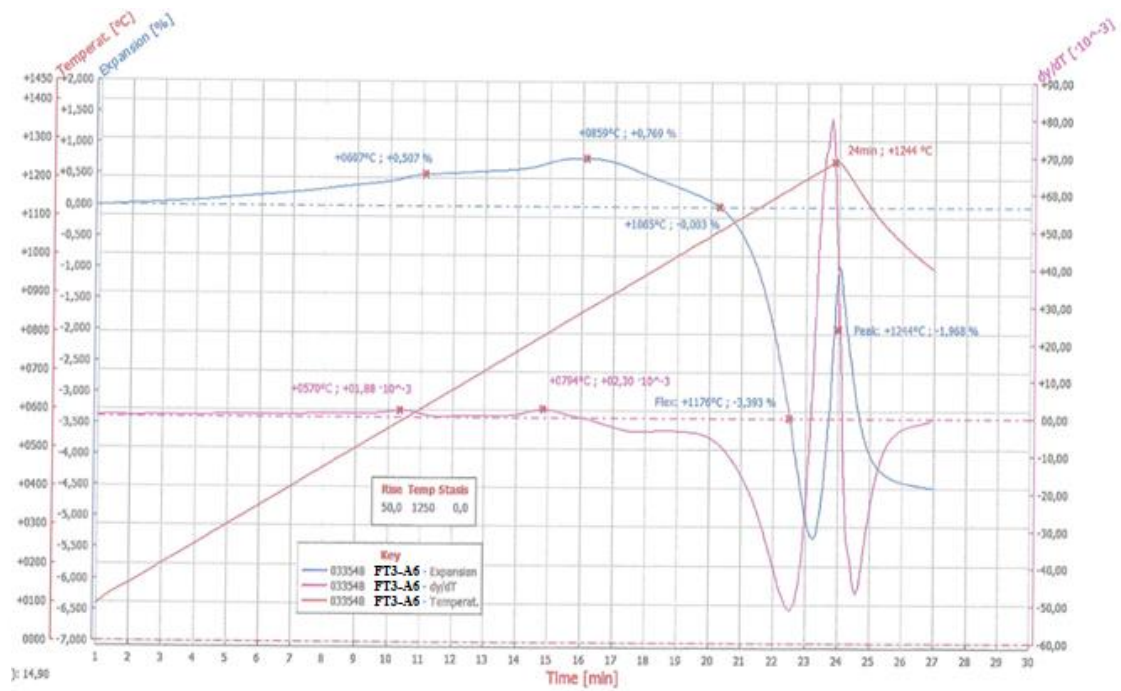


Figure 10.4 Sintering behaviour graph of FT3-A6 under continuous firing condition

Further inspections on FT3-A6 body was continued with the establishment of the peak value as final step and FT-STD body was subjected that heat for 4 minutes (Fig. 10.5). Peak temperature was set to 1170 °C which is 6 °C lower than FT3-A6's flex temperature. After the holding, body was completely sintered.

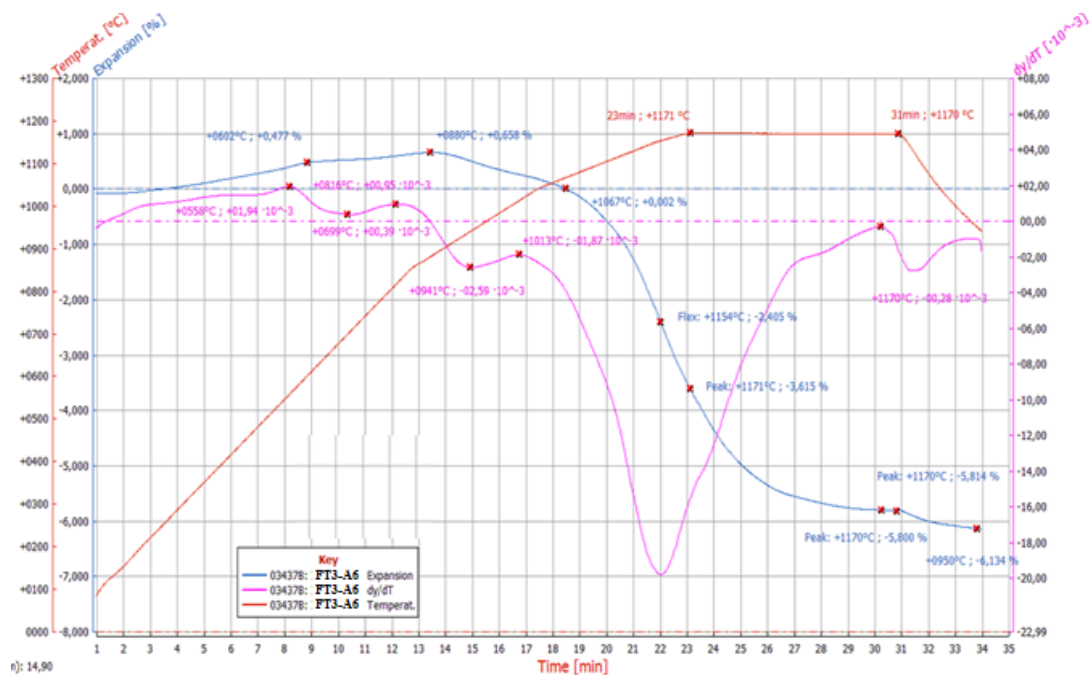


Figure 10.5 Sintering behaviour graph of FT3-A6 with a peak temperature and holding time.

Furthermore, concerning the mentioned 30 °C difference between optical dilatometer and furnace, firing examinations were conducted under 1140 °C. But the sintering of the FT3-A6 body was already completed at 1130 °C, which is 65 °C lower than the FT-STD body.

✓ *Phase and Microstructural Evaluation*

In order to determine the phase distributions, fired FT-STD and FT3-A6 bodies were subjected to a XRD analysis (Fig. 10.6). According to the XRD results, four different phases, anorthite, albite, mullite and quartz were seen in both bodies. In FT3-A6 body, peaks owned by anorthite and albite (Plagioclase phases) were more intense when compared with that of FT-STD. Anorthite phase is encouraged in a Ca-rich environment and this increase can be explained by the high Ca content of the added waste (A6).

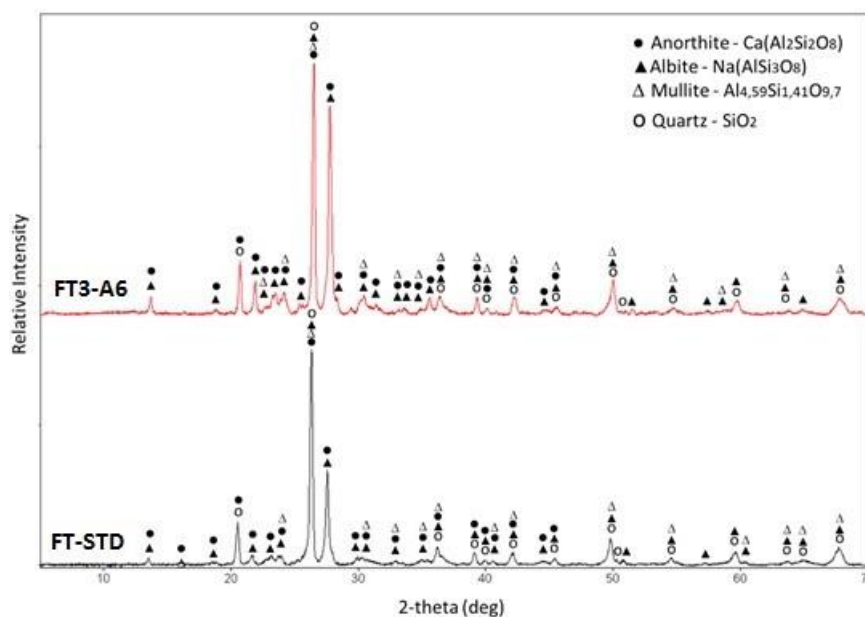
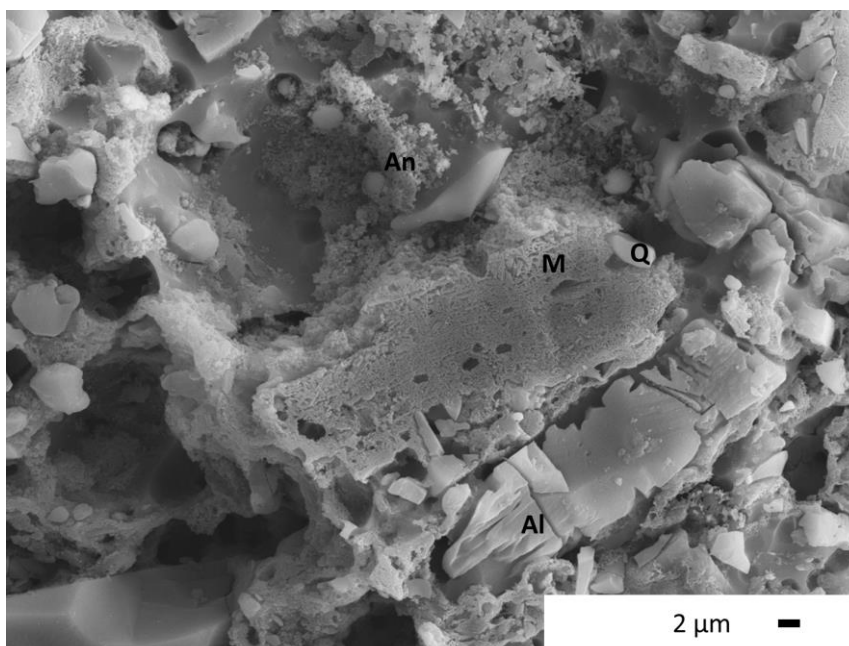
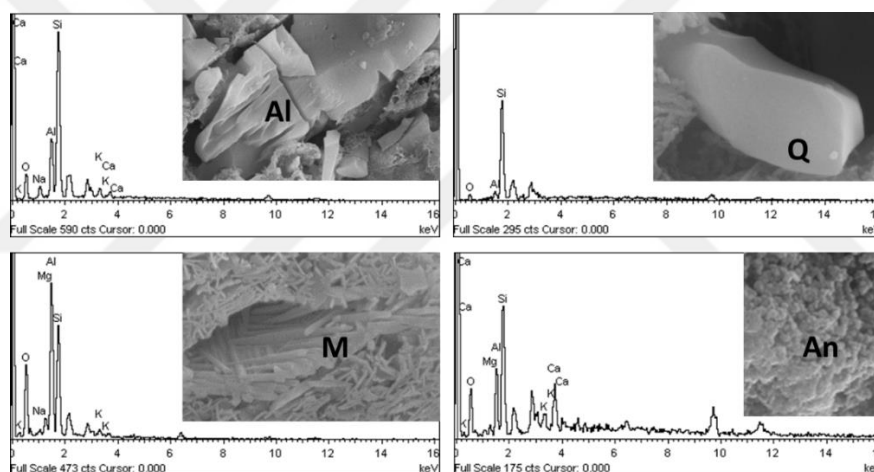


Figure 10.6 XRD patterns of fired FT3-A6 and FT-STD bodies

For further investigations on formed phases and microstructures of the FT-STD and FT3-A6, SEM/EDS analysis was applied to both bodies. Obtained SEM images and EDX results of fired FT-STD and FT3-STD bodies shown in Fig. 10.7 and Fig. 10.8 respectively. After the investigations, “An” areas in the microstructures were specified as anorthite ($\text{Ca}(\text{Al}_2\text{Si}_2\text{O}_8)$), concerning the spherical shape and high amounts of Si, Al and Ca. Where “Q” areas were referred as quartz (SiO_2), in connection with the high Si content of the regions. Regarding the content of Na, Al and Si, “Al” areas were ascertained as albite ($\text{Na}(\text{AlSi}_3\text{O}_8)$) and finally “M” areas were defined as mullite ($\text{Al}_{4,59}\text{Si}_{1,41}\text{O}_{9,7}$) related to the acicular shape of the regions and content of high Si and Al. In this case, applied SEM/EDX analyses approved the phases ascertained from XRD patterns. Results proved that the waste addition encouraged the forming of plagioclase (anorthite and albite) phases. The main constituents of this phase group are Ca and Na which are also present (especially Ca) in the composition of added A6 waste. Increasing amount of Ca in the composition created a suitable environment for the forming of plagioclase [52].

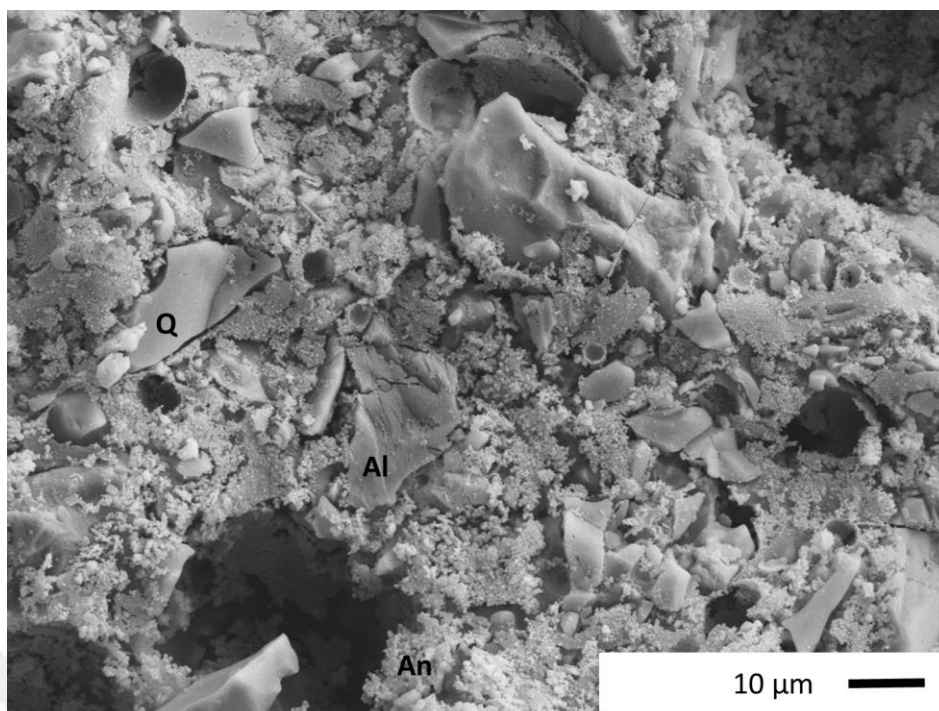


(a)

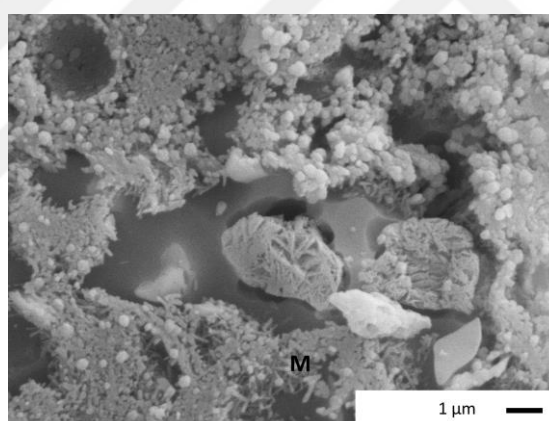


(b)

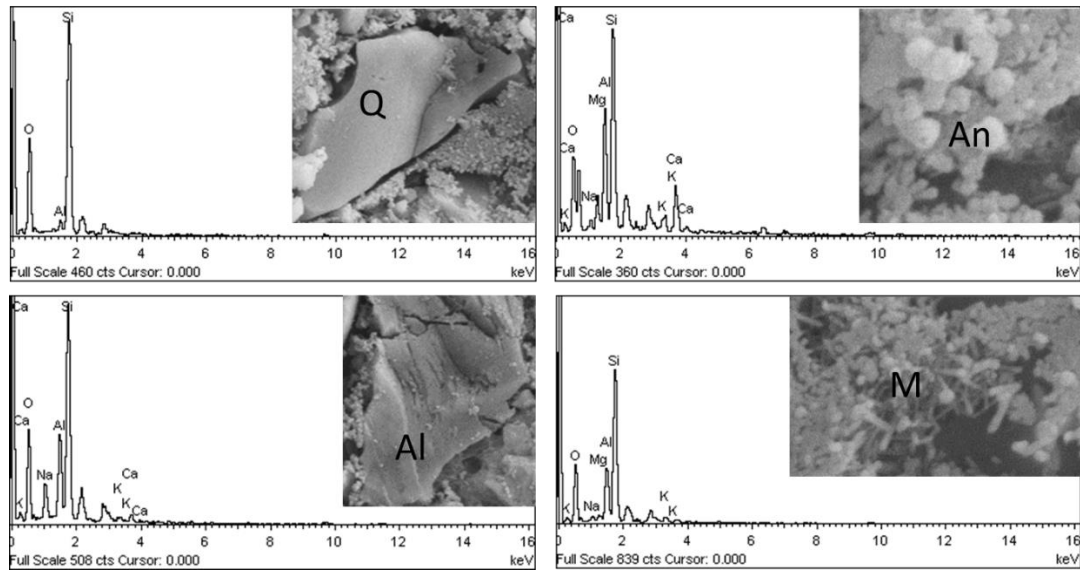
Figure 10.7 (a) SEM image of fired FT-STD body. (b) EDX analysis results of pointed regions in SEM image.



(a)



(b)



(c)

Figure 10.8 (a) SEM image of fired FT3-A6 body (10 μm). (b) SEM image of fired FT3-A6 body (2 μm). (c) EDX analysis results of pointed regions in SEM images.

✓ *Optical and Mechanical Properties*

Optical, mechanical and thermal properties of both bodies are shown in Table 10.12. According to the table, water absorpsivity value of the FT3-A6 is much lower than FT-STD, which is desirable for floor tiles. Firing shrinkage value of both bodies are similar. Fired strength of FT3-A6 is lower than FT-STD which can be explained by the over-formed plagioclase. Plagioclase phases are hard but brittle. Color values of both bodies are similar to each other. It was also seen that whiteness of the FT3-A6 was better.

Table 10.12 Optical, mechanical and thermal properties of FT-STD and FT3-A6

	Flex Point Tempera tures (°C)	Furnace Sintering Temperat ures (°C)	Water Absorb sivity (%)	Firing Shrin kage (%)	Fired Strength (N/mm²)	Color Values
FT- STD	1225	1195	1.6	6.4	51.89	L: 57.00 a: 2.52 b: 11.02
FT3- A6	1176	1130	0.49	6.8	38.43	L: 60.82 a: 3.77 b: 12.18

10.4.2.2 Wall Tiles

- General Thermal Analysis

In order to determine the sintering temperature of WT compositions, optical dilatometer was not needed, because the acquired flex temperature is the point where sintering rate at its highest and water absorbtion at its lowest and for wall tiles, it's not needed to go up to those temperatures. Because certain amounts of water absorption is desired for wall tiles. Instead of optical dilatometer analysis, peak temperature of the laboratory furnaces was set to a temperature between 1000 – 1120 °C, which is the peak temperature of establishments furnaces, and sintering behavior of WT compositions were ascertained by applying different firing regimes.

After all characterizations, WT3-A6 composition showed the lowest sintering temperature and suitable mechanical properties. Following characterization will continue with the benchmarking of WT-STD and WT3-A6.

- Benchmarking of WT-STD and WT3-A6 Compositions

✓ *Sintering Behaviour*

Depending on the furnace experiments, the sintering temperature of WT3-A6 was 1050 °C, being lower by 70 °C compared to that of WT-STD. This again proved the fluxing ability of the boron-containing wastes.

✓ *Phase and Microstructural Evaluation*

Phase analysis of the fired WT-STD and WT3-A6 bodies was performed by XRD; the XRD patterns are shown in Fig. 10.9. Major phases were anorthite, albite and quartz.

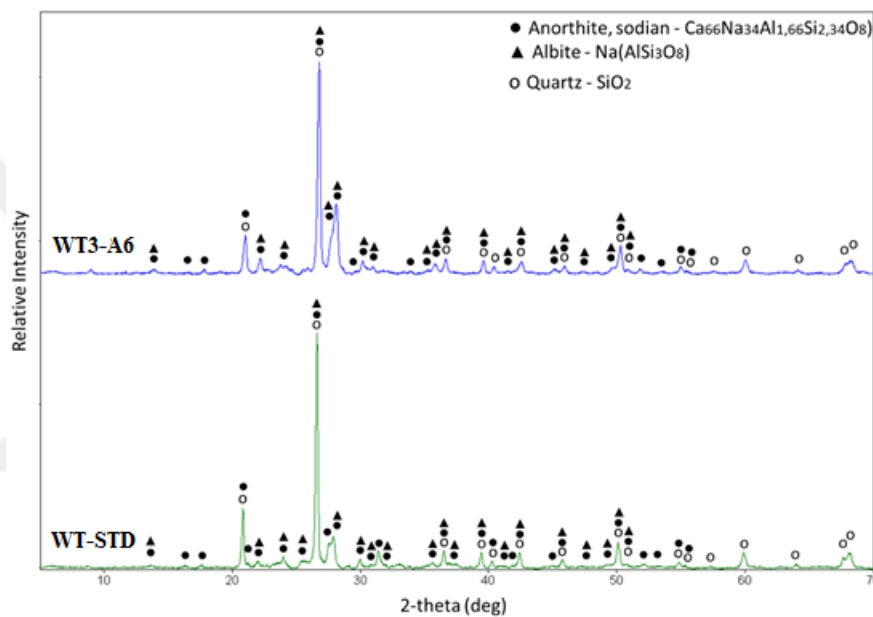
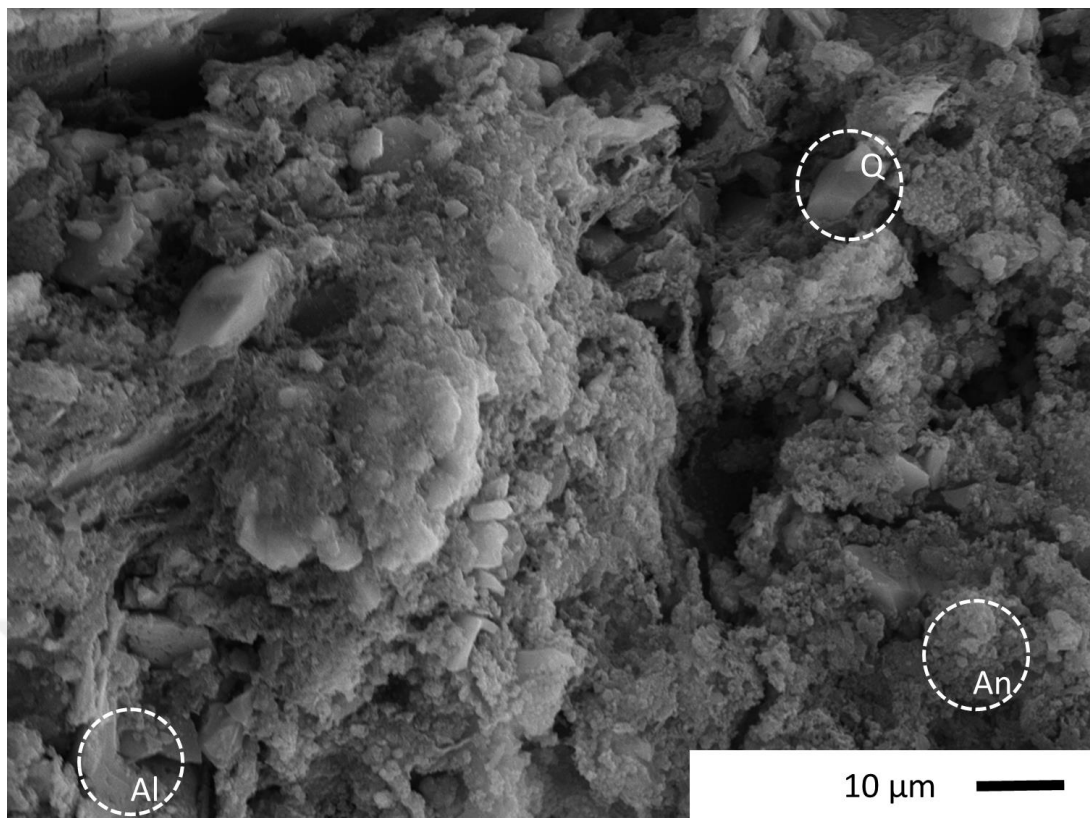
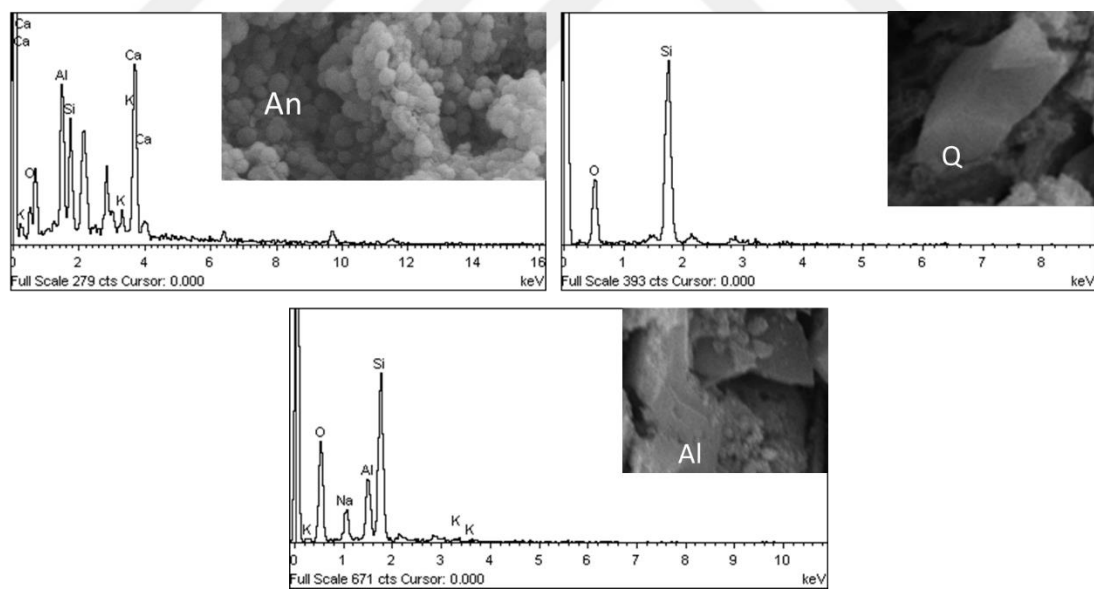


Figure 10.9 XRD patterns of fired WT-STD and WT3-A6 bodies

SEM images and EDX results of the etched fractured surfaces of WT-STD and WT3-A6 are given in Figs. 10.10 and 10.11 respectively. As in the FT bodies, 'Q' represents the quartz phase and 'Al' represents the albite phase. However, in this case, the 'An' region denotes the anorthite-sodium phase ($\text{Ca}_{66}\text{Na}_{34}\text{Al}_{1,66}\text{Si}_{2,34}\text{O}_8$). This phase belongs again to the family of plagioclase phases series but it is a mixture of albite and anorthite phases containing both Ca and Na. Finally, caused by the formation of anorthite-sodium phase, albite was absent in the structure.

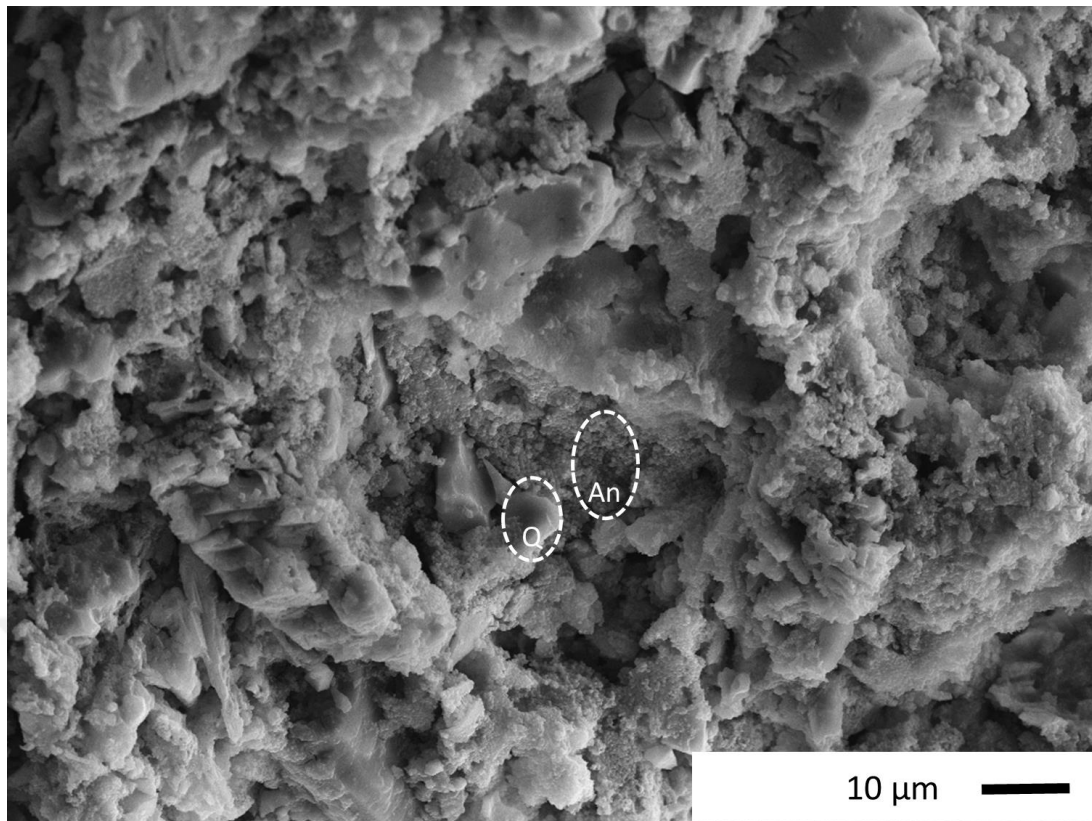


(a)

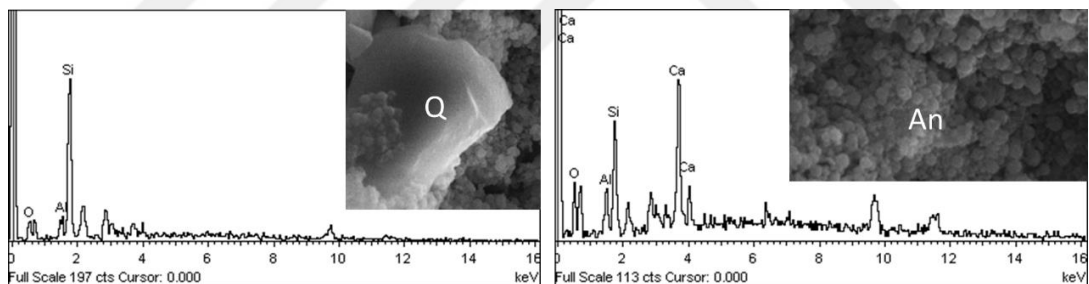


(b)

Figure 10.10 (a) SEM image of fired WT-STD body. (b) EDX analysis results of pointed regions in SEM image



(a)



(b)

Figure 10.11 (a) SEM image of fired WT3-A6 body. (b) EDX analysis results of pointed regions in SEM image

✓ *Optical and Mechanical Properties*

Optical, mechanical and thermal properties of the WT3-A6 and WT-STD body are given in Table 10.13. Addition of the boron waste A6 waste did not adversely affect the strength of the WT3-A6. Opposingly, BW addition slightly increased the strength of fired WT3-A6. This can be explained by the restricted formation of the anorthite phase at lower sintering temperatures. As for the colour values, there was no undesirable change, although a slight decrease in whiteness was observed.

Table 10.13 Optical, mechanical and thermal properties of FT-STD and FT3-A6

	Laboratory Firing Temperatures (°C)	Water Absorbance vity (%)	Firing Shrinkage (%)	Fired Strength (N/mm ²)	Color Values
WT-STD	1120	20	0.4	19.79	L: 81.12 a: 5.67 b: 16.17
WT3-A6	1050	19.39	0.6	20.46	L: 77.03 a: 7.7 b: 17.57

10.4.2.3 Porcelain Tiles

- General Thermal Analysis

Sintering behaviour results of the waste-containing PT compositions are given in Table 10.13. Concerning the outputs of the applied mechanical tests and sintering behaviours, PT3-A6 composition showed promising properties. Hence, PT3-A6 composition was further investigated.

Table 10.14 Sintering behaviour of waste-containing PT compositions in comparison with PT-STD

Composition	Flex Point	Firing Temperature	Tried Furnace
PT-STD	1233	1233	1
PT3-A6	1214	1210 - 1185	14
PT4-A6	1218	1220 - 1200	4
PT5-A6	1217	1230 - 1190	10
PT1-A5	1219	1220 - 1195	9

PT2-A5	1190	1220 - 1180	13
PT3-A5	1211	1220 - 1190	10
PT1-A1	1202	1210 - 1195	4
PT1-A2	1206	1210 - 1195	4
PT1-A3	1213	1210 - 1195	4
PT1-A4	1224	1220 - 1195	4

- Benchmarking of PT-STD and PT3-A6 Compositions

✓ *Sintering Behaviour*

The sintering behavior of the PT-STD body was obtained by optical dilatometry under continuous sintering conditions with a heating rate of 50 °C/min up to 1250 °C. The flex point of the PT-STD was determined to be 1233 °C. (Fig. 10.12).

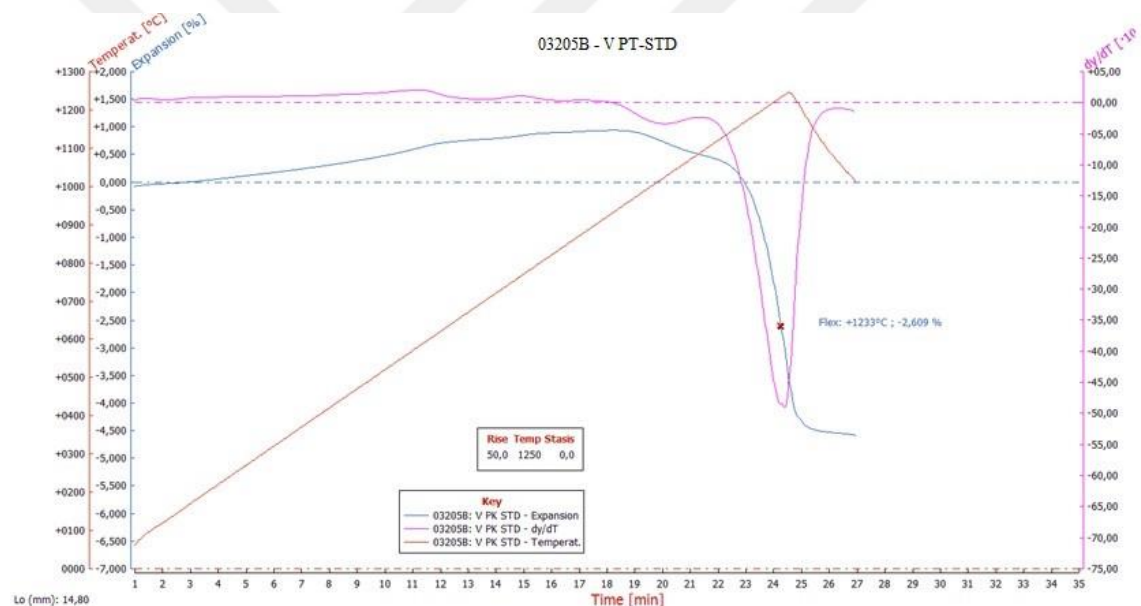


Figure 10.12 Sintering behavior of PT-STD under continuous firing conditions

For a detailed thermal characterizaton, asmeasured flex point (1233 °C) was set as a peak temperature and PT-STD body was subjected to the heat for 5 mins.

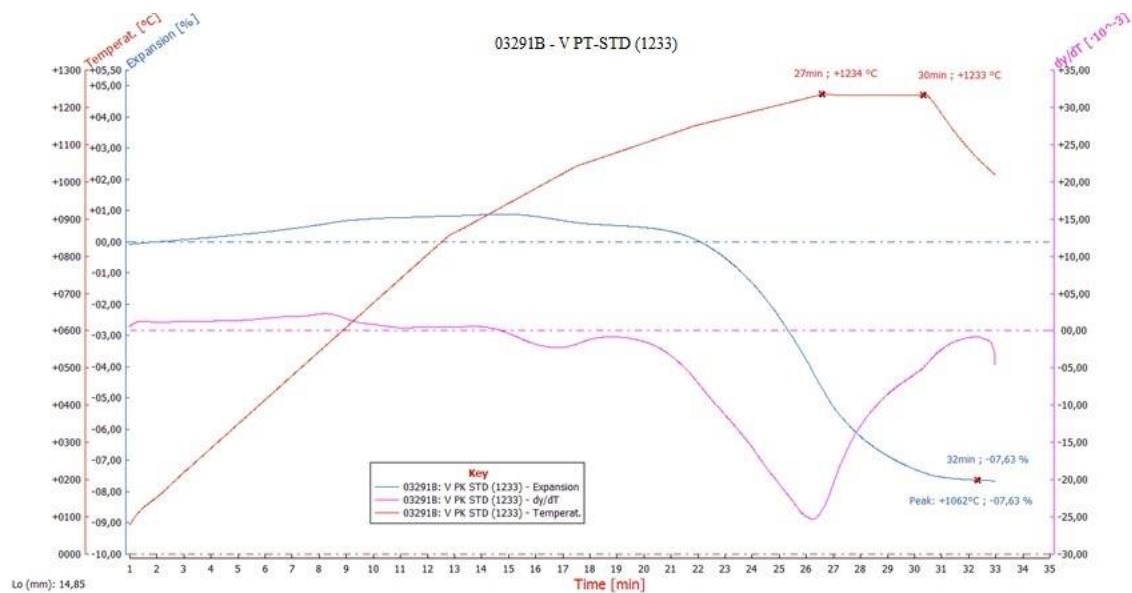


Figure 10.13 Sintering behaviour of PT-STD as a function of the peak temperature and holding time

Figure 10.14 shows the sintering behavior of PT3-A6 under continuous firing conditions, showcasing the peak temperature as 1214 °C which is 19 °C lower than that of PT-STD.

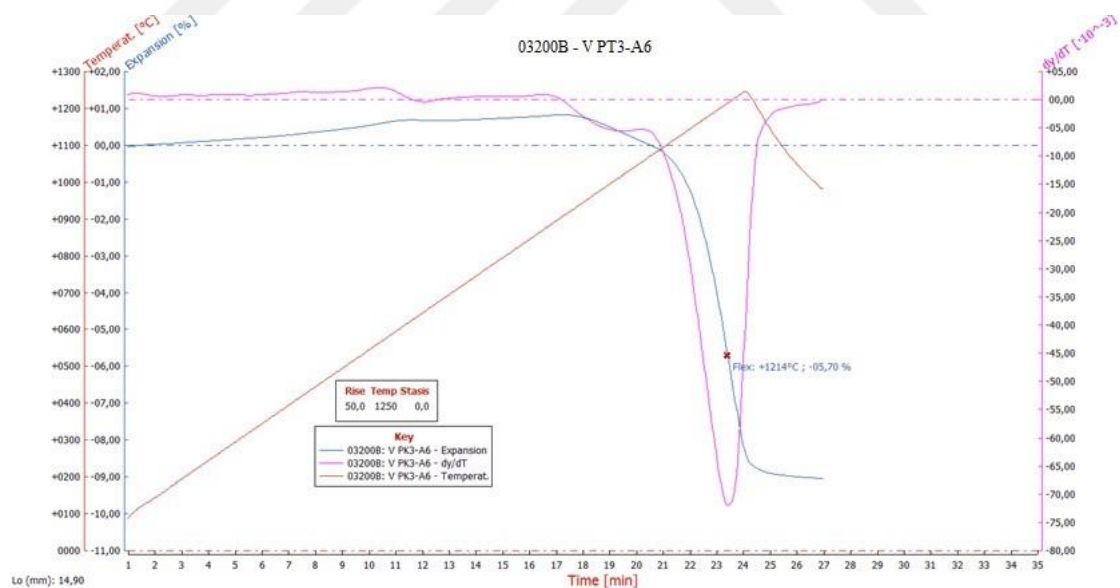


Figure 10.14 Sintering behaviour of PT3-A6 under continuous sintering conditions

To determine the sintering behavior of the PT3-A6 and avoid the effect of differences between lab furnace and optical dilatometer-determined temperatures, the flex point was lowered to 1210 °C, as the peak temperature was 4 °C lower than the previous one obtained at a holding time of 4 min, which resulted in a decreased

extent of sinterization. To better observe the sinterization mechanism and avoid the effect of the above differences, the peak temperature was increased to 1220 °C, and samples were compared. Figure 10.15 shows that the shrinkage value stabilized at the 28th minute of the sintering process. For this reason, the furnace cycle was designed to feature a flex point of 1210 °C and a holding time of 5 min.

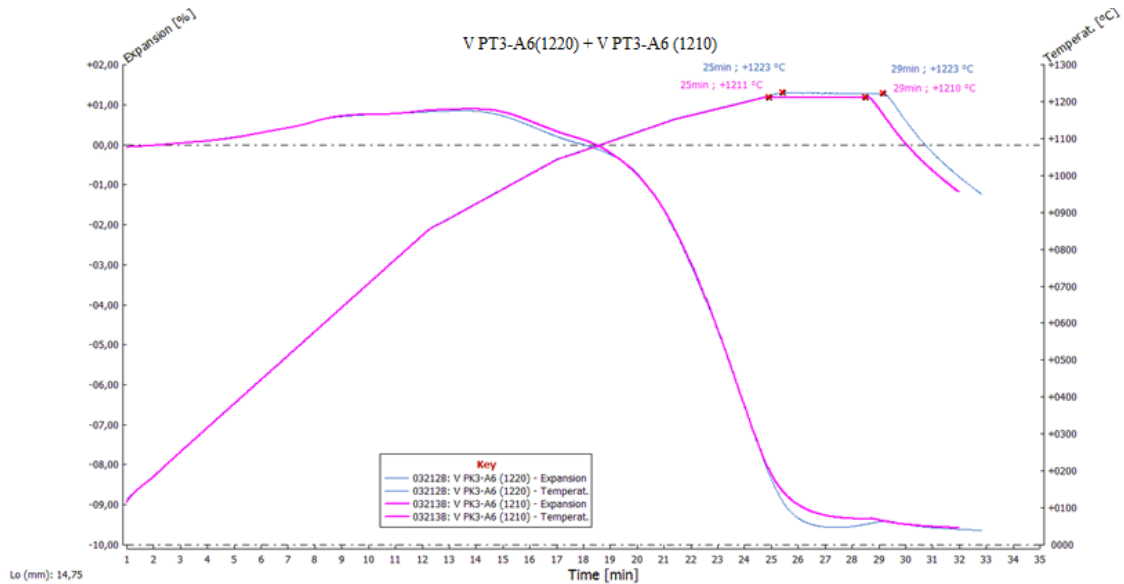


Figure 10.15 Sintering behaviour of PT3-A6 as a function of the peak temperature and holding time (1210-1220 °C)

According to the results of optical dilatometry, the sintering temperature of PT3- A6 was 19 °C lower than that of PT-STD, equaling 1195 °C. However, the above decrease was estimated as 38 °C by in-furnace measurements, which was ascribed to the temperature difference between the furnace and the dilatometer. Therefore, the lowest sintering temperature achieved for PT3-A6 was concluded to equal 1195 °C.

✓ *Phase and Microstructural Evaluation*

Crystalline phase compositions of the sintered PT-STD and PT3-A6 bodies were determined by a XRD analysis (Figure 10.16). Major phases present in the bodies were quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and plagioclase (albite to anorthite) ($\text{NaAlSi}_3\text{O}_8$ to $\text{CaAl}_2\text{Si}_2\text{O}_8$). Closer look on the XRD patterns, plagioclase peaks in 22° and 28° were decreased in PT3-A6 body. Concerning the high amounts of Ca present in the employed A6 waste, excess amounts Ca encouraged the formation of anorthite and discouraged the formation of albite. Total amount of the plagioclase may be

decreased in PT3-A6 body but the anorthite amount was increased. The increase in anorthite phase is the reason behind the decrease in sintering temperature because Ca based phases encourages the mechanism of viscous sintering [52]. Also it can be seen that the crystallinity of the PT3-A6 composition is lower than the standard composition. The reason for the occurrence of a more amorphous structure is the bonds formed between Ca-B, Si-B and Na-B which are basic glass bonds [53], [54].

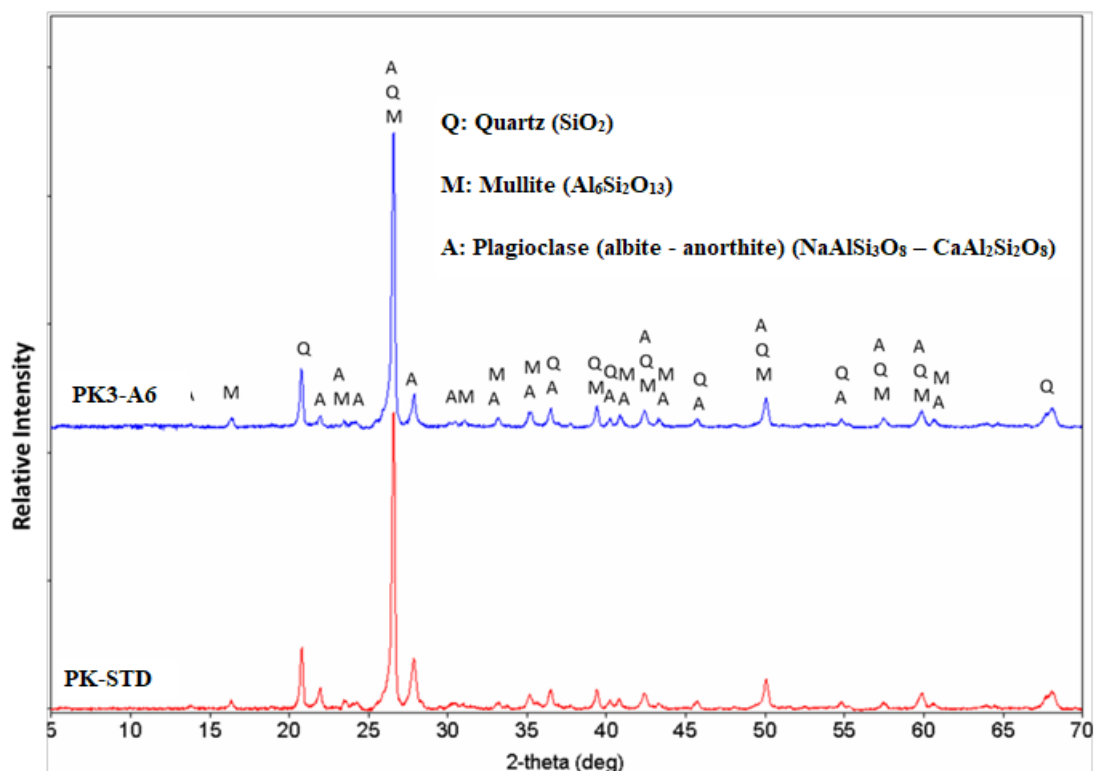


Figure 10.16 XRD patterns of fired PT-STD and PT3-A6 bodies

The microstructures of both PT-STD and PT3-A6 were assessed by SEM/EDX analysis. Figure 10.17 and 10.18 show the SEM images and EDX results of the PT-STD and PT3-A6 bodies respectively. In both structures, anorthite phase was detected (A), concerning the spherical shape and the content of Si, Al and Ca of the region. The “K” regions were specified as quartz (SiO_2), concerning the high amounts of Si present. “Al” regions were determined as albite ($\text{NaAlSi}_3\text{O}_8$), because of the Si, Al and Na content. Finally “M” regions were attributed to mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), based on their acicular shape and high content of Si and Al. Amorphous structure determined in the XRD patterns can also be seen in the SEM images. In PT3-A6 microstructure, there are sponge-like glassy areas which could not totally

crystallized due to viscous sintering caused by Ca-B, Si-B and Na-B glass bonds. Applied SEM/EDX analysis also approved the phases determined in the XRD analysis.



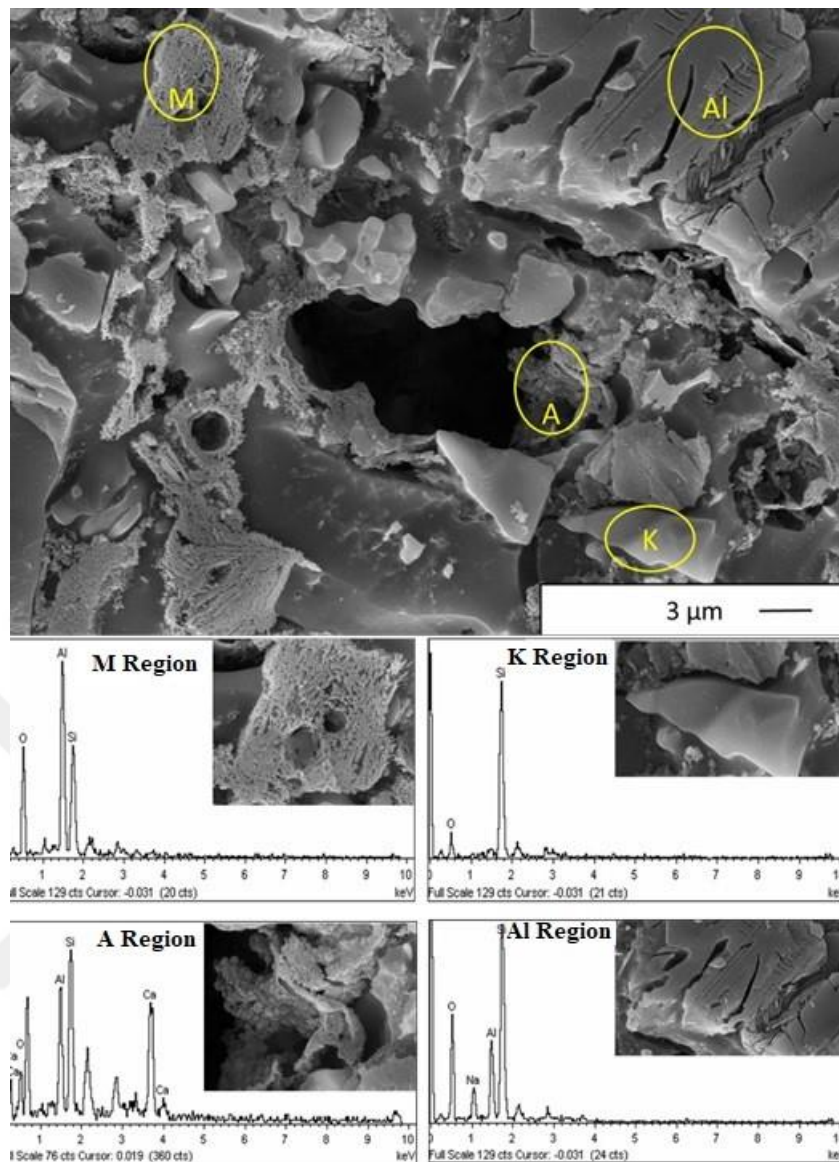


Figure 10.17 SEM image of fired PT-STD body and EDX analysis results of pointed regions in SEM image

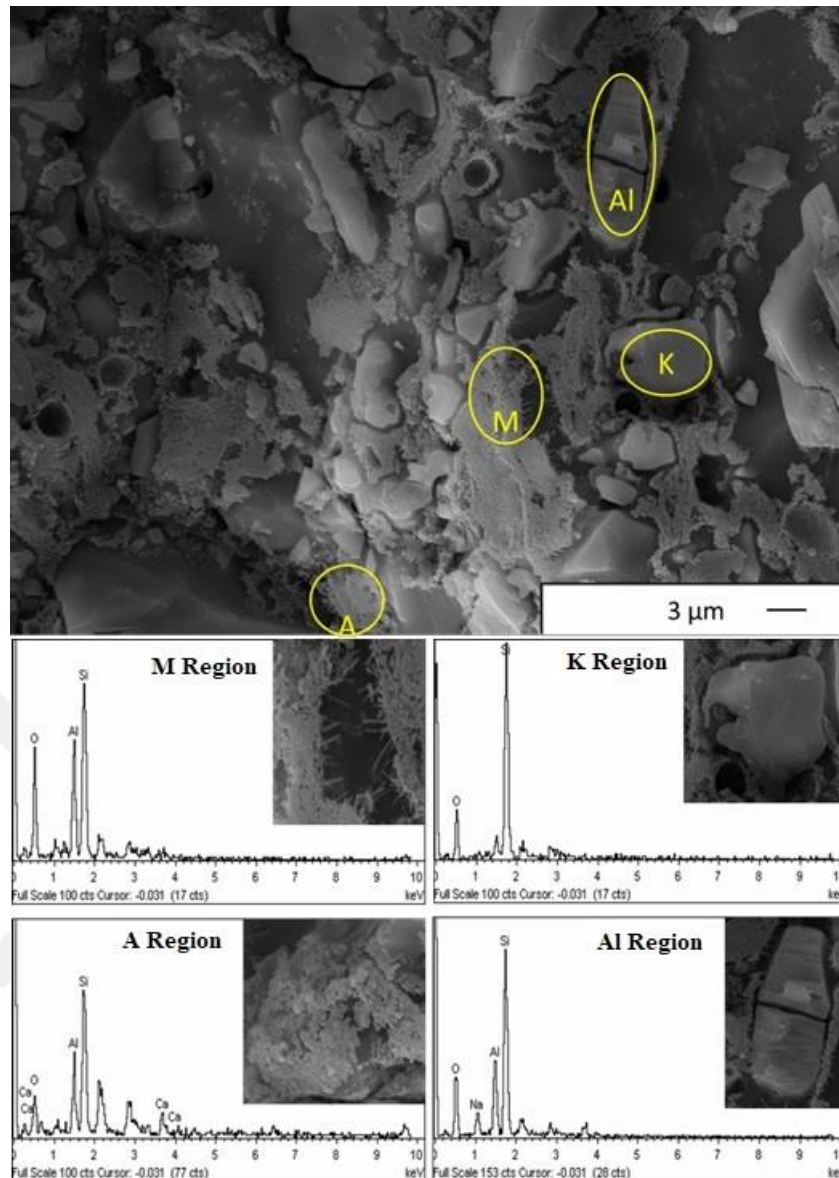


Figure 10.18 SEM image of fired PT3-A6 body and EDX analysis results of pointed regions in SEM image.

In Figure 10.19, SEM images of the polished cross-sections of both PT-STD and PT3-A6 bodies were given. The image showed that the pores in PT-STD structure are small, dense, mostly stucked with each other and irregularly shaped, but for the PT3-A6, pores mostly spherical and located independently in the structure. The difference in the shapes and the distribution of the pores can be caused by the low sintering temperature of the PT3-A6 body. Less intense sintering causes pores to not to stick with each other and have more stable shape [55].

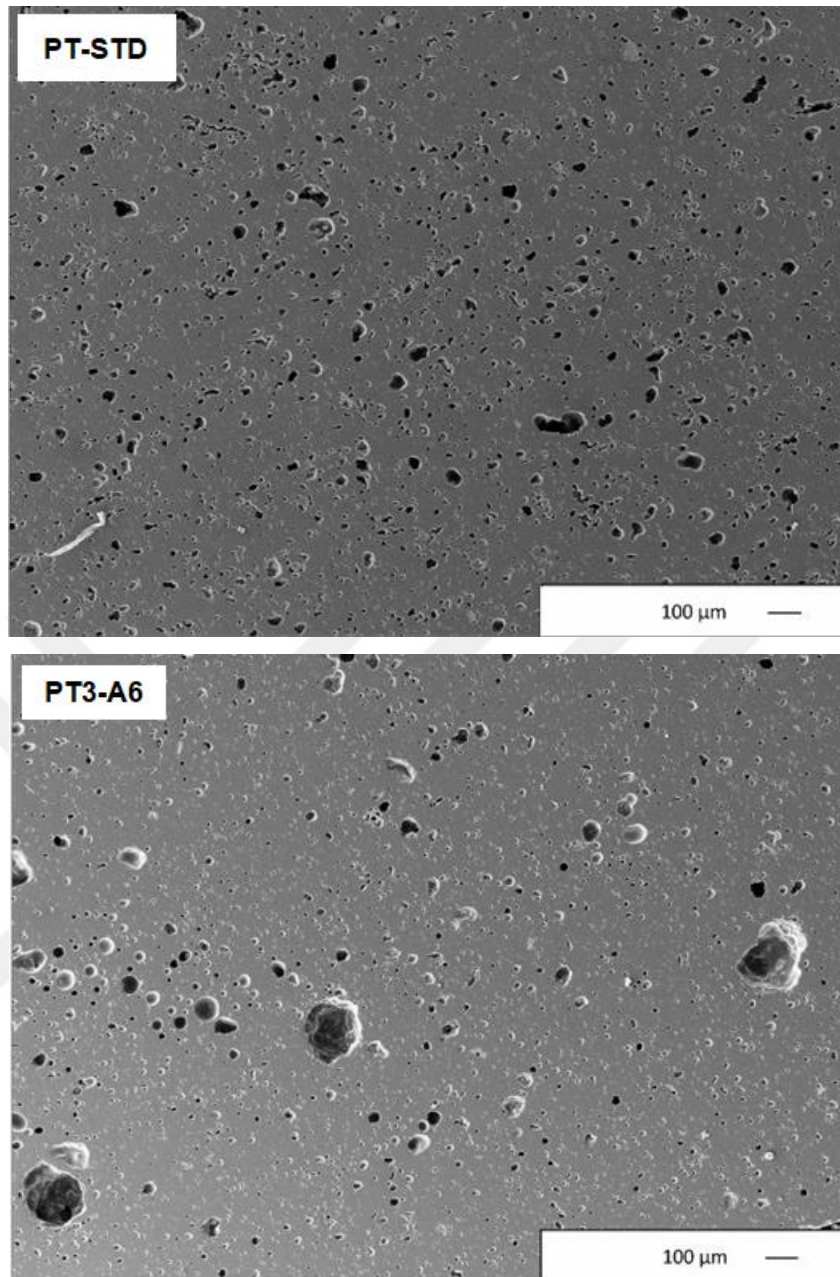


Figure 10.19 SEM images from the cross-sections of the sintered PT-STD and PT3-A6 bodies

✓ *Optical and Mechanical Properties*

Optical, mechanical and thermal properties of the PT3-A6 and PT-STD body are given in Table 10.13. Results showcased that the water absorption and sintered strength values were improved in PT3-A6 composition. Sintering shrinkage and color values showed similarity between two compositions. Only the whiteness value showed a decrease in PT3-A6 which can be caused by the Fe_2O_3 oxide present in the wastes content.

Table 10.15 Optical, mechanical and thermal properties of FT-STD and FT3-A6

	Flex Point Temperatures (°C)	Furnace Sintering Temperatures (°C)	Water Absorbance ivity (%)	Firing Shrinkage (%)	Fired Strength (N/mm ²)	Color Values
PT-STD	1233	1233	0,05	7,5	38,26	L: 79,23 a: 1,42 b: 10,26
PT3-A6	1214	1195	0,01	7,4	44,80	L: 74,95 a: 1,97 b: 9,78

10.5 Characterization Results of Waste-Containing Frits and Glazes

10.5.1 Transparent Frits

- **Thermal Analysis**

In order to observe the sintering behaviours of the samples heat microscope was used. Temperatures of sintering, softening, sphere, half sphere and melting temperatures were obtained by going up to 400 °C with 30 °C/minute and 1400 °C with 10 °C/minute.

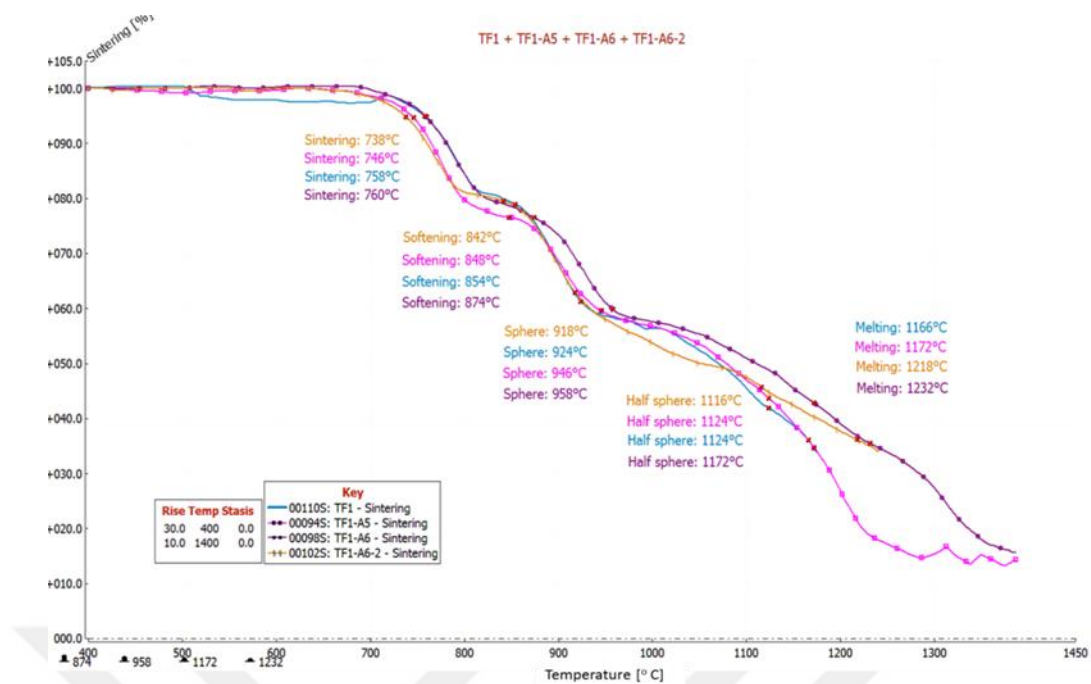


Figure 10.20 Result of thermal analysis applied to frits by using heat microscope

Sintering curves of the waste-containing frits are similar to that of standard frits. Sintering, softening, sphere, half sphere and melting temperatures of the compositions are given in Table 10.14.

Table 10.16 Results of the thermal analysis applied to developed frits

FRIT	Sintering Temperature	Softening Temperature	Sphere Temperature	Half Sphere Temperature	Melting Temperature
	°C	°C	°C	°C	°C
TF1	758	854	924	1124	1166
TF1-A5	746	848	946	1124	1172
TF1-A6	760	874	958	1172	1232

TF1-A6-2	738	842	918	1116	1218
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✓ Phase and Microstructural Evaluation

In Figure 10.21, XRD patterns of the TF1, TF1-A5, TF1-A6 and TF1-A6-2 glazes are given. There was no clue of a crystal phase in the patterns, an amorphous structure.

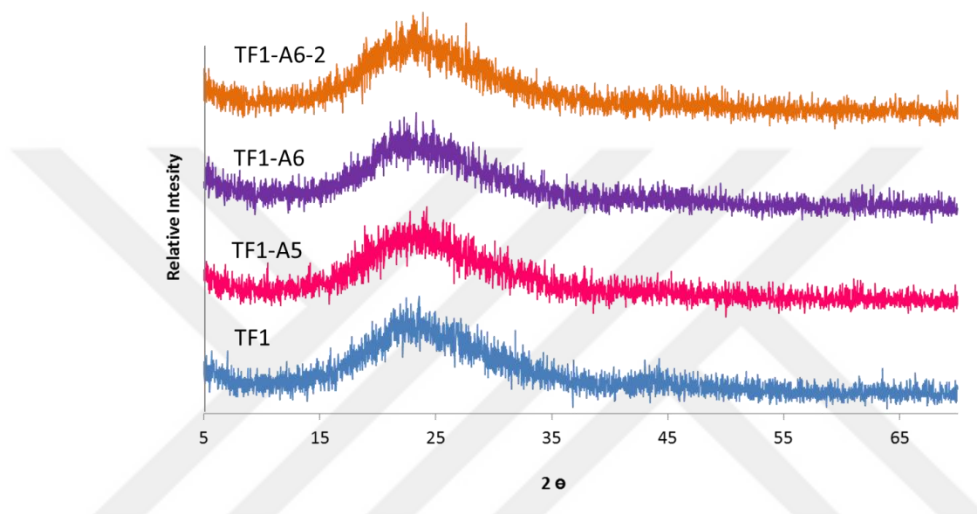


Figure 10.21 XRD patterns of TF1, TF1-A5, TF1-A6, TF1-A6-2

In Figure 10.22 SEM images taken from the surface of TF1, TF1-A5, TF1-A6, TF1-A6-2 glazes are given. There were no clue of a crystal structure and this images also proves the amorphous structure which is obtained from XRD results.

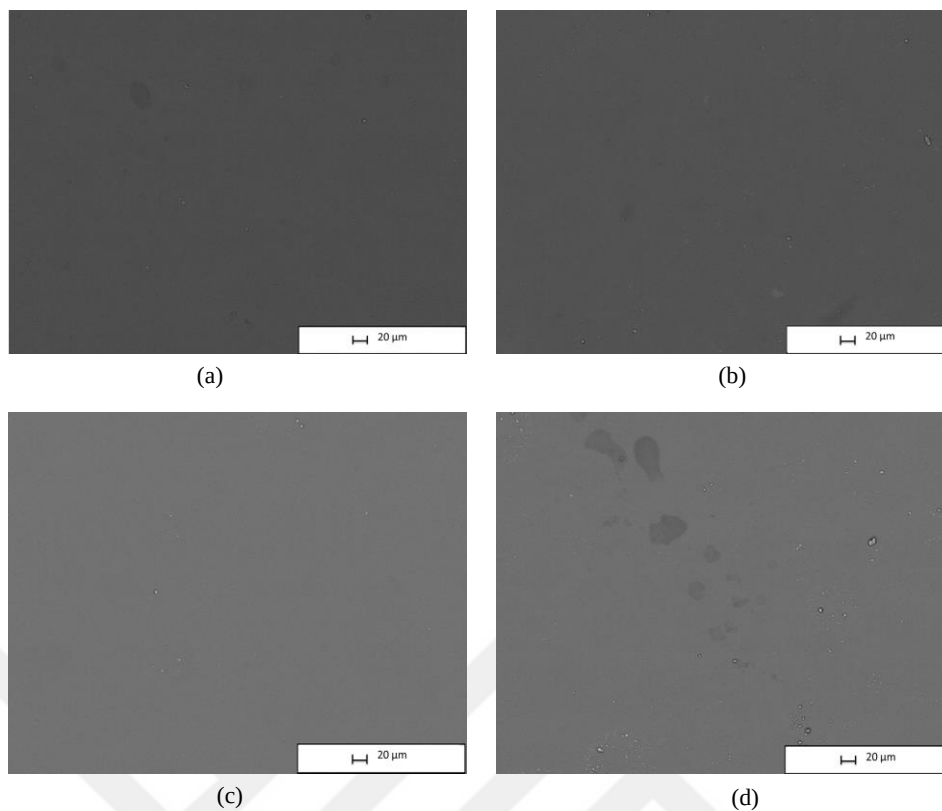


Figure 10.22 SEM images taken from the surface of TF1 (a), TF1-A5 (b), TF1-A6 (c), TF1-A6-2 (d).

In Fig. 5 SEM images taken from the cross-section of TF1, TF1-A5, TF1-A6, TF1-A6-2 glazes are given. Images showed that the porous structure and quartz crystals which are present in the standard TF1 glaze are also present in the TF1-A5, TF1-A6 and TF1-A6-2 glazes.

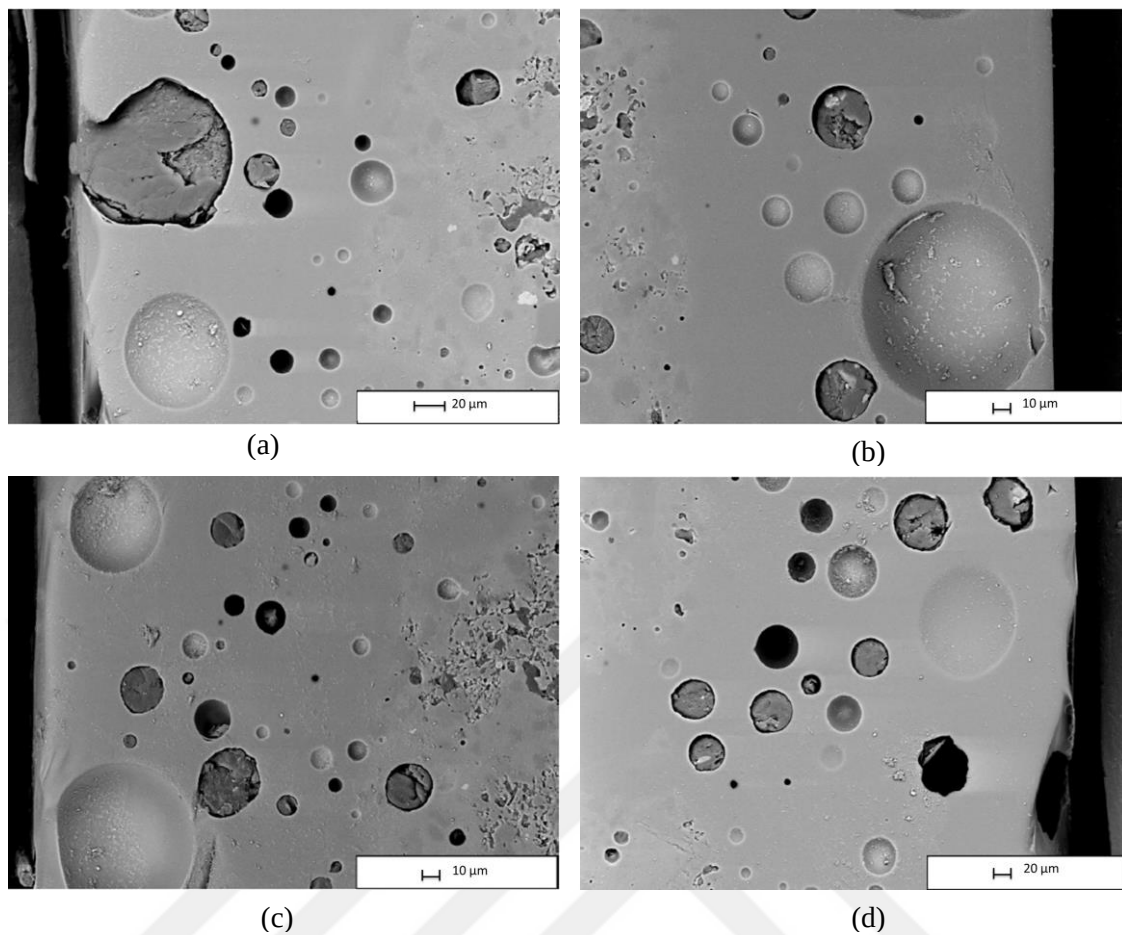


Figure 10.23 SEM images taken from the cross-section of TF1 (a), TF1-A5 (b), TF1-A6 (c), TF1-A6-2 (d)

✓ **Physical-Visual Properties**

Digital photos of the final glaze layer occurred after firing are given in Fig. 6 in comparison with TF1 glaze.

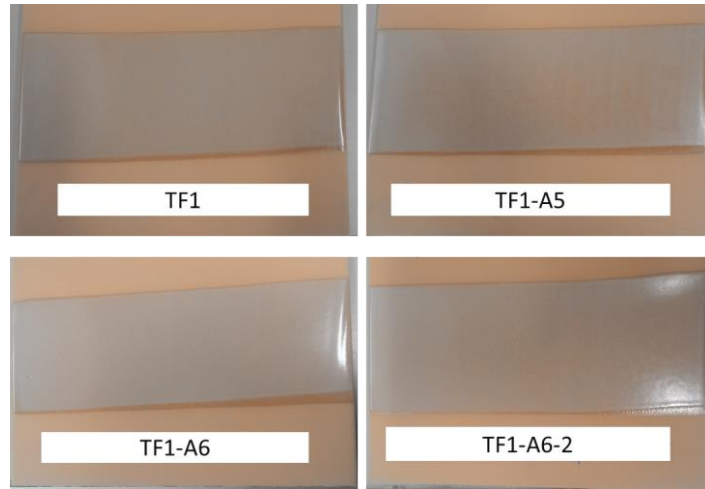


Figure 10.24 Digital photos of the glazes TF1, TF1-A5, TF1-A6, TF1-A6-2 applied on the tile surface.

As a result of the color, surface roughness and brightness analysis, Table 3 is formed. Whiteness of the glazes derived from frits including wastes are increased and this caused a small decrease in transparency of the glazes. The brightness values of developed glazes are similar to those of standard glaze but the surface roughness of the new glazes were slightly increased, most significant increase was seen at TF1-A6-2 glaze.

Table 10.17 Color, brightness and roughness values of developed glazes.

FRIT	COLOR			BRIGHTNESS			ROUGHNESS
	L	a	b	20 °	60 °	80 °	μm
TF1	69,3	4,41	12,49	21	56,1	71,7	1,67
TF1-A5	70,61	4,03	11	27,1	58,3	73,5	2,82
TF1-A6	72,38	3,84	10,53	21	55,4	74,7	2,05
TF1-A6-2	73,31	4,67	11,98	22,5	56,1	71,7	3,18

10.5.2 Matt Opaque Frits

✓ Thermal Analysis

The sintering curves (Figure 16 and 17) received from the BW-containing frits exhibit that critical temperatures are lower than those of a standard frit (Table 3). The critical temperatures of the MOF1-A4 frit, which yielded the brightest glaze, are the lowest. B₂O₃ and CaO present in the structures were responsible for the decline in the critical temperatures, owing to their fluxing abilities.

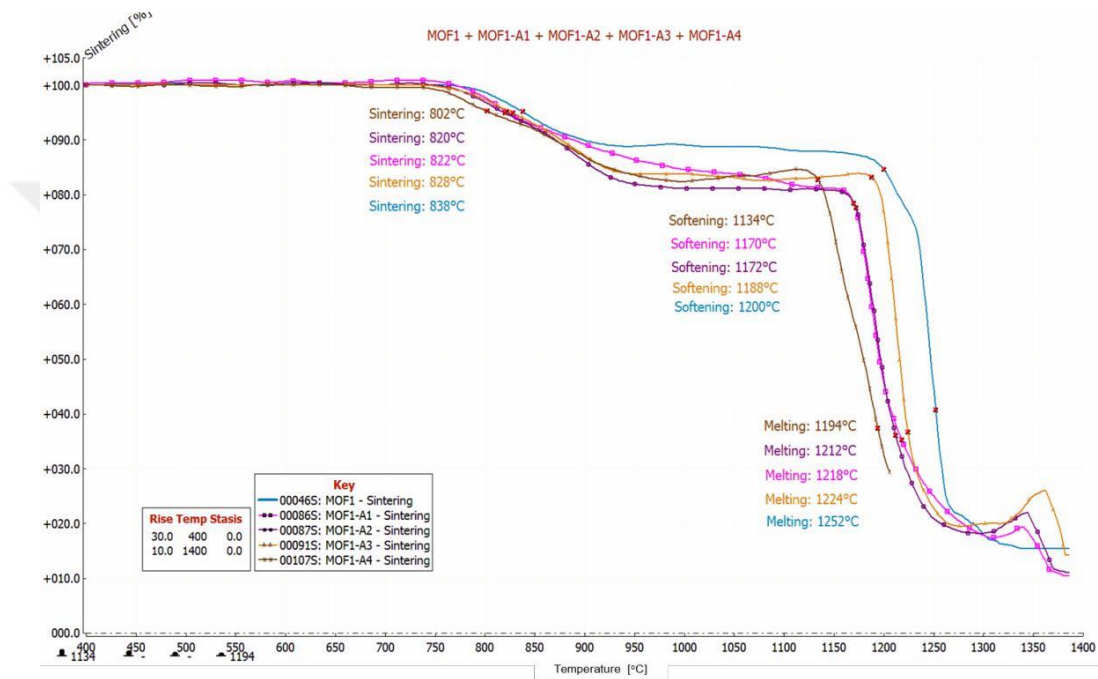


Figure 10.25 Results of thermal analysis of frits using heat microscope

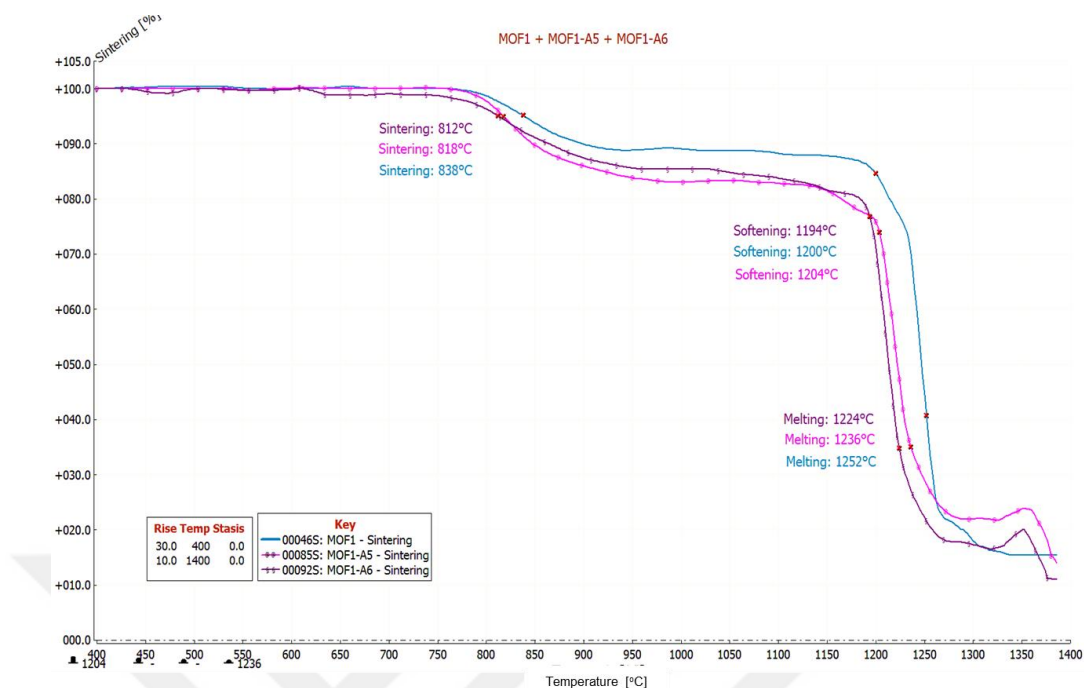


Figure 10.26 Results of thermal analysis of frits using heat microscope

Table 10.18 Results of thermal analysis of developed frits.

FRIT	Sintering Temperature	Softening Temperature	Melting Temperature
	°C	°C	°C
MOF1	838	1200	1252
MOF1-A1	822	1170	1218
MOF1-A2	820	1172	1212
MOF1-A3	828	1188	1224
MOF1-A4	802	1134	1194
MOF1-A5	818	1204	1236
MOF1-A6	812	1194	1224

As DTA graphs showcased (Figs. 18 and 19), temperatures needed for crystallization were similar (around 950 °C) for both bodies. However, the crystallization peak of the standard MOF1 frit is sharper and more intense when

compared to BW added frits. Situation can be explained by the viscous sintering mechanism, encouraged by the B_2O_3 and CaO , resulting in a more amorphous material.

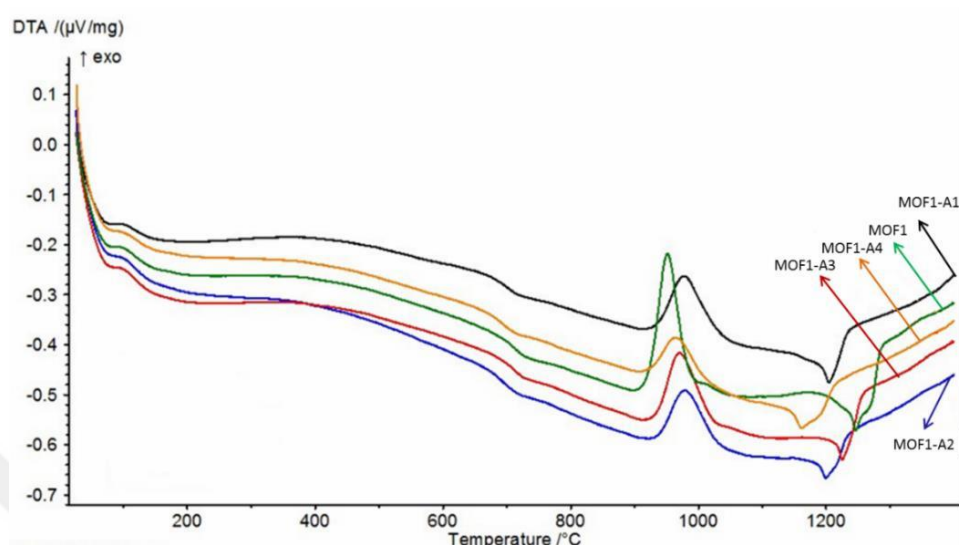


Figure 10.27 Results of DTA analysis of frits

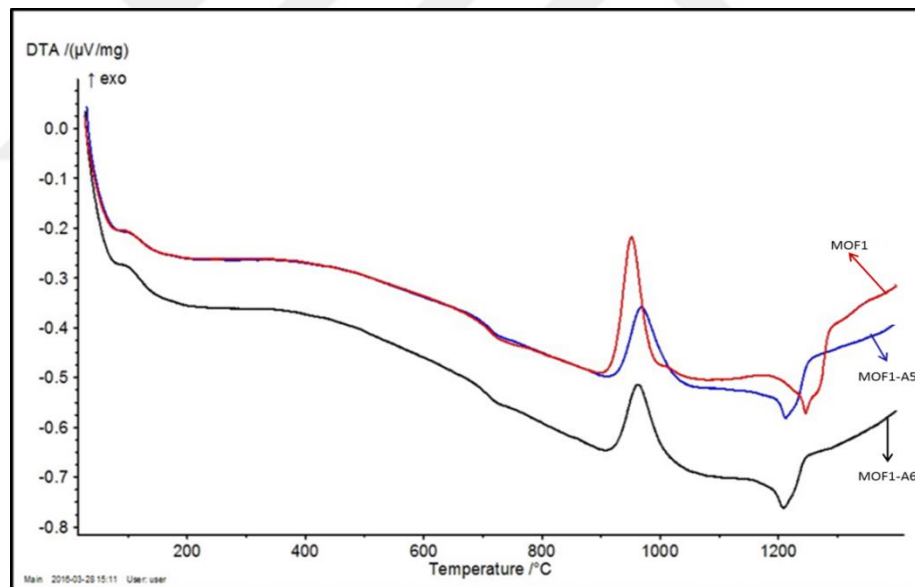


Figure 10.28 Results of DTA analysis of frits

The sintering graph (Fig. 20) of BOG-A3 and BOG-A5 showcased similar critical temperatures to that of BOG. Small differences are caused by the complex composition of the wastes, especially by the changing amount of oxides. Further, as can be determined from the DTA curves (Fig. 21), between 950–980 °C, the sintering mechanism stopped due to the exothermic peak which corresponds to the formation

of zircon crystals in the structures. The forming of the zircon crystals increased the viscosity of the glaze and blocked the bulk flow, which caused a break in the sintering. Once the system reached 1070 °C, the softening point, the glaze became viscous again and the sintering continued. The endothermic peak around 1200 °C can be explained as corresponding to the melting of the zircon crystals in the amorphous (glassy) phase.



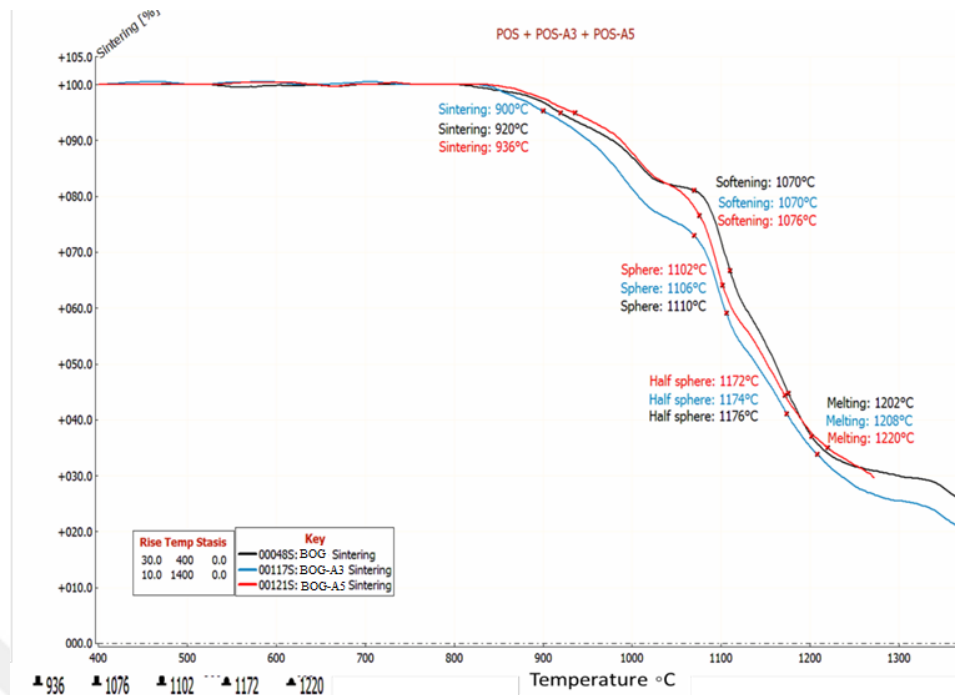


Figure 10.29 Results of thermal analysis of bright opaque glazes using heat microscope

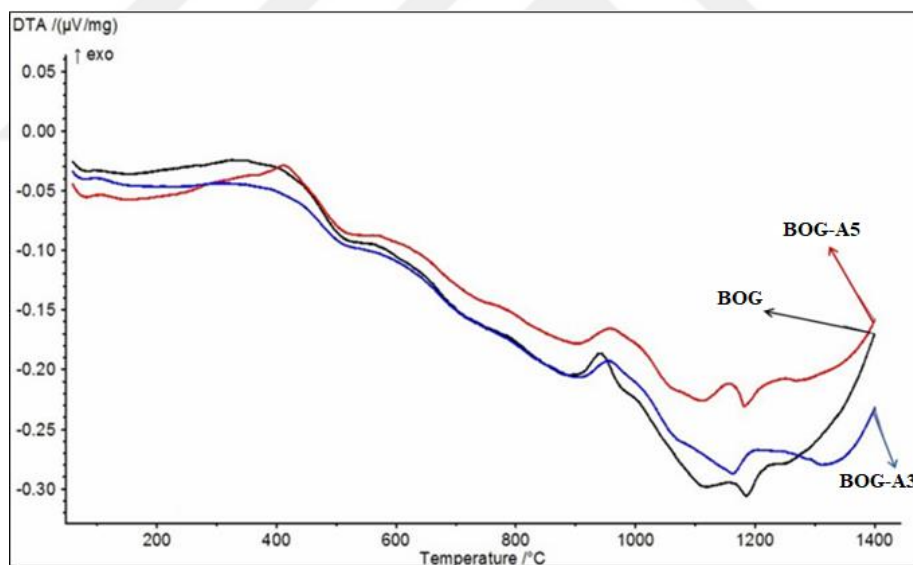


Figure 10.30 Results of DTA analysis of bright opaque frits

✓ Phase and Microstructural Evaluation

The XRD patterns, shown in Fig. 3 and Fig. 4, indicate that small amounts of diopside ($\text{MgCaSi}_2\text{O}_6$) and zircon (ZrSiO_4) crystals were present in the waste-containing frits, in the same way as in a standard MOF1 glaze. The width of the peak of the amorphous phase was higher for the waste-containing frits than for MOF1, given

that the elements present in the waste tend to form compounds with an amorphous structure (CaO and B_2O_3). In the pattern for the standard MOF1 glaze, the intensity of the peak related to the diopside crystals is higher than that of the peak attributable to the zircon crystals. However, in the pattern for MOF1-A5, the intensities of the two peaks are similar. Further, owing to the presence of the glass-forming fluxes, the degree of crystallization of the waste-containing frits was lower, as evidenced by the low intensity of the crystallization peaks.



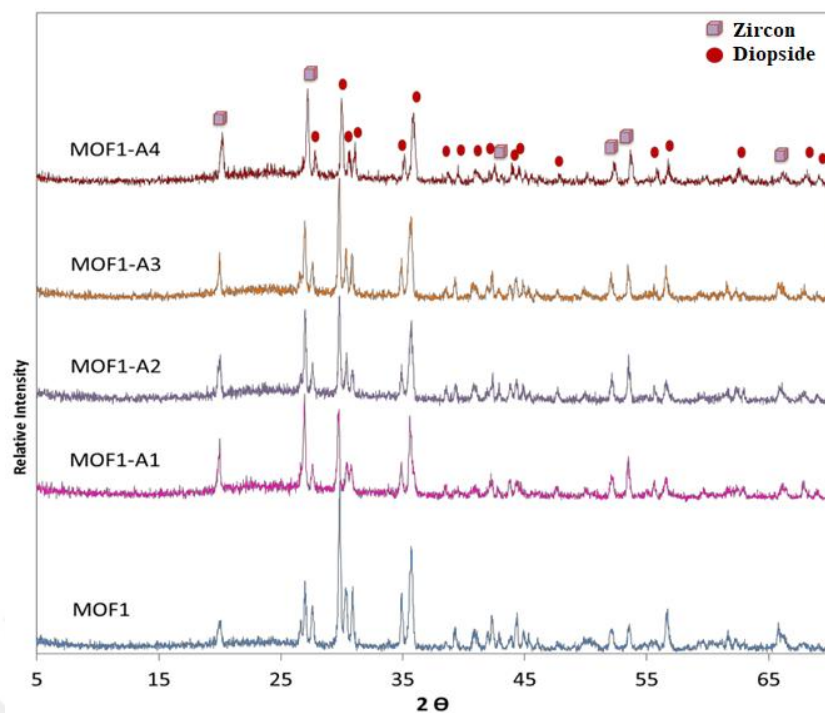


Figure 10.31 XRD patterns of MOF1, MOF1-A1, MOF1-A2, MOF1-A3 and MOF1-A4

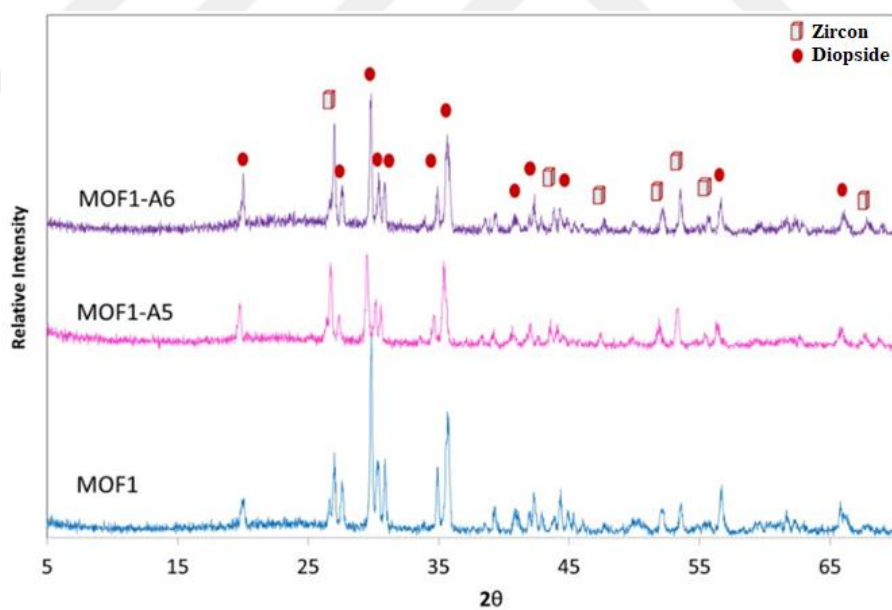


Figure 10.32 XRD patterns of MOF1, MOF1-A5, and MOF1-A6

XRD analysis of the surface of the BOG-A3 and BOG-A5 showed that they only include zircon crystals in addition to the amorphous phase, in the same way as BOG.

Mineralogical analysis proved that the addition of boron waste to the frit composition has no undesired effect on the type of crystals forming on the surface.

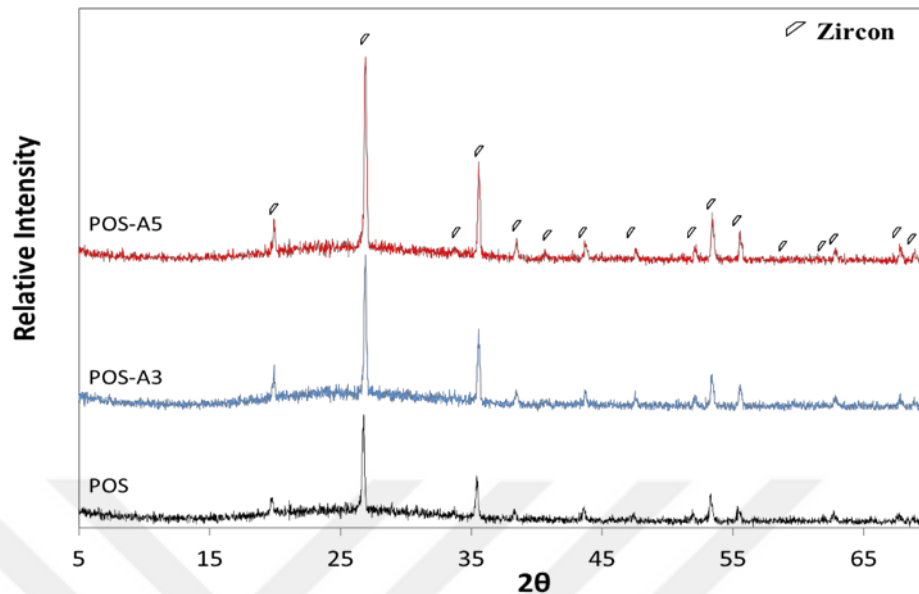
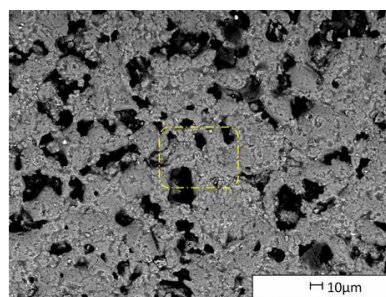
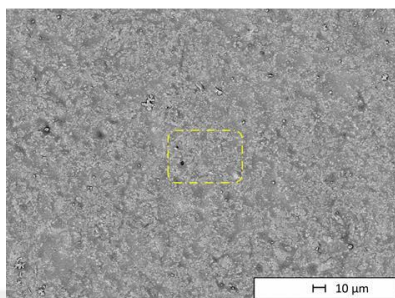


Figure 10.33 XRD patterns of BOG, BOG-A3 and BOG-A5 glazes

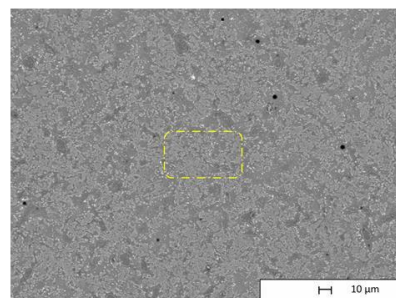
Figures 6 and 7 indicate SEM pictures of the surfaces of waste-containing frits and in addition that of the MOF1 frit. Figures 8 and 9 demonstrates higher-amplification pictures of the territories set apart with the specked lines in Figs. 6 and 7. The SEM pictures demonstrate that the delivered frit don't have exceptionally permeable surfaces, for example, that of the standard MOF1 frit. The shape and thickness of the pores can be credited to the impact of the gooey sintering process. At temperatures higher than the glass-change temperature (roughly 1100 °C),¹⁸ the thickness of the frits diminishes. Further, at higher temperatures, the vast measure of Ca present in the structure begins to go about as a motion alongside the B₂O₃. Attributable to these motions, the degree of sintering and densification builds, prompting littler pores.



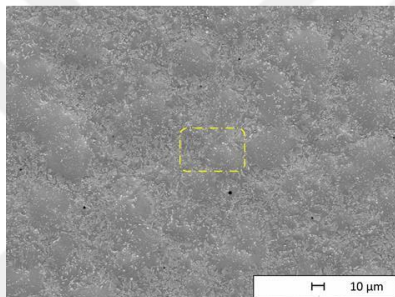
(a)



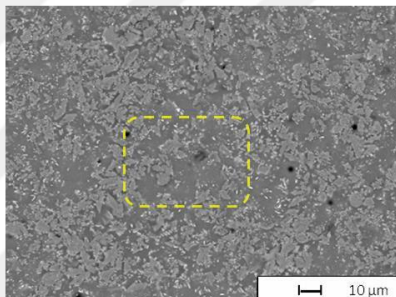
(b)



(c)

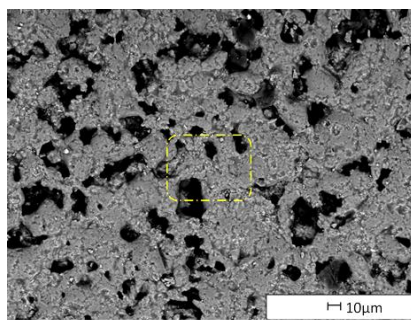


(d)

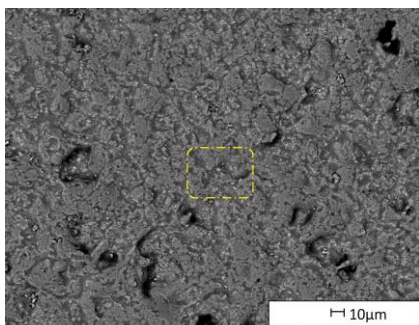


(e)

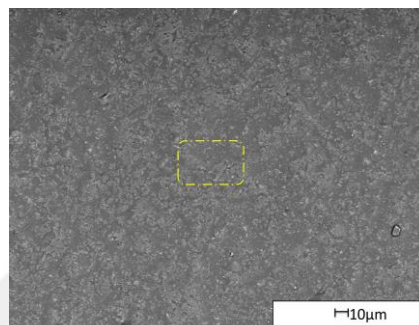
Figure 10.34 SEM images of surfaces of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4



(a)

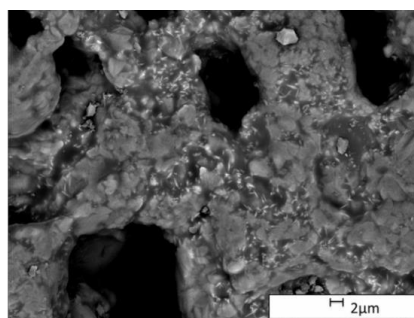


(b)

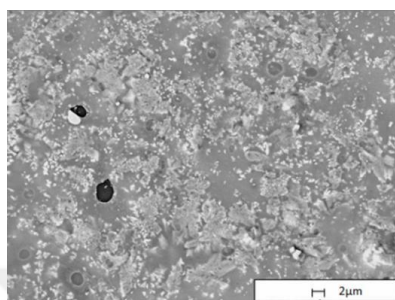


(c)

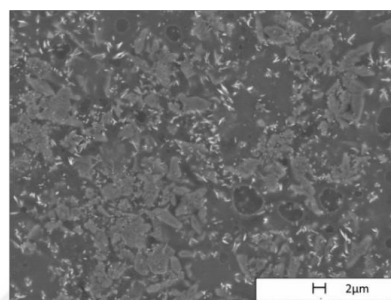
Figure 10.35 SEM images of surfaces of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6



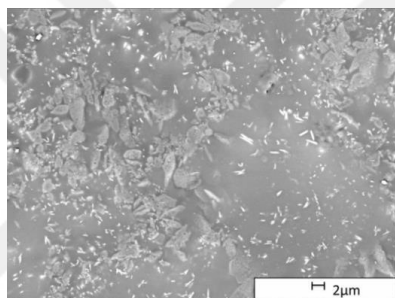
(a)



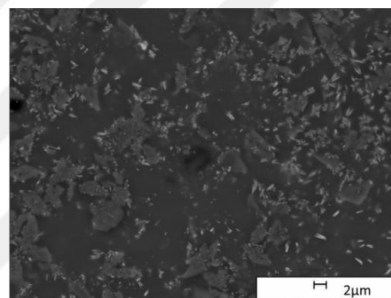
(b)



(c)



(d)



(e)

Figure 10.36 SEM images of surfaces of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4

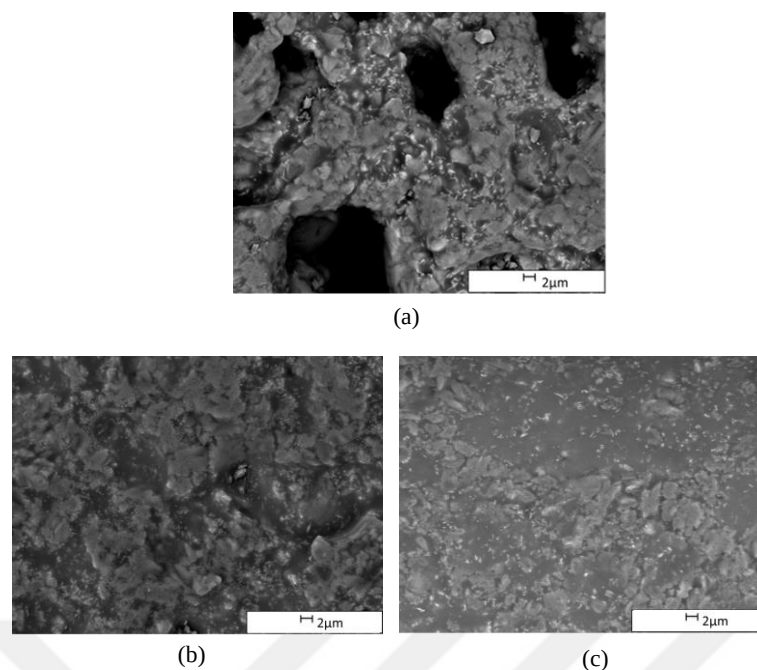
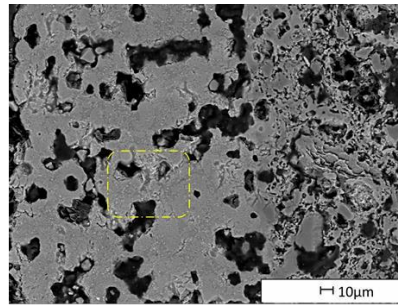
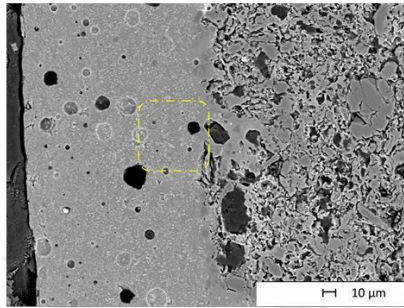


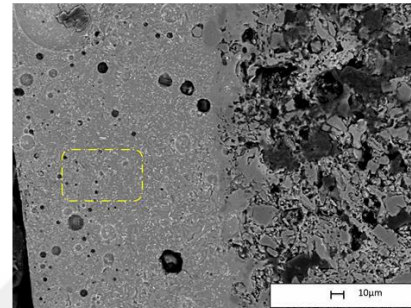
Figure 10.37 SEM images of surfaces of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6. Figures 10 and 11 demonstrate SEM pictures of cross-segments of the frits including waste and in addition that of MOF1, while Figs. 12 and 13 demonstrate higher-amplification pictures of the territories set apart by the yellow lines in Figs. 10 and 11. It tends to be seen that the pores in the standard coating are interconnected; however, those in the recently created frits are most certainly not. Further, the last are littler than the pores in the standard frit.



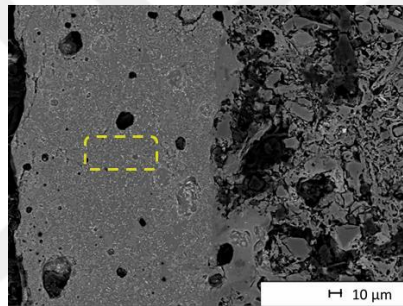
(a)



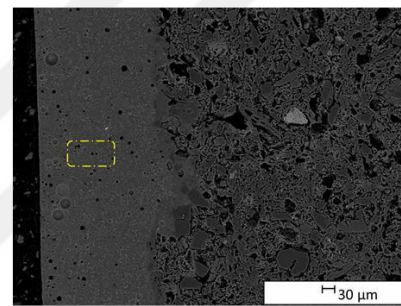
(b)



(c)

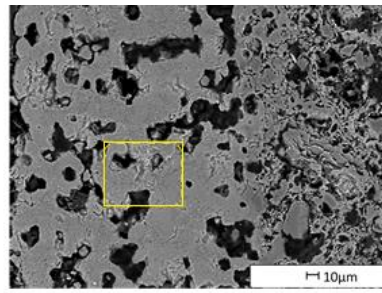


(d)

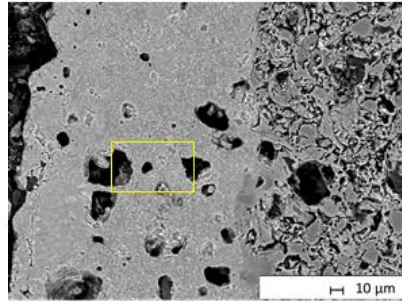


(e)

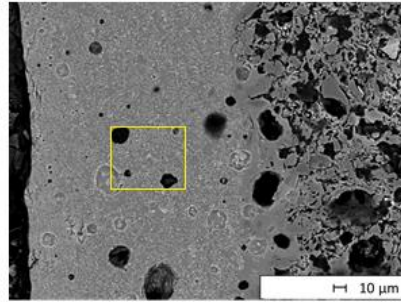
Figure 10.38 SEM images of cross-sections of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4



(a)



(b)



(c)

Figure 10.39 SEM images of cross-sections of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6

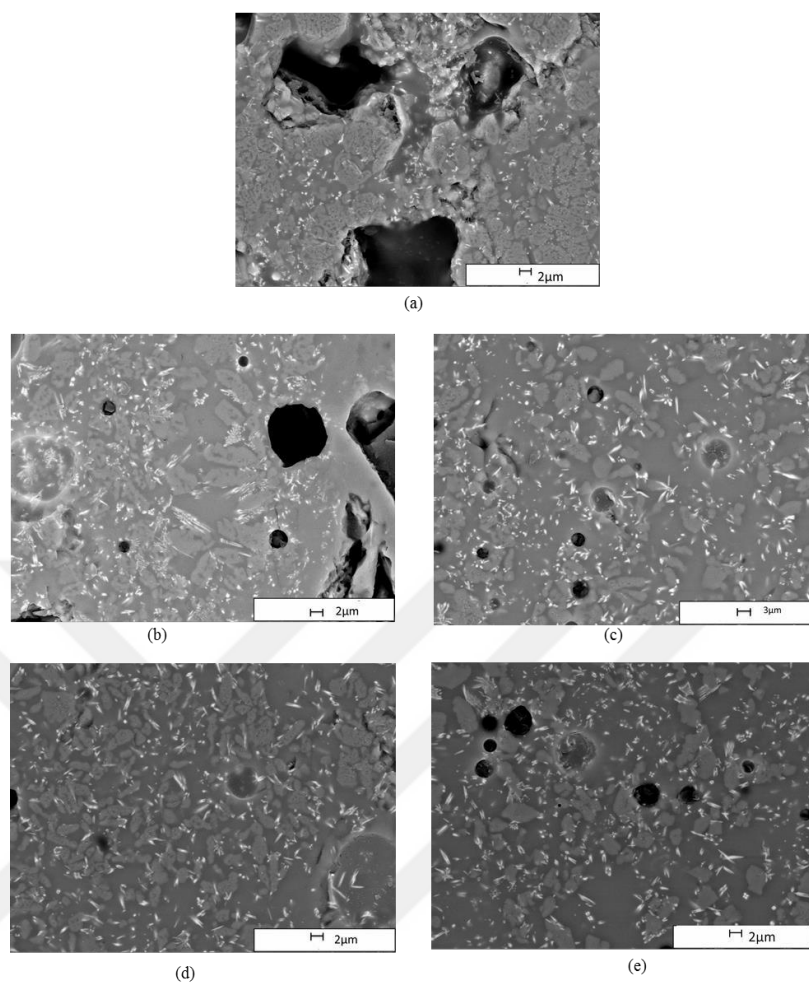
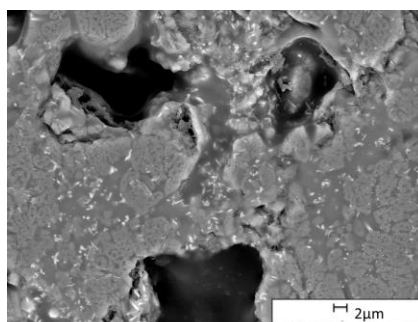
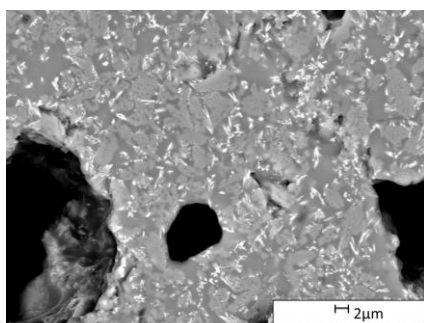


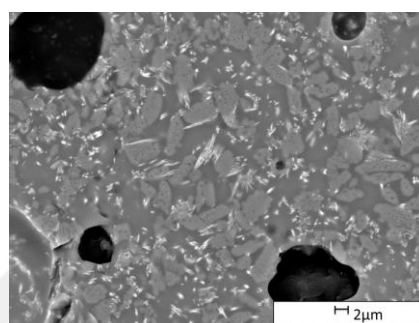
Figure 10.40 SEM images of cross-sections of (a) MOF1, (b) MOF1-A1, (c) MOF1-A2, (d) MOF1-A3, and (e) MOF1-A4



(a)



(b)



(c)

Figure 10.41 SEM images of cross-sections of (a) MOF1, (b) MOF1-A5, and (c) MOF1-A6

As can be seen from Figs. 14 and 15, the size, shape, and distribution of the crystals in all the bright opaque glazes are very similar, without being dependent on the image area. An EDS analysis of the crystals also proved the presence of zircon crystals in the structures.

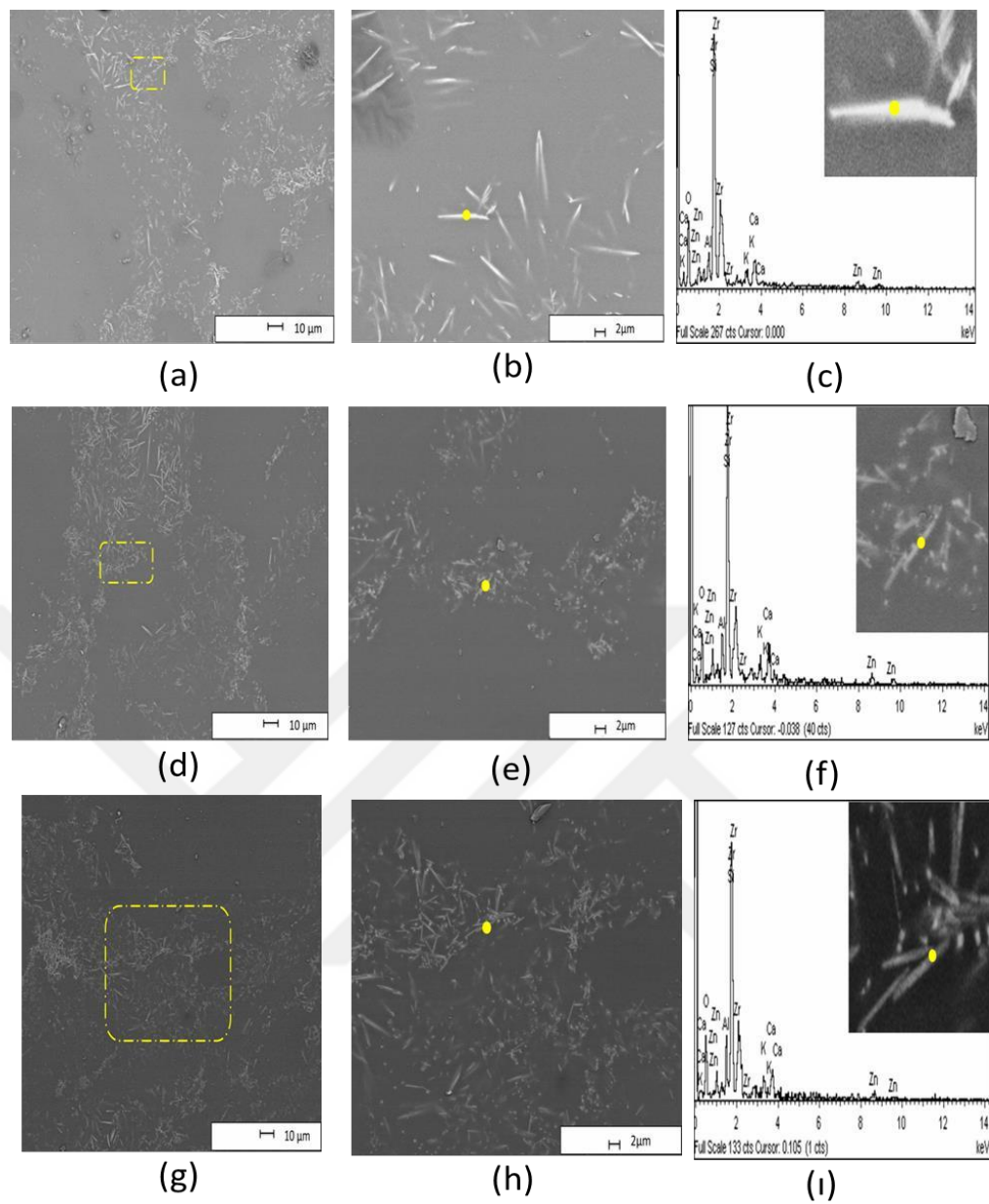


Figure 10.42 (a), (d), (g) SEM (backscattered electron) images of surfaces of BOG, BOG-A3, and BOG-A5. (b), (e), (h) SEM (backscattered electron) images of marked

areas in (a), (d), and (g) at higher magnification. (c), (f), (i) EDX analysis of dotted crystals in (b), (e), and (h)

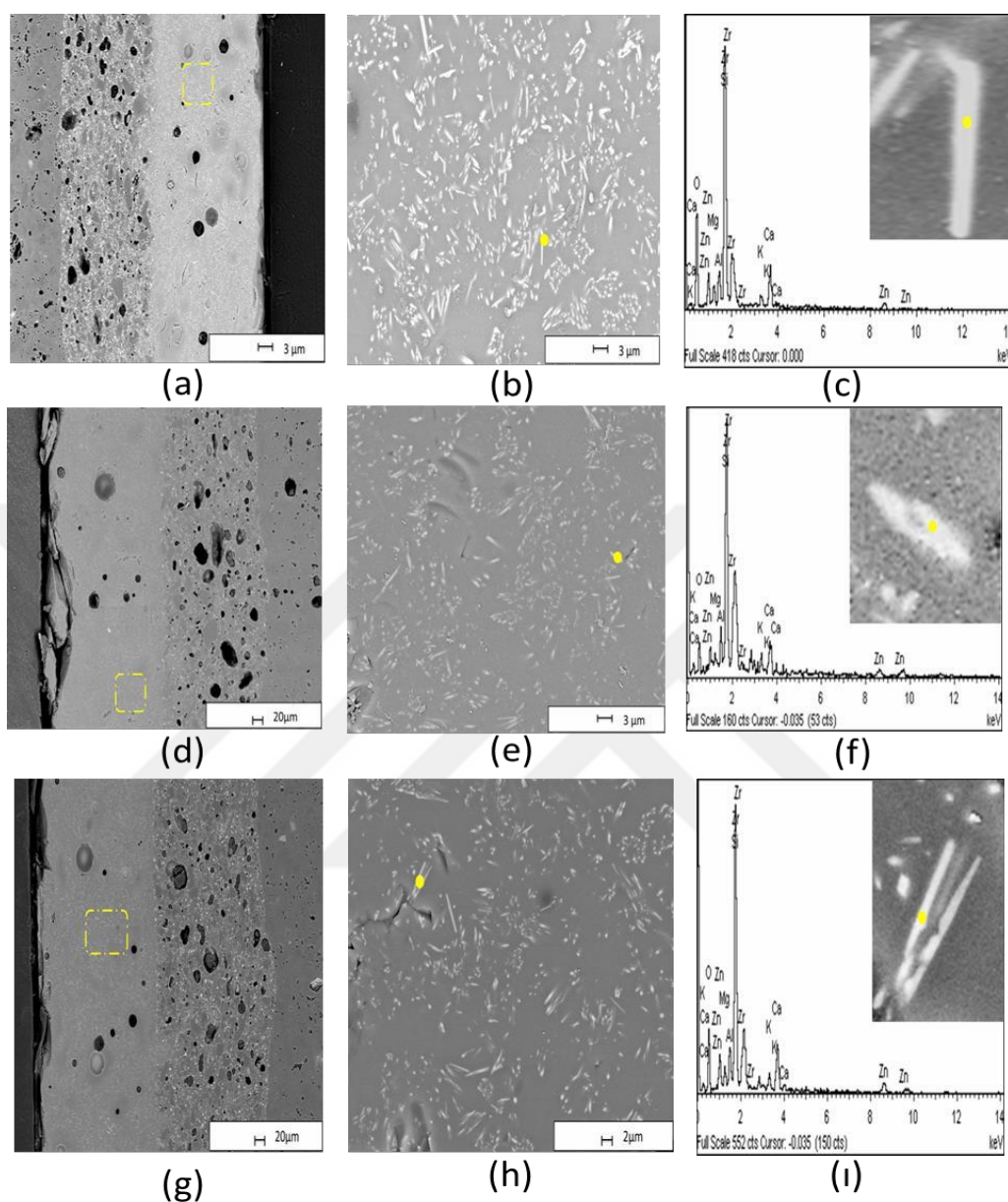


Figure 10.43 (a), (d), (g) SEM (backscattered electron) images of cross-sections of BOG, BOG-A3 and BOG-A5. (b), (e), (h) SEM (backscattered electron) images of the marked areas in (a), (d) and (g) in higher magnification. (c), (f), (i) EDX analysis of dotted crystals in (b), (e) and (h)

✓ **Optical, Mechanical and Chemical Properties**

Digital photographs of the developed glaze layers are given in Fig. 22 together with standard glaze.



Figure 10.44 Digital photographs of MOF1, MOF1-A5, and MOF1-A6 glazes, applied to tile surfaces.

The results of the color, surface roughness, and brightness analyses are listed in Table 4. The brightness and roughness values for MOF1-A3 and MOF1-A5 are very similar to those of the standard glaze, while the others are brighter and smoother than the standard glaze. The seven glazes could be arranged in order of brightness and roughness, follows: $\text{MOF1-A4} > \text{MOF1-A2} > \text{MOF1-A1} > \text{MOF1-A6} > \text{MOF1-A3} > \text{MOF1-A5} > \text{MOF1}$ and $\text{MOF1-A5} > \text{MOF1} > \text{MOF1-A6} > \text{MOF1-A1} > \text{MOF1-A2} > \text{MOF1-A4}$. This also shows that there is an inverse relationship between the roughness and brightness.

Table 10.19 Color, brightness, and roughness values of developed glazes

GLAZE	COLOR			BRIGHTNESS			ROUGHNESS
	L*	a*	b*	20 °	60 °	80 °	μm
MOF1	92.47	-0.1	0.76	1.1	2.4	2.4	18.72
MOF1-A1	89	0.4	1.45	2.4	16.2	38.9	4.97
MOF1-A2	89.28	0.6	2.24	4.1	23.8	55.8	4.02
MOF1-A3	89.3	0.72	2.5	1.3	5.2	6.9	12.19
MOF1-A4	88.31	0.6	2.27	6.9	33.2	64.1	2.21
MOF1-A5	90.94	0.22	1.4	1.1	2.7	2.9	19.35
MOF1-A6	90.45	0.32	1.64	1.4	6.2	7.2	10.13

In Table 5, color and brightness values for BOG-A3 and BOG-A5 are compared with those of BOG. As expected, the visual properties of the waste-containing bright opaque glazes are very similar to the standard BOG. BOG-A3 exhibits a greater brightness than BOG-A5.

Table 10.20 Color and brightness values of bright opaque glazes

GLAZE	COLOR			BRIGHTNESS		
	L*	a*	b*	20 °	60 °	80 °
BOG	92.05	-0.78	2.28	75	93.4	94.3
BOG-A3	91.72	-0.76	2.77	72.5	91.1	96.2
BOG-A5	91.53	-0.76	2.91	75	90.9	93.5

The results of the applied ISO 10545 tests are listed in Table 6. The waste-containing bright opaque glazes showcased very similar characteristics to those of a standard glaze. Regarding the decorative use of the glazes and areas in which they are likely

to be applied, staining resistance and chemical resistance are important both visually and technically. The test results showed that the waste-containing glazes are well suited to such applications.

Table 10.21 ISO 10545 test results of the BOG, BOG-A3 and BOG-A5

TEST	DESCRIPTION			BOG	BOG-A3	BOG-A5
Surface Abrasion Value (PEI)				3 (1500 rpm)	3 (1500 rpm)	3 (1500 rpm)
(TS EN ISO 10545-7)						
Chemical Resistance	House Chemicals	Amonium Chloride	1 day	GA	GA	GA
		(100 g/l)				
(ISO 10545-13)	Swimming Pool	Sodium Hypochloride	1 day	GLA	GLA	GLA
	Salts	(20 mg/l)				
	Low-Concentration	HCl (%3)	4 days	GLA	GLA	GLA
	Acids and	KOH (30g/l)	4 days	GLC	GLC	GLC
	Alkalis	Citric Acid	1 day	GLA	GLA	GLA
		(100 g/l)				
	High-Concentration	HCl (%18)	4 days	GHA	GHA	GHA

	Acids and Alkalies	KOH (100gr/l)	4 days	GHC	GHC	GHC
		Lactic Acid	4 days	GHA	GHA	GHA
		-5%				
Cement Joint Cleaner				GA	GA	GA
Thermal Shock Resistance				Suitable	Suitable	Suitable
(ISO 10545-9)						
Staining Tests	Iron Oxide			5	5	5
(ISO 10545-14)	Olive Oil			5	5	5
	Alcohol Iodide			5	5	5
	Methylene Blue			5	5	5
	Potassium Permanganate			5	5	5
	Black Joint Filler			5	5	5
	Pencil Test			5	5	5
	Shoe Mark			5	5	5

Mohs (Surface Hardness)		4	4	4
Crazing Resistance		Suitable	Suitable	Suitable



Conclusion and Recommendation

As a result of the study, BWs were successfully employed in the fabrication of ceramic tiles with 3 main findings; i) production at lower and more sustainable temperatures, ii) a green product also supplying environmental and ecological benefit, iii) decrease in the raw material costs by recycling. Used waste materials were obtained from landfills located near borate mines, with a daily 80 tons of occurrence amount.

BW containing tiles were fabricated in respect with industrial processes and standards. In floor tiles production, developed compositions containing 5.66 wt% BW showed 65 °C lower sintering temperature than the standard production. Sintering shrinkage (6.8%), colour values (L: 57.00, a: 2.52b: 11.02) and water absorption values (0.49%) were within acceptable industrial standards. However, the 38.43 N/mm² of strength was relatively lower compared to the standard tiles. This was connected to the high CaO amount, resulting as an increase in porosity, hence, future research should concentrate on solving this problem.

In wall tile compositions containing 5.64 wt% of BW, the sintering temperature was decreased by 70 °C. Samples had acceptable sintering shrinkage (0.6%), colour values (L: 77.00, a: 7.7b: 17.57), water absorption (19.39%) and strength (20.46 N/mm²) properties, providing the necessary industrial standards.

Developed porcelain tile compositions including 3 wt% BW showcased 38 °C decrease in sintering temperature when compared to standard composition. Water absorption (0.01%), firing shrinkage (7.4%), fired strength (44.80 N/mm²) and color values (L:74.95, a:1.97, b:9.78) were within industrial standards.

The fluxing effect of B₂O₃ current in wastes provide liquid phase at lower temperatures, thus promoting viscous sintering below the industrial sintering temperatures, providing the expected final characteristics.

For the frits, it was proved BW can be used as an alternative source of B₂O₃, substituting boric acid in the industrial production of matt opaque frit and bright opaque glaze. The obtained final product could be applied to conventional tile production, even at lower sintering temperatures. A low CaO content in transparent frits allows only a limited addition of waste. Full or partial substitution also decreases the firing temperature. Yielded bright opaque glaze compositions met the EN ISO 10545 standards, exhibiting desirable surface abrasion, chemical resistance, thermal shock resistance, and staining characteristics.

Utilization of boron-containing wastes in the production of both ceramic tiles and frits serves as an auspicious recycling option for the removal of these wastes along with bringing additional benefits to both environment and industry.

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Publications From The Thesis

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Papers

1. Bugra Cicek, Emirhan Karadagli, Fatma Duman, Use of boron mining waste as an alternative to boric acid (H_3BO_3) in opaque frit production, *Ceramics International* 44 (2018) 14264–14280
2. Bugra Cicek, Emirhan Karadagli, Fatma Duman, Valorisation of boron mining wastes in the production of wall and floor tiles, *Construction and Building Materials* 179 (2018) 232–244

Conference Papers

1. Fatma Duman, Tuğçe Yağyemez, Emirhan Karadağlı, Buğra Çiçek, Utilization of Bandırma Colemanite Enrichment Wastes in the Production of Transparent Frits, *Acta Materialia Turcica* 1 (2018) 45-49