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Innovative cleaner production technique: foam glass production from lead crystal glass sludge

Hussein Abdel Fattah ElKersh

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INNOVATIVE CLEANER PRODUCTION TECHNIQUE:
FOAM GLASS PRODUCTION FROM LEAD CRYSTAL GLASS SLUDGE

BY
HUSSEIN ABDEL FATAH MOHAMED RAMADAN ELKERSH
B.Sc. Mechanical Power Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Mechanical Engineering

Under the supervision of:

Dr. Salah M. El Haggar
Professor, Department of Mechanical Engineering
The American University in Cairo

January 2014
ACKNOWLEDGMENT

I would like to dedicate this work to my parents whom without their encouragement this work would not have been possible. I would like to profoundly thank Dr. Salah El-Haggar for his continuous guidance and support throughout the thesis work. I would like to thank Mr. Mohamed Saeed (Waste Management Lab), Mr. Zakaria Yehia (Materials Testing Lab) and Mr. Ahmed Saad (Environmental Lab). I am also thankful to ASFOUR Crystal team for their cooperation and support for this research.
ABSTRACT

An innovative cleaner production technique that adopts open-recycling system of the grinding and polishing sludge of lead crystal glass was applied in this study. Foam glass with good properties that can be used in the thermal insulation applications was produced from the grinding and polishing sludge. The leaching test of the sludge showed that it is a hazardous waste because its leachate has a lead concentration of 7.5 mg/l, while the leachate of the produced foam glass was proved to have a negligible lead concentration of less than 0.02 mg/l. The effect of the heating method, sintering temperature, holding time and additives of Silicon Carbide SiC and granite powder on the properties of the foam glass was investigated. The investigated properties are foam bulk density, porosity percentage, compressive strength and thermal conductivity. Sintering the samples by direct insertion to the oven resulted in lower compressive strength and lower density compared to the low heating rate of around 1.5 °C/min adopted in this study. Sintering temperature of 750 °C at a holding time of 30 minutes produced foam glass with bulk density of 0.485 g/cm³, porosity of 84.6%, compressive strength of 2.21 MPa and thermal conductivity of 0.051 W/m. K. These properties are comparable to those of commercial foam glass. Lower temperatures resulted in foam glass with significantly higher bulk density, while higher temperatures led to deterioration in the foam glass properties due to the coalescence phenomenon.

The addition of SiC leads to increase foam glass porosity and reduce its bulk density, compressive strength and thermal conductivity. Adding SiC from 2 to 8 wt.% produced a foam glass with porosity 89.4-91.9%, bulk density 0.256-0.334 g/cm³, compressive strength 0.89-1.44 MPa and thermal conductivity 0.039-0.058 W/m.K. In contrast, the addition of granite powder reduces the foam glass porosity and increases its bulk density, compressive strength and thermal conductivity. Adding granite powder from 2 to 8 wt.% produced a foam glass with porosity 76.1-83.2%, bulk density 0.529-0.747 g/cm³, compressive strength 2.43-5.09 MPa, thermal conductivity 0.074-0.135 W/m. K. It can be concluded that the foam glass prepared by adding SiC is suitable to the applications that need very low thermal conductivity, while the foam glass prepared by adding granite powder is suitable to the applications where compressive strength is of more importance.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. iii
LIST OF TABLES ........................................................................................................... vii
LIST OF FIGURES ....................................................................................................... ix
LIST OF ABBREVIATIONS ........................................................................................ xiii
NOMENCLATURE ...................................................................................................... xiv

## CHAPTER 1: INTRODUCTION .................................................................................. 1

1.1 Glass .................................................................................................................... 1

1.2 Glass Types, Compositions and Applications .................................................. 2
  1.2.1 Soda-lime glass .............................................................................................. 3
  1.2.2 Borosilicate glass ......................................................................................... 3
  1.2.3 Lead glass ..................................................................................................... 3

1.3 Lead in the Crystal Glass Industry ................................................................. 5

1.4 Health Hazardous Associated with Lead ..................................................... 7
  1.4.1 Lead dust in lead crystal manufacturing .................................................... 9
  1.4.2 Lead release from lead crystal to food and beverages ....................... 10

1.5 Lead-Free Crystal Glass ................................................................................. 11

1.6 Viscosity-Temperature Characteristics of Glass ......................................... 13

1.7 Glass Manufacturing ....................................................................................... 14
  1.7.1 Batch preparation ....................................................................................... 15
  1.7.2 Melting ......................................................................................................... 15
  1.7.3 Forming ........................................................................................................ 15
  1.7.4 Annealing .................................................................................................... 17
  1.7.5 Finishing ...................................................................................................... 17

1.8 Pollution Associated with Glass Manufacturing ......................................... 18
  1.8.1 Air emissions .............................................................................................. 18
  1.8.2 Wastewater ................................................................................................. 19
  1.8.3 Solid waste .................................................................................................. 20

## CHAPTER 2: LITERATURE REVIEW ..................................................................... 22

2.1 Cleaner Production Techniques in Lead Crystal Glass ................................. 22
  2.1.1 Air emissions .............................................................................................. 23
  2.1.2 Wastewater ................................................................................................. 24
2.1.3 Solid waste ............................................................. 26

2.2 Utilization of Grinding Sludge to Produce Foam Glass ................. 28

2.3 Foam Glass ............................................................ 28

  2.3.1 Foaming agents ................................................. 29

  2.3.2 Foam Glass Properties .......................................... 30

  2.3.3 Compressive stress model for open and closed cells ............... 34

2.4 Parameters Affecting the Properties of Foam Glass ..................... 36

  2.4.1 Heating & cooling rate .......................................... 36

  2.4.2 Amount of foaming agent ....................................... 39

  2.4.3 Holding time .................................................... 41

  2.4.4 Sintering temperature .......................................... 43

2.5 Measuring Compressive Strength ........................................ 47

  2.5.1 Stress-strain curve of foam glass ................................ 47

  2.5.2 Sample size and cross head speed ................................ 51

2.6 Leaching of Lead Silicate Glass ...................................... 52

CHAPTER 3: Experimental Procedure ........................................ 60

3.1 Characteristics of Raw Material ....................................... 60

  3.1.1 Chemical analysis .............................................. 60

  3.1.2 Particle size analysis .......................................... 60

  3.1.3 Powder density measurement .................................. 62

  3.1.4 Leaching test ................................................... 62

3.2 Foam Glass Preparation Procedure .................................... 67

3.3 Experimental Matrix .................................................. 73

3.4 Testing of the Produced Foam Glass ................................... 74

  3.4.1 Compression test ............................................... 74

  3.4.2 Bulk density measurement ..................................... 75

  3.4.3 Thermal conductivity measurement ............................. 75

  3.4.4 Leaching test ................................................... 75

CHAPTER 4: RESULTS AND DISCUSSION ................................ 76

4.1 Physical Properties of Powders ....................................... 76

4.2 The Effect of Low Heating Rate vs. Direct Insertion .................. 78

4.3 The Effect of Sintering Temperature on the Foam Glass Properties .... 80
LIST OF TABLES

Table 1.1: Summary of unique glass characteristics ........................................ 2
Table 1.2: Chemical composition of soda-lime glass, lead crystal glass and borosilicate glass ................................................................. 2
Table 1.3: Chemical Composition of CRT glass parts .................................. 4
Table 1.4: Chemical composition of different lead glass .............................. 5
Table 1.5: Crystal glass categories ............................................................. 7
Table 1.6: List of lead-free crystal patents achieving refractive index greater or equal to 1.545 ................................................................. 11
Table 1.7: Air emissions guideline values for glass manufacturing ............... 19
Table 1.8: Effluent levels for glass manufacturing to discharged to surface water 20
Table 1.9: Maximum allowable concentrations for contaminants from leaching tests of solid wastes ............................................................ 21
Table 2.1: Economic analysis of the cleaner production process (US$) ..... 25
Table 2.2: Properties of some selected commercial foam glass .................. 31
Table 2.3: Size of compression test samples and the adopted cross head speeds ................................................................. 52
Table 2.4: Lead leachate values for 30 CRTs ........................................... 54
Table 2.5: Samples composition, their porosity and their lead leachate value 55
Table 3.1: Sieves used in the particle size analysis of the sludge ................. 60
Table 3.2: Experimental matrix ............................................................... 73
Table 4.1: Chemical composition of the sludge ....................................... 76
Table 4.2: Particle size of the sludge powder from sieve analysis tests ....... 77
Table 4.3: The results of measured powder density (ρ) ........................... 77
Table 4.4: The effect of heating method on the foam glass density and porosity 78
Table 4.5: The effect of heating method on the foam glass compressive strength 79
Table 4.6: The variation of bulk density and porosity with sintering temperature 81
Table 4.7: The variation of compressive strength with sintering temperature .... 82
Table 4.8: The variation of thermal conductivity with sintering temperature .... 83
Table 4.9: The variation of bulk density and porosity with holding time ........ 85
Table 4.10: The variation of compressive strength with holding time .......... 86
Table 4.11: The variation of thermal conductivity with holding time ........... 87
Table 4.12: The variation of bulk density and porosity with SiC content .......... 89
Table 4.13: The variation of compressive strength with SiC content .......... 90
Table 4.14: The variation of thermal conductivity with SiC content .................. 91
Table 4.15: The variation of bulk density and porosity with granite content ........ 93
Table 4.16: The variation of compressive strength with granite content ............. 94
Table 4.17: The variation of thermal conductivity with granite content ............. 95
Table 4.18: The variation of compressive strength with relative density............. 97
Table 4.19: Measured pH value and Pb concentration of the sludge leachate........ 98
Table 4.20: Measured pH value and Pb concentration of the leachate of foam glass sample#2 ................................................................. 99
LIST OF FIGURES

Figure 1.1: Behavior of crystalline and non-crystalline materials during cooling 1
Figure 1.2: Components of CRTs ................................................. 4
Figure 1.3: The relationship between glass density, refractive index and lead content ................................................. 6
Figure 1.4: The organ systems affected by lead exposure ......................... 8
Figure 1.5: The lowest observable levels for lead concentration in blood in adults and children resulting in negative health effects .................. 9
Figure 1.6: Relationship between concentration of BaCO$_3$ and refractive index of glass ................................................. 12
Figure 1.7: The effect of temperature on the viscosity of glass ............. 13
Figure 1.8: Overview of glass manufacturing .................................. 14
Figure 1.9: Producing glass bottle by using the blowing method ............ 16
Figure 1.10: Schematic diagram showing the float process for making sheet glass ................................................. 17
Figure 1.11: Conventional treatment process for wastewater in the glass industry ................................................. 20
Figure 2.1: Proposed membrane system to recycle the wastewater in glass industry ................................................. 24
Figure 2.2: Typical manufacturing process and conventional wastewater treatment system in crystal glass industry ................................................. 24
Figure 2.3: Cleaner production zero-discharge wastewater system in crystal glass industry ................................................. 25
Figure 2.4: Schematic diagram for utilizing polishing waste of lead crystal glass ................................................. 26
Figure 2.5: Schematic diagram for utilizing grinding waste of lead crystal glass ................................................. 27
Figure 2.6: The range of properties for foams .................................. 31
Figure 2.7: Variation of compressive strength and density of glass foams with the strut thickness of cells ................................................. 32
Figure 2.8: Variation of compressive strength with the square root of the pore diameter ................................................. 33
Figure 2.9: The relationship between thermal conductivity and porosity .... 33
Figure 2.10: Cubic cell model for open and closed cells ..................... 34
Figure 2.11: Comparison between the experimental results of foam glass prepared from CRT glass with Gibson and Ashby model ............. 35
Figure 2.12: Comparison between the experimental results of foam glass prepared from soda-lime glass with Gibson and Ashby model

Figure 2.13: Morphology of foam glass sintered at 725 °C and holding time 15 minute prepared by a) Heating rate 20 °C/min b) Direct insertion

Figure 2.14: The variation of the mechanical strength with different SiC content

Figure 2.15: Morphology of foam glass with different content of SiC: a) 1 wt% b) 5 wt% c) 9 wt%

Figure 2.16: The variation of foam glass density with different content of foaming agent egg shell containing 95wt% CaCO₃

Figure 2.17: Morphology of foam glass at different holding time: a) 5 minutes b) 10 minutes c) 15 minutes d) 30 minutes

Figure 2.18: Morphology of foam glass at different holding time: 30 minutes b) 60 minutes c) 90 minutes

Figure 2.19: Morphology of foam glass at sintering temperature: a) 750 °C b) 850 °C c) 950 °C

Figure 2.20: Morphology of foam glass at sintering temperature: a) 600 °C b) 700 °C

Figure 2.21: The variation of a) density b) compressive strength with sintering temperature

Figure 2.22: Effect of sintering temperature on relative density under various pressures

Figure 2.23: The morphology of foam glass prepared from soda-lime glass at: (a) 750 °C, (b) 800 °C, (c) 850 °C (d) 900 °C

Figure 2.24: Metal lead content in wt% of unreduced lead initially present before foaming vs. the sintering temperature

Figure 2.25: Compressive stress-strain curve for elastic-brittle foams

Figure 2.26: Compression stress-strain curve for foam glass prepared from soda-lime glass

Figure 2.27: Compression stress-strain curve for different samples of foam glass prepared from soda-lime glass, aluminosilicate glass powder and SiC as foaming agent

Figure 2.28: Compression stress-strain curve for foam glass with different particle size prepared from soda-lime glass with 12wt% sodium silicate at sintering temperature of 850 °C, holding time 30 minutes

Figure 2.29: Compression stress-strain curve for foam glass prepared from CRT panel and funnel glass with SiC and TiN as foaming agent

Figure 2.30: Metal lead content in wt% of unreduced lead initially present before foaming vs. the foaming agent content
Figure 2.31: Small lead bubbles generated on the surface of the pores of the foam glass

Figure 2.32: Magnified droplet of the generated metal lead

Figure 3.1: Used set of sieves in the particle size analysis of the sludge

Figure 3.2: The set of sieves with the pan installed in the mechanical shaker

Figure 3.3: Plan view of the assembled mechanism used for the shake extraction

Figure 3.4: Example Extractor

Figure 3.5: The simovert connected to the motor to adjust the rpm

Figure 3.6: Filtering the sample through 0.45-μm membrane filter by using a vacuum pump

Figure 3.7: The five consecutive filters used in the filtration process (first filter on the left)

Figure 3.8: The sample before filtration (on the left) and after filtration (on the right)

Figure 3.9: the pH-meter used to measure the pH

Figure 3.10: The Atomic Absorption Spectrometer used to measure the lead concentration

Figure 3.11: Rotary mixer to obtain the sludge powder

Figure 3.12: Drying oven and its temperature control unit

Figure 3.13: Rotary mixer to mix the sludge powder with additives

Figure 3.14: The hydraulic press and the mould used in sample preparation

Figure 3.15: The pressed sample before sintering

Figure 3.16: Electric oven for foam glass sintering

Figure 3.17: The heating rate of the electric oven used for sintering

Figure 3.18: Slow cooling rate of foam glass

Figure 3.19: A sample of the produced foam glass

Figure 3.20: Bench-type circular saw

Figure 3.21: Foam glass 20 mm cube samples prepared for the compression test

Figure 3.22: Foam glass 100*30*30 mm samples prepared for measuring the thermal conductivity

Figure 3.23: The universal testing machine used in the compression test

Figure 3.24: The foam glass sample suffering from catastrophic failure after the compression test

Figure 4.1: Particle-size distribution of sludge using sieve analysis

Figure 4.2: Compressive stress-strain curve for the foam glass prepared by low heating rate and direct insertion
Figure 4.3: The effect of low heating rate and direct insertion on the foam glass properties
Figure 4.4: The variation of bulk density and porosity with sintering temperature
Figure 4.5: Compressive stress-strain curves at different sintering temperatures
Figure 4.6: The variation of compressive strength with sintering temperature
Figure 4.7: The variation of thermal conductivity with sintering temperature
Figure 4.8: The variation of bulk density and porosity with holding time
Figure 4.9: Compressive stress-strain curves at different holding times
Figure 4.10: The variation of compressive strength with holding time
Figure 4.11: The variation of thermal conductivity with holding time
Figure 4.12: The variation of bulk density and porosity with SiC content
Figure 4.13: Compressive stress-strain curves at different wt.% SiC
Figure 4.14: The variation of compressive strength with SiC content
Figure 4.15: The variation of thermal conductivity with SiC content
Figure 4.16: The variation of bulk density and porosity with granite content
Figure 4.17: Compressive stress-strain curves at different wt.% granite
Figure 4.18: The variation of compressive strength with granite content
Figure 4.19: The variation of thermal conductivity with granite content
Figure 4.20: Compressive strength vs. relative density of the samples along with Gibson and Ashby model
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CLM</td>
<td>Complex Lead-bearing Material</td>
</tr>
<tr>
<td>CPCB</td>
<td>Central Pollution Control Board</td>
</tr>
<tr>
<td>CRT</td>
<td>Cathode Ray Tube</td>
</tr>
<tr>
<td>EP</td>
<td>Extraction Procedure Toxicity Characteristic</td>
</tr>
<tr>
<td>IFC</td>
<td>International Finance Corporation</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>LCA</td>
<td>Life Cycle Assessment</td>
</tr>
<tr>
<td>MF</td>
<td>Micro-Filtration</td>
</tr>
<tr>
<td>SCR</td>
<td>Selective Catalytic Reduction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STDEV</td>
<td>Standard Deviation</td>
</tr>
<tr>
<td>TCLP</td>
<td>Toxicity Characteristic Leaching Procedure</td>
</tr>
<tr>
<td>UF</td>
<td>Ultra-Filtration</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environmental Program</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>WDX</td>
<td>Wavelength Dispersive X-ray</td>
</tr>
</tbody>
</table>
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mass of sample after drying, g</td>
</tr>
<tr>
<td>B</td>
<td>Original mass of sample, g</td>
</tr>
<tr>
<td>M</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>m</td>
<td>Mass, g</td>
</tr>
<tr>
<td>S</td>
<td>Solid content</td>
</tr>
<tr>
<td>V</td>
<td>Volume, cm$^3$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Powder density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Foam glass bulk density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_{rel}$</td>
<td>Relative density</td>
</tr>
<tr>
<td>$\sigma_{cr}$</td>
<td>Crushing/compressive strength of foam glass, MPa</td>
</tr>
<tr>
<td>$\sigma_{bs}$</td>
<td>Bending strength of solid glass, MPa</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Fraction of the solid contained in the cell edges</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION

1.1 Glass

Glass is a ceramic material made from inorganic materials at high temperature. The solidification behavior of glass is what makes it non-crystalline (amorphous) material as it is cooled without crystallization. When cooling a crystalline material it solidifies at its specified melting temperature $T_m$ with a significant decrease in its specific volume. However, when cooling glass the liquid transforms to glass at the glass transition temperature $T_g$. At this temperature the liquid changes from rubbery soft plastic state to a brittle rigid glass state (Callister and Rethwisch, 2009; Smith, 1996). This is presented in Figure 1.1.

![Figure 1.1: Behavior of crystalline and non-crystalline materials during cooling (Callister and Rethwisch, 2009)](image)

Glass has some unique characteristics. It’s necessary to know these characteristics in order to properly choose the suitable applications for glass. Table 1.1 qualitatively summarizes these characteristics.
Table 1.1: Summary of unique glass characteristics

<table>
<thead>
<tr>
<th>Property</th>
<th>Unique Characteristics of Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Glass is highly resistant to chemical attack, and many chemicals and foods/beverages can be stored for decades without corrosion of the glass. Only a few chemicals aggressively attack glass (hydrofluoric acid, phosphoric acid, hot alkali solutions, superheated water).</td>
</tr>
<tr>
<td>Elasticity</td>
<td>Glass is perfectly elastic. After bending or stretching it returns exactly to its original shape when the force is removed. Glass will break, however, when the force applied exceeds the ultimate strength of the glass.</td>
</tr>
<tr>
<td>Strength</td>
<td>Glass is brittle, and will break rather than deform when subjected to severe impacts. However, in compression, glass is very strong (e.g., glass spheres are used in undersea applications where they are subjected to intense compressive forces). The tensile strength of glass can be increased by thermal tempering, chemical modification, or laminating.</td>
</tr>
<tr>
<td>Hardness</td>
<td>Glass is a hard material, with hardness values comparable to steel, and can withstand significant abrasion over its lifetime. Glasses with aluminum oxide are some of the hardest.</td>
</tr>
<tr>
<td>Optical</td>
<td>Glass is transparent or translucent to light, and some glasses are selectively transparent, transmitting light of one wavelength or color more efficiently than any other. Other glasses are designed to absorb infrared light and transmit visible light, or to transmit either ultraviolet or infrared while absorbing visible light. Glass can also bend light (as in a lens).</td>
</tr>
<tr>
<td>Electrical</td>
<td>Glass is a good insulator, and provides high resistance to the passage of electricity.</td>
</tr>
<tr>
<td>Thermal</td>
<td>Glasses with low thermal expansion have high thermal shock resistance.</td>
</tr>
</tbody>
</table>

Source: (Energetics, 2002)

1.2 Glass Types, Compositions and Applications

Silicon dioxide (SiO₂) derived from sand is the main constituent of glass. Glass can be classified based on its chemical composition to three main types that represent more than 95% of the produced glass. These three types are; soda-lime glass, lead glass, borosilicate glass (Vieitez et al., 2011). Table 1.2 shows the chemical composition of these three types.

Table 1.2: Chemical composition of soda-lime glass, lead crystal glass and borosilicate glass

<table>
<thead>
<tr>
<th></th>
<th>Soda-lime glass</th>
<th>Borosilicate glass</th>
<th>Lead glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO₂)</td>
<td>71-75%</td>
<td>70-80%</td>
<td>54-65%</td>
</tr>
<tr>
<td>Boron trioxide (B₂O₃)</td>
<td></td>
<td>7-15%</td>
<td></td>
</tr>
<tr>
<td>Lead oxide (PbO)</td>
<td></td>
<td></td>
<td>25-30%</td>
</tr>
<tr>
<td>Sodium oxide (Na₂O)</td>
<td>12-16%</td>
<td>4-8%</td>
<td>13-15%</td>
</tr>
<tr>
<td>Potassium oxide (K₂O)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>10-15%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum trioxide (Al₂O₃)</td>
<td></td>
<td></td>
<td>7%</td>
</tr>
</tbody>
</table>

Source: (Vieitez et al., 2011)
1.2.1 Soda-lime glass

The main constituents of soda–lime glass, other than silicon dioxide, are Na₂O derived from sodium carbonates Na₂CO₃ (soda ash) and CaO from Calcium carbonate CaCO₃ (limestone). The function of Na₂O is to lower the melting point of silica to 1500 °C while CaO is added to enhance the chemical durability of the glass. Soda-lime glass is used in three main applications: Container glass (packing bottles and jars), flat glass (windows of buildings and automotive) and domestic glass (drinkware and dishes) (Vieitez et al., 2011).

1.2.2 Borosilicate glass

As shown in Table 1.2 borosilicate glass contains 7-15% Boron trioxide. Adding boron provides superior durability and resistance against chemicals and heat. It also changes the viscosity of glass which facilitates the manufacturing process. Typical applications of borosilicate glass can be found in laboratories and pharmaceutical tools such as syringes, ampoules and vials. It’s also used in cookware and as bulbs for high-power lamps and in the fire protection windows (Vieitez et al., 2011).

1.2.3 Lead glass

Lead oxides PbO (litharge) and Pb₃O₄ (red lead) are added to glass to increase the refractive index which gives brilliance to glass. It also eases the workability of handmade glass by lowering the required working temperature and viscosity (Vieitez et al., 2011). Table 1.2 shows that the typical lead oxide PbO content in lead glass is about 25-30%, however higher percentage can be found in certain applications like optical glasses. There are four main applications of lead glass (Hynes and Jonson, 1997):

- Lead Crystal: According to the European Community Directive on crystal glass 69/493/EEC, in order to market glass as ‘full crystal’, the glass should contain at least 24% PbO with a minimum refractive index and density of 1.545 and 2.9 g/cm³, respectively (EU Directive 69/493/EEC, 1969). This will be discussed later in more details.
- Cathode ray tube CRT: Lead is added to CRT to absorb the UV and X-ray radiation produced by the electron gun. It should be noticed however that CRT
contains three main different glass parts as shown in Figure 1.2: the panel, funnel and neck glass. Only the latter two parts are the ones that contain lead. The panel glass, however, includes barium and strontium instead of lead because lead silicate glass is brown while barium-strontium silicate is transparent under X-ray radiation. In color CRTs the panel glass should be colorless when the electrons hit it, thus the lead silicate is replaced by barium-strontium silicate. Solder glass called frit is used to join the neck, funnel and panel glass of CRT. This frit seal includes 85% lead (Méar et al., 2006a). Table 1.3 shows the typical chemical composition of three main glass parts of the color CRT.

![Diagram of CRT components](image)

**Figure 1.2: Components of CRTs (Méar et al., 2006a)**

<table>
<thead>
<tr>
<th></th>
<th>Panel glass (Ba containing)</th>
<th>Funnel glass (Pb containing)</th>
<th>Neck glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>60.7</td>
<td>54.10</td>
<td>38.00</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.70</td>
<td>1.80</td>
<td>0.90</td>
</tr>
<tr>
<td>Na₂O</td>
<td>7.50</td>
<td>6.20</td>
<td>2.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>6.90</td>
<td>8.20</td>
<td>16.50</td>
</tr>
<tr>
<td>CaO</td>
<td>0.10</td>
<td>3.50</td>
<td>0.10</td>
</tr>
<tr>
<td>BaO</td>
<td>9.90</td>
<td>0.80</td>
<td>0.70</td>
</tr>
<tr>
<td>SrO</td>
<td>8.60</td>
<td>0.70</td>
<td>4.80</td>
</tr>
<tr>
<td>PbO</td>
<td>0.01</td>
<td>22.00</td>
<td>35.00</td>
</tr>
</tbody>
</table>

**Table 1.3: Chemical Composition of CRT glass parts**

Source: (Bernardo et al., 2007b)
• Optical Glass: The optical properties of glass are important in the application of optical glasses. Lead is added in different percentages (from small masses to more than 50%) to control and enhance the refractive index and dispersion (Hynes and Jonson, 1997).

• Sealing / solder glass: This type of glass is used when joining metals to glasses like in light bulbs. The sealing glass should have a matching thermal expansion and good adhesion properties (Frieser, 1975; Hynes and Jonson, 1997).

Table 1.4 shows the typical chemical compositions of optical glass, sealing glass and lead crystal glass.

Table 1.4: Chemical composition of different lead glass

<table>
<thead>
<tr>
<th>Composition</th>
<th>Chemical Composition (mass %)</th>
<th>Lead Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Optical glass*</td>
<td>Sealing glass</td>
</tr>
<tr>
<td>SiO₂</td>
<td>50.2</td>
<td>57.1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.8</td>
<td>4.9</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.6</td>
<td>7.0</td>
</tr>
<tr>
<td>PbO</td>
<td>39.7</td>
<td>29.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Refractive index=1.5955 & Dispersion = 39.18
Source: (Hynes and Jonson, 1997)

1.3 Lead in the Crystal Glass Industry

Lead is used in many industries and it is ranked fifth in tonnage consumed after iron, copper, aluminum and zinc. It has some unique properties such as low melting point (327.5 °C), high density (11.35 g/cm³), good resistance to acids and chemical stability in air and water. Lead oxide PbO, known as litharge, is formed by heating lead in air or blowing air into molten lead (El-Sayed 2011). The price of PbO was doubled between 2000 and 2008 to reach 3000 Euro/ton (Rada, 2009). As previously stated, adding lead oxide to glass results in increasing the refractive index. It also leads to increase the glass density. Figure 1.3 shows the relationship between glass density, refractive index and the lead content.
The European Community Directive on crystal glass 69/493/EEC set certain criteria for glass to be marketed as “full crystal” or “crystal” (KEMI, 2007; UNEP, 2010). The directive divides crystal glass into four categories. In the first two categories the content of lead oxide PbO must be greater than or equal to 30% and 24% with density greater than or equal to 3 and 2.9 g/cm² respectively and a refractive index greater than or equal to 1.545. These two categories can be marketed as “full crystal” with a gold round label. In the second two categories lead oxide PbO and/or other oxides such as Barium Oxide BaO and Potassium Oxide K₂O can be used with a total percentage of 10% (EU Directive 69/493/EEC, 1969). The crystal glass categories as decided by the European Community directive on crystal glass are shown in Table 1.5.
Table 1.5: Crystal glass categories

<table>
<thead>
<tr>
<th>Description</th>
<th>Metal oxide%</th>
<th>Density (g/cm^3)</th>
<th>Refractive index</th>
<th>Surface Hardness</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full Crystal</td>
<td>PbO ≥ 30%</td>
<td>≥ 3</td>
<td>1.545</td>
<td></td>
<td>Round golden label</td>
</tr>
<tr>
<td>Full Crystal</td>
<td>PbO ≥ 24%</td>
<td>≥ 2.9</td>
<td>1.545</td>
<td></td>
<td>Round golden label</td>
</tr>
<tr>
<td>Crystal</td>
<td>ZnO, BaO, PbO, K₂O single or together ≥ 10%</td>
<td>≥ 2.45</td>
<td>1.52</td>
<td></td>
<td>Square silver label</td>
</tr>
<tr>
<td>Crystal</td>
<td>BaO, PbO, K₂O single or together ≥ 10%</td>
<td>≥ 2.4</td>
<td>Vickers 500 ± 20</td>
<td></td>
<td>Equilateral triangle silver label</td>
</tr>
</tbody>
</table>


The UNEP review of scientific information on lead describes the European Community directive on crystal glass as a directive that advocates the use of lead (UNEP, 2010). This is because the directive asks for certain amounts of lead oxide to be used in order to market crystal glass as “full crystal” with the round golden label. This can conflict with the environmental policies in countries that try to minimize the usage of such toxic substances. For example, the Swedish government indicates that the requirements in this directive clash with the Swedish environmental policy and thus the Swedish government aims to change this crystal directive (KEMI, 2007). Rada (2009) proposed alternative directive that doesn’t ask for using lead oxide, but it specifies other important parameters. These parameters include impact resistance, chemical durability, absence of bubbles and cores as well as the refractive index. In contrary to the European Community Directive on crystal glass, the proposed directive didn’t include density in its criteria.

1.4 Health Hazardous Associated with Lead

Lead is considered as pure toxic element and it has no beneficial effects to the body (UNEP, 2013). Figure 1.4 shows the human organ systems that can be affected by exposure to lead. Countries such as Germany, Australia and Canada have guidelines to lead levels in blood as low as 10-15 μg/dl for general population (UNEP, 2013).
Studies have shown that there is no threshold for safe exposure to lead since even the lowest dose can affect the human nervous system (UNEP, 2013). However, Figure 1.5 shows the lowest observable levels of lead in blood that can cause negative health effects in adults as well as children.
Figure 1.5: The lowest observable levels for lead concentration in blood in adults and children resulting in negative health effects (Hynes and Jonson, 1997)

1.4.1 Lead dust in lead crystal manufacturing

Air measurements in lead crystal manufacturing facilities showed that the lead concentration in the air can reach as high as 110 μg/m$^3$ (WHO-IARC, 1993). This is significantly higher than the threshold set by countries like Sweden which is 50 μg/m$^3$ (Andersson et al., 1990). Pierre et al. (2002) investigated the relationship between the exposure to lead crystal dust on blood lead level in employees working in finishing and grinding of crystal pieces. They concluded that exposure to dust particles in the finishing workshops results in increasing the lead levels in blood. The highest measured value was 60 μg/dl which can lead to poisoning. They also concluded that the lead blood levels are higher for the employees working at crystal grinding stations than at polishing stations. WHO-IARC (1993) listed several studies that investigated the lead concentration in the blood of the employees working in the different...
segments of the lead crystal manufacturing industry. The studies showed high lead levels in the blood of the workers.

1.4.2 Lead release from lead crystal to food and beverages

Lead can be released to the food and beverages when stored in lead crystal glass. Acidic foods and beverages such as pickles and fruit juices have an increased potential for releasing lead, while less acidic foods and beverages, such as cheese and milk have less potential (Health Canada, 2003). Also increasing the storage temperature and/or the storage duration can result in increasing the potential for lead release (So, 1997). Several studies have investigated the release of lead from lead crystal glass used to store beverages, especially wine, and they concluded that lead is released when the lead crystalware get in contact with acidic beverages (Graziano and Blum, 1991; Jones et al., 1992; Barbee and Constantine, 1994; Hight, 1996; So, 1997; Guadagnino et al., 2000). Such release of lead to food and beverages can cause health risks, however certain coatings can be used to coat the internal surface of the lead crystalware to reduce the amount of the released lead (Ahmed et al., 1998). The quantity of the released lead depends on four main factors (Health Canada, 2003; So, 1997):

1. The amount of lead in the glass
2. The type of food or beverage
3. The duration which the lead crystalware is in contact with the food or beverage
4. The storage temperature

Testing the release of lead from lead glass used to store drinks or foods is usually done in accordance with ISO 7086-1 “Glass hollowware in contact with food- Release of lead and cadmium- Part 1: Test method” (ISO 7086-1, 2000). The new version of this standard was released in 2000 and its second part ISO 7086-2 “Glass hollowware in contact with food- Release of lead and cadmium-Part 2: Permissible limits” provides guideline values that should not be exceeded as follows (ISO 7086-2, 2000):

- 1.5 mg/l for small hollowware (<600 ml volume)
- 0.75 mg/l for large hollowware (≥600 ml volume but less than 3000 ml)
- 0.5 mg/l for very large hollowware (≥3000 ml volume)
It should be noted, however, that the earlier version of ISO 7086-2 released in 1982 provided higher guideline values (5 mg/l for small hollowware and 2.5 for large hollowware) (ISO 7086-2, 1982), which were significantly higher than the maximum permissible limits set by many countries like Canada and Australia (0.2 mg/l) (So, 1997).

The aforementioned discussion shows the necessity to produce lead free crystal glass to eliminate the health hazardous associated with using lead in manufacturing full crystal glass.

### 1.5 Lead-Free Crystal Glass

There are two ways that can be adopted to manufacture lead-free crystal glass with high refractive index. The first way is to use a certain group of oxides, while the second way is to use barium compounds (Hynes and Jonson, 1997). There are many patents that used alternative group of oxides to PbO and managed to achieve refractive index greater than or equal to 1.545 as required by the European Community Directive on crystal glass 69/493/EEC. A list of some of these patents are presented in Table 1.6

**Table 1.6: List of lead-free crystal patents achieving refractive index greater or equal to 1.545**

<table>
<thead>
<tr>
<th>Patent</th>
<th>Applicant</th>
<th>Main oxides</th>
<th>Refractive index</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP 0553586 A1</td>
<td>Baccarat</td>
<td>ZnO, SrO, CaO</td>
<td>&gt;1.545</td>
<td>&gt;2.9</td>
</tr>
<tr>
<td>GB 2280432 A</td>
<td>British Glass</td>
<td>Bi₂O₃, TiO₂, SrO</td>
<td>&gt;1.55</td>
<td>&gt;2.7</td>
</tr>
<tr>
<td>EP 0797550 A1</td>
<td>Calp</td>
<td>ZnO, BaO, Bi₂O₃, La₂O₃, Nb₂O₅, TiO₂</td>
<td>&gt;1.545</td>
<td>&gt;2.9</td>
</tr>
<tr>
<td>EP 0657391 A1</td>
<td>Corning</td>
<td>BaO, SrO, ZnO</td>
<td>&gt;1.545</td>
<td>&gt;2.9</td>
</tr>
<tr>
<td>US 7202188 B2</td>
<td>Swarovski</td>
<td>ZnO, CaO, Al₂O₃, B₂O₃, TiO₂, La₂O₃</td>
<td>&gt;1.55</td>
<td>&gt;2.7</td>
</tr>
<tr>
<td>EP 0594422 A1</td>
<td>Toyo Glass</td>
<td>BaO, ZnO, TiO₂</td>
<td>&gt;1.55</td>
<td>&gt;2.9</td>
</tr>
<tr>
<td>EP 0893417 A1</td>
<td>Toyo Glass</td>
<td>BaO, CaO, TiO₂</td>
<td>&gt;1.55</td>
<td>&gt;2.9</td>
</tr>
</tbody>
</table>

Source: (Rada, 2009)

Regarding the second way, Dararutana and Sirikulrat (2010) managed to replace lead oxide PbO by Barium carbonates BaCO₃ and achieved high refractive index. The refractive index was found to increase linearly with increasing the percentage of barium carbonates as shown in Figure 1.6.

11
Rada (2009) suggests that the approach of lead-free crystal can be a possible solution to the problems associated with manufacturing lead crystal such as the volatilization of lead dust, the disposal of hazardous toxic slurries coming from glass grinding and polishing as well as the disposal of contaminated refractories from shut-down furnaces. However, Hynes et. al (2004) indicate that some of the components used as alternatives for lead oxide might prove to be toxic as well. For example, the toxicity of soluble barium compounds hinders the widespread of using them as alternative to lead oxide (Hynes and Jonson, 1997). There is a need to carry out assessments in order to decide whether lead-free crystals will enhance the workers and environmental safety in comparison with lead crystals or not (Hynes et. al, 2004). One more important point regarding switching from lead crystals to lead-free crystals is the major changes that will be required in processes like cutting, grinding and polishing. This is because these processes have been already well-established and optimized for the lead crystals and switching to lead-free crystals that have different surface properties will require major changes in these processes (Hynes and Jonson, 1997).
1.6 Viscosity-Temperature Characteristics of Glass

The viscosity–temperature characteristics of glass are important in glass manufacturing. Figure 1.7 shows the relationship between viscosity and temperature for different glass types. Four points are indicated in the figure that correspond to certain viscosity values (Callister and Rethwisch, 2009; Smith, 1996):

![Graph showing viscosity-temperature characteristics of glass](image)

Figure 1.7: The effect of temperature on the viscosity of glass (Callister and Rethwisch, 2009)

- Melting point (at 10 Pa.s): At this point the glass becomes fluid enough to be considered as a liquid.
- Working point (at $10^3$ Pa.s): Glass is easily deformed at this viscosity and this is the reason why the glass fabrication operations are carried out at this point.
- Softening point (4x$10^6$ Pa.s): Represents the maximum temperature at which a glass piece may be handled without resulting in significant dimensional changes. At this point the glass can flow under its own weight.
- Annealing point \((10^{12} \text{ Pa.s})\): At this temperature internal stresses can be removed within 15 minutes. This temperature is 565 °C for borosilicate glass, 552 °C for soda-lime glass and 450 °C for full lead crystal (Cummings, 1997)
- Strain point \((3 \times 10^{13} \text{ Pa.s})\): The annealing range of glass is the interval between this point and the annealing point. The strain temperature is 530 °C for borosilicate glass, 525 °C for soda-lime glass and 420 °C for full lead crystal (Cummings, 1997). The glass transition temperature is higher than the strain point below which glass becomes rigid and can easily be fractured.

1.7 Glass Manufacturing

Glass manufacturing includes five main processes: batch preparation, melting, forming, annealing and finishing. After these processes glass is inspected and then packed and shipped. Figure 1.8 shows a flow diagram for the processes of glass manufacturing.

![Diagram of glass manufacturing processes](image-url)

Figure 1.8: Overview of glass manufacturing (WHO – IARC, 1993; Energetics, 2002)
1.7.1 Batch preparation

Silica sand is the major constituent of almost all glasses. Other additives such as soda ash or limestone can be added to achieve certain required properties of the produced glass. Waste glass or cullet is added to the batch to facilitate the melting process. Raw materials are crushed, ground, and sieved before being delivered to the glass plant. Efficient mixing of materials is necessary because inefficient mixing can result in increasing the melting time and reducing the glass quality. Efficient mixing is usually assured by mechanical stirring (WHO – IARC, 1993; Energetics, 2002).

1.7.2 Melting

The cold batch is then charged to the melting furnace and melted at 1200-1650 °C. Generally there are two main types of melting furnaces: discontinuous and continuous furnaces. The discontinuous furnaces are used with small glass production quantities (less than five tons per day) while continuous furnaces are used with larger production quantities and are designed to be used continuously over a period of years. Melting rate depends on the furnace temperature, composition of the batch, particle size of the batch ingredients, amount of cullet, and homogeneity of the batch. The smaller the particle size is, the quicker the melting occurs. Imperfections that are described as cords or stones in the produced glass can happen because of the large particle size or due to the inefficient mixing of the batch. Such imperfections as well as any gas bubbles should be eliminated (WHO – IARC, 1993; Energetics, 2002).

1.7.3 Forming

In this process the molten glass coming out of the melting furnace is formed in order to have its final shape. The forming process should be carried out quickly because molten glass becomes rigid as it cools. Five forming methods are used depending on the required shape of the produced glass; pressing, blowing, drawing, sheet forming and fiber forming. These methods can be summarized as follows (Callister and Rethwisch, 2009):

- Pressing: Glasses with thick-wall such as plates or dishes can be formed by pressing. Pressure is applied by using cast iron molds coated with graphite. Different shapes of molds can be used depending on the desired shape of the produced glass.
• Blowing: Glass jars, bottles and light bulbs are formed by using blowing which can be carried out manually or automatically. Firstly, glass is mechanically pressed in a mold then a finishing mold is used along with a blast of air. The pressure produced from the blast of air ensures that the glass conforms the finishing mold contours. This is shown in Figure 1.9.

![Figure 1.9: Producing glass bottle by using the blowing method](image)

(Callister and Rethwisch, 2009)

• Drawing: Glass shapes that have a constant cross section such as rod and tubing can be formed by using drawing.

• Sheet forming: The float glass technique patented in 1959 in England is used in this method to form sheet glass. In this technique the molten glass is moved by using rollers from the melting furnace to the float bath furnace where it floats over the surface of molten tin as shown in Figure 1.10. Perfectly flat and parallel faces as well as uniform thickness sheet glass is attained due to the gravitational and surface tension forces.
Fiber forming: This method is a sophisticated form of the drawing operation. In this method molten glass is placed in a platinum chamber and passes through small orifices at the bottom of the chamber. Controlling the temperature of the chamber and the orifices is critical in order to control the glass viscosity.

1.7.4 Annealing

Cooling glass from high temperature with a high cooling rate results in internal stresses (thermal stresses) that weaken the glass and can lead to fracture. After the forming operation, the glass should be annealed in order to eliminate or reduce such thermal stresses by cooling the glass at a slow rate. If these stresses have already been introduced to glass then an annealing heat treatment should be carried out by heating the glass to its annealing point, then slowly cooling it to the room temperature (Callister and Rethwisch, 2009). Usually long continuous electric ovens called lehrs are used for this purpose (WHO – IARC, 1993).

1.7.5 Finishing

The finishing stage includes grinding and polishing of the produced glass. Grinding is carried out to remove the upper layer of the glass surface. Natural abrasive grits such as diamonds or synthetic grits like silicon carbide can be used. During the grinding operation water or other suitable cutting fluid is used. Polishing is then carried out either mechanically or chemically. In the mechanical polishing fine
abrasive powders such as ferric oxide and cerium oxide are used and they operate on the same principle as the abrasives used in the grinding operation. In chemical polishing the glass is subjected to a mixture of acids such as hydrofluoric and concentrated sulfuric acids (WHO – IARC, 1993).

1.8 Pollution Associated with Glass Manufacturing

The pollution associated with glass manufacturing can be categorized in three elements: air emissions, wastewater and solid waste (IFC, 2007). It is worth noticing that in the case of lead crystal glass manufacturing a substantial amount of lead is released to the environment during the manufacturing process. Typically at least 15% of lead escapes during batch preparation and transportation. Another 10-14% of lead compounds are released during the melting process in the furnaces while additional 2-3% of lead is discharged to wastewater after the grinding and polishing process (Pechnikov et al., 1996). This means that around 30% of the lead used in the production of lead crystal is released to the environment during its manufacturing. Pechnikov et al. (1996) investigated the lead pollution around a lead crystal manufacturing plant in Russia that produces 7325 tons/year of crystal having a lead oxide content of 18%. They found that around 408 tons/year of lead is released to the environment.

1.8.1 Air emissions

The air emissions in glass industry include sulfur dioxide, nitrogen oxides, carbon dioxide as well as Particulate Matter PM that may have some metals. The PM from lead crystal plants may have a lead content of 20–60%. Melting furnaces are considered the main contributor to air emissions since almost 80-90% of the total plant air emissions are because of these furnaces (IFC, 2007). Table1.7 shows the World Bank group guideline values of air emissions in glass industry.
Table 1.7: Air emissions guideline values for glass manufacturing

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Guideline value (mg/Nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particulates</td>
<td></td>
</tr>
<tr>
<td>- Natural Gas</td>
<td>100*</td>
</tr>
<tr>
<td>- Oil</td>
<td>50*</td>
</tr>
<tr>
<td>SO$_2$</td>
<td></td>
</tr>
<tr>
<td>- Natural Gas</td>
<td>700</td>
</tr>
<tr>
<td>- Oil</td>
<td>500</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>1000</td>
</tr>
<tr>
<td>HCl</td>
<td>30</td>
</tr>
<tr>
<td>Fluorides</td>
<td>5</td>
</tr>
<tr>
<td>Lead</td>
<td>5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1</td>
</tr>
<tr>
<td>Other heavy metals (total)</td>
<td>5**</td>
</tr>
</tbody>
</table>

*Where toxic metals are present, not to exceed 20 mg/Nm$^3$

**1 mg/Nm$^3$ for selenium

Source: (IFC, 2007)

Dust emission is another form of air emission. However, this form of air emission is associated with raw material transportation, handling, storage and mixing. The dust released in these processes has coarser particulates than those emitted from hot processes which usually have a size smaller than 1 $\mu$m. The release of PM though dust emission during the aforementioned processes represents an Occupational Health and Safety OHS concern, while the release of PM during hot processes represents an environmental concern (IFC, 2007).

1.8.2 Wastewater

The effluent from glass manufacturing plants can contain pollutants because this water was used in several processes like grinding and polishing before being discharged. The conventional practice for dealing with wastewater in the glass industry is to use the coagulation and sedimentation techniques before discharging the effluent (Kang and Choo, 2003). This conventional practice is shown in Figure 1.1.1. Different primary coagulants such as Aluminum Sulfate Al$_2$(SO$_4$)$_3$ can be added to neutralize the electrical charges of particles in the wastewater which makes the particles clump together. Coagulant aids such as lime stone CaCO$_3$ can be used to add density to the slow-settling particles and add toughness to the particles so that they will not break up during the mixing and settling processes (ME, 2013).
The World Bank Group has set guideline values for the treated effluent from glass manufacturing plants to be discharged to surface water as shown in Table 1.8.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Guideline Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6-9</td>
</tr>
<tr>
<td>Total suspended solids</td>
<td>30 mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>130 mg/L</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>Lead</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.3 mg/L</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.1 mg/L</td>
</tr>
<tr>
<td>Fluorides</td>
<td>5 mg/L</td>
</tr>
<tr>
<td>Boric acid</td>
<td>2 mg/L</td>
</tr>
<tr>
<td>Temperature increase</td>
<td>&lt;3 °C</td>
</tr>
</tbody>
</table>

Source: (IFC, 2007)

On the other hand, the allowable limit for the lead content if the effluent is discharged to public sewer system is in the range of 1-5 mg/l in countries like Canada (Coronado, 2003) and India (CPCB, 1986).

1.8.3 Solid waste

Solid waste in glass industry consists of cullet that can be recycled and mixed in the batch preparation stage. Also the solid waste includes refractory waste as a result of maintenance and repair for the furnace that is typically carried out every 5-15 years. This refractory waste can be recycled as feedstock for brick manufacturing (IFC, 2007). Moreover, the wastewater includes significant amount of solids. The lime-treatment and sedimentation of wastewater results in sludge that is dried then
sent to landfills. If the sludge contains heavy metals such as Pb then there are concerns that these heavy metals can leach and be released to groundwater causing serious environmental problems. It is necessary to carry out leaching test for any lead glass or any glass containing heavy metals to determine if it’s safe to landfill it in the municipal solid waste landfills. According to the US legislations, the solid waste has toxicity characteristic and is considered hazardous waste if the extract from any approved leaching test has any of the listed contaminants at a concentration equal to or greater than the values shown in Table 1.9 (Baba and Kaya, 2004).

Table 1.9: Maximum allowable concentrations for contaminants from leaching tests of solid wastes

<table>
<thead>
<tr>
<th>USEPA hazardous Waste number</th>
<th>Contaminant</th>
<th>Maximum Concentration (mg/l^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D004</td>
<td>Arsenic</td>
<td>5.0</td>
</tr>
<tr>
<td>D005</td>
<td>Barium</td>
<td>100.0</td>
</tr>
<tr>
<td>D006</td>
<td>Cadmium</td>
<td>1.0</td>
</tr>
<tr>
<td>D007</td>
<td>Chromium</td>
<td>5.0</td>
</tr>
<tr>
<td>D008</td>
<td>Lead</td>
<td>5.0</td>
</tr>
<tr>
<td>D009</td>
<td>Mercury</td>
<td>0.2</td>
</tr>
<tr>
<td>D010</td>
<td>Selenium</td>
<td>1.0</td>
</tr>
<tr>
<td>D011</td>
<td>Silver</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Source: (Baba and Kaya, 2004)

If the leaching test results showed that the solid waste contains 5 mg/l or higher concentration of lead as shown in Table 1.9, then this solid waste is considered hazardous. If such solid waste has to be landfilled, then it should be directed to a hazardous waste landfill (Bodger, 2003). The hazardous waste landfills are designed in a way to avoid the leakage of the leachate of the hazardous waste to groundwater (Zhao and Richardson, 2003).

The sludge in this research is provided by ASFOUR Crystal. The plant produces about 20 tons/day of sludge resulting from the grinding and polishing of lead crystal glass. The grinding and polishing processes are carried out by using synthetic diamonds and cerium oxide, respectively. The objective of the present research is to produce foam glass with comparable properties to those of commercial foam glass from this sludge. This can be applied by adopting one of the cleaner production techniques that will be discussed in the next chapter.
CHAPTER 2

LITERATURE REVIEW

2.1 Cleaner Production Techniques in Lead Crystal Glass

Applying Life Cycle Assessment LCA for crystal glass can be beneficial. LCA is a methodology for assessing the environmental impacts related to any product. It evaluates these impacts for the entire life cycle of products starting from collecting raw materials, until all residuals are returned to the earth for “disposal” based on the cradle-to-grave life cycle (El-Haggar, 2007). Applying LCA in any industry helps to identify the critical aspects from an energetic and environmental point of view. The first documented LCA for crystal glass was carried out by Pulselli et al. (2009). The LCA showed that the manufacturing stage is the one with the highest environmental impacts and that it accounts for about 89% of the energy consumption and 93% of the material use.

Adopting the cleaner production techniques in the manufacturing stage can minimize the environmental impacts associated with production of lead crystal. Cleaner production can be defined as “the continuous application of an integrated preventive environmental strategy to processes, products and services to increase overall efficiency and to reduce risks to humans and the environment” (UNEP, 2002). Cleaner production techniques can be broadly classified to three techniques: pollution reduction, product modification and recycling (El-Haggar, 2007). The recycling technique means using materials in closed loop system (cradle-to-cradle) instead of the linear open system (cradle-to-grave) to save resources and mitigate negative environmental impacts. This can be attained by adopting either open or closed-recycling systems. In closed-recycling systems products waste is used to further re-manufacture the same products, while in open-recycling systems the waste is used to manufacture other products (Heart, 2008). On-site recycling and off-site recycling is another classification for the recycling systems. In on-site recycling the waste materials are returned within the same factory as an input material to the original process or another process. In off-site recycling the recycling process is carried out outside the factory usually by another party to produce other products (El-Haggar, 2007). Adopting any of these recycling systems in the manufacturing of lead crystal
can mitigate the negative environmental impacts due to air emissions, wastewater and solid waste and achieve many economical benefits.

2.1.1 Air emissions

Recycling techniques can be adopted with regard to air emissions. There are already some practical applications that have been successfully carried out to produce useful products from harmful emissions. A good example is the industrial symbiosis of Kalundborg in Denmark where sulfur emissions are used to manufacture liquid fertilizers and synthetic gypsum (El-Haggar, 2007). Another example is the innovative proprietary technology developed by the California based company “Calera” to manufacture useful products such as Calcium Carbonate cement out of the CO₂ emissions (Calera, 2013). With regard to the specific industry of lead crystal, the filter dust of the flue gases can be recycled. When sulfur-containing oil is used in the lead crystal furnaces, lead sulfate is released as one of the main air emissions components. This lead sulfate can be chemically treated to remove the sulfate content and obtain lead carbonate that can be used to partially replace the lead oxide used in the manufacturing of lead crystal (Porcham, 1995).

Several pollution reduction techniques can also be used to reduce air emissions in the manufacturing of glass in general. Such techniques include using low NOx burners or selective catalytic reduction (SCR), choosing fuels with low sulfur and carbon content especially natural gas, and installing waste heat recovery units from furnace flue gases (IFC, 2007). Moreover, using cyclones or cloth bag filters can be used to remove the particulate matter from the flue gas emissions (Pechnikov et al., 1996).

Several specific techniques exist in the area of lead crystal manufacturing to avoid lead loss that happens due to air emissions during batch preparation and transportation to the melting furnaces. These techniques include compaction of batch material and using enclosed automatic conveyor to transport the batch material directly to the furnace (Pechnikov et al., 1996). In addition, enclosed silos can be used to store the batch material. Furthermore, the amount of fine particles can be reduced by humidifying the batch with water or with alkali solution such as sodium hydroxide NaOH or sodium carbonate Na₂CO₃ (IFC, 2007).
2.1.2 Wastewater

Several researches have been carried out to investigate the practicality of recycling the wastewater in the glass industry to reuse it in the manufacturing process. Kang and Choo (2003) investigated the use of a hybrid system of Microfiltration (MF) and Ultrafiltration (UF) membrane to reclaim the glass industry wastewater as shown in Figure 2.1.

![Figure 2.1: Proposed membrane system to recycle the wastewater in glass industry (Kang and Choo, 2003)](image)

Lee et al. (1997) managed to recycle the wastewater of a lead crystal manufacturing plant in Korea by replacing the conventional treatment system shown in Figure 2.2 with a new cleaner production technique that uses microfiltration / nanofiltration hybrid system as shown in Figure 2.3. This system resulted in zero discharge of wastewater. It’s worth noting, however, that although this cleaner production technique managed to recycle all the wastewater, it resulted in sludge that is directed to landfills without any recycling.

![Figure 2.2: Typical manufacturing process and conventional wastewater treatment system in crystal glass industry (Lee et al., 1997)](image)
This cleaner production system had an investment of $137000 for 10 m$^3$/day of generated wastewater with a payback period of less than two years as shown in Table 2.1. This system ensured not to violate the strict effluent standards in Korea that has a limit of 3 ppm of fluoride and 0.2 ppm of lead. Such strict limits were very difficult to comply with by using the conventional system (Lee et al., 1997).

**Table 2.1: Economic analysis of the cleaner production process (US$)**

<table>
<thead>
<tr>
<th></th>
<th>Conventional process</th>
<th>Cleaner production process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment</td>
<td></td>
<td>137000</td>
</tr>
<tr>
<td>Operating cost per year</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw materials</td>
<td>16000</td>
<td>15200</td>
</tr>
<tr>
<td>Energy</td>
<td>1300</td>
<td>5000</td>
</tr>
<tr>
<td>Miscellaneous expenditure</td>
<td>128000</td>
<td>48600</td>
</tr>
<tr>
<td>Membrane exchange</td>
<td>0</td>
<td>4900</td>
</tr>
<tr>
<td>Pollution penalties</td>
<td>5000</td>
<td>0</td>
</tr>
<tr>
<td>Total operating cost</td>
<td>150300</td>
<td>73700</td>
</tr>
<tr>
<td>Payback Period</td>
<td></td>
<td>1.8 years</td>
</tr>
</tbody>
</table>

Source: (Lee et al., 1997)
2.1.3 Solid waste

Several cleaner production techniques exist that can utilize or recycle the sludge that results from lime-treatment and sedimentation of wastewater instead of directing it to landfills. Figure 2.4 shows a proposed scheme to use the polishing waste of lead crystal glass. It includes acid discharge that can be used after neutralization as gypsum binder and glass opacifier. The polishing waste also includes pickling sediment. The lead sulfate PbSO₄ in the pickling sediment can be used to produce Complex Lead-bearing Material CLM that proved to be used successfully to replace up to 10% of the red lead used in lead crystal manufacturing without altering the quality of the produced crystals. CLM can also be used to produce low-melting glasses that can be used in different applications like glass solders (Zhernovaya and Onishchuk, 2005).

Figure 2.4: Schematic diagram for utilizing polishing waste of lead crystal glass (Zhernovaya and Onishchuk, 2005)

Another way to recycle the lead sulfate content resulting from the chemical polishing of lead crystal is to chemically treat it to obtain lead carbonate concentrate that can be used to replace up to 35% of the used red lead. This technology has
already been adopted many years ago by Swarovski which is one of the world leading crystal glass manufacturers. Over 18 years the company managed to process 3500 tons of polishing sludge to produce 1400 tons of lead carbonate concentrate that saved 900 tons of the red lead used in the manufacturing of lead crystal. This technology has already been licensed to other companies in Europe and Asia (Porcham, 1995).

Grinding or cutting of glass also produces considerable amounts of solid wastes suspended in the wastewater. For example, the diamond cutting of crystal glass results in significant amount of solid waste in the form of glass particles that are flushed into the sink of the grinding machine and discharged to the sewage system. These solid wastes can be used to produce foam materials and materials for tinting household glass as shown in Figure 2.5. Adding 15-20% of the crystal cutting slime to household soda-lime glass proved to give glass a pale blue color and significantly improve its optical characteristics (Zhernovaya and Onishchuk, 2005).

![Diagram](image)

**Figure 2.5:** Schematic diagram for utilizing grinding waste of lead crystal glass (Zhernovaya and Onishchuk, 2005)
2.2 Utilization of Grinding and Polishing Sludge to Produce Foam Glass

Solid waste in the form of the sludge resulting from the grinding and polishing processes of lead crystal can be used to manufacture foam glass. This is considered as an open-recycling technique that has many advantages in comparison with landfiling. Utilization of waste materials in closed loops either through closed-recycling or open-recycling is a far better practice than landfiling. This is true from an environmental and economical point of view. From an environmental point of view waste utilization saves resources and eliminates potential risks that can be associated with improper waste disposal. From economical point of view, it provides free raw material to produce products. It also eliminates the costs associated with waste landfiling especially if the waste leaching results were above the regulatory limits, which means it has to be directed to a special landfill as explained in Chapter 1. Moreover, waste utilization ensures that manufacturers will avoid any penalties with regard to improper waste disposal (El Kersh and El-Haggar, 2012).

To the best of the author knowledge there is no literature available about the characteristics of the foam glass that can be produced from the grinding and polishing sludge of lead crystal. The chemical composition of lead crystal is similar to the funnel and neck glass used in CRT as described in Chapter 1. Thus, the literature about the foam glass produced from the funnel and neck glass of CRT glass will be presented. Also the literature about the foam glass produced from CRT panel glass which has barium-strontium silicate instead of lead silicate will be included. This is because both barium and lead are toxic metals that can be used to produce crystal glass with high refractive index as previously discussed. Literature about foam glass produced from other waste glass like soda-lime glass will also be considered when necessary for comparison and illustration purposes.

2.3 Foam Glass

Foam glass from waste glass is usually produced by using gas-generating agents that are called foaming agents. These foaming agents usually include carbon and are dry mixed with the glass powder then heated to a temperature at which gas evolves from these foaming agents. The evolved gas results in forming small
spherical bubbles that expand under the increasing gas pressure to form pores in the produced foam glass (Scarinci et al., 2006).

2.3.1 Foaming agents

Literature shows that two foaming agent groups are used to produce foam glass from waste glass: neutralization and redox agents (Spiridonov and Orlova, 2003).

The neutralization agents release the gas that causes the foaming effect by thermal decomposition. This includes Calcium Carbonates CaCO$_3$ that thermally decomposes by heating resulting in the release of CO$_2$ (Spiridonov and Orlova, 2003; Scarinci et al., 2006) as shown in the following equation (Bernardo et al., 2005):

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

This type of foaming agents has intense gas release during the decomposition which results in breaking the walls of the individual pores leading to create maze-like cavities. The produced foam glass by using this type of foaming agents has high water absorption and is usually used in the soundproof applications (Spiridonov and Orlova, 2003). Several studies have been carried out to produce foam glass from CRT glass by using CaCO$_3$ (Brusatin et al., 2004; Bernardo et al., 2005; Bernardo and Albertini, 2006; Fernandes et al., 2013).

On the other hand, the foaming process happens in the redox agents like Silicon Carbide SiC and Titanium nitride TiN through chemical reactions (Scarinci et al., 2006). This type of foaming agents is usually used to produce foams with prevailing closed pores that are used in the thermal insulation applications. Gases are released because of the oxidation reaction of the foaming agent (Spiridonov and Orlova, 2003). Several studies have been carried out to produce foam glass from CRT glass by using redox agents (Méar et al., 2005a; Méar et al., 2005b; Méar et al., 2006b; Méar et al., 2006c; Méar et al., 2007; Yot and Méar, 2009; Guo et al., 2010a; Guo et al., 2010b; Chen et al., 2011). When using SiC with glass that contains lead, CO$_2$ is released as shown in the following equation (Yot and Méar, 2009):

\[
2\text{PbO}(s) + \text{SiC} (s) + \text{O}_2(g) \rightarrow 2\text{Pb}(s) + \text{SiO}_2(s) + \text{CO}_2(g)
\]

And when using TiN, N$_2$ is released as shown in the following equation (Yot and Méar, 2009):

\[
2\text{PbO}(s) + 2\text{TiN}(s) + \text{O}_2(g) \rightarrow 2\text{Pb}(s) + 2\text{TiO}_2(s) + \text{N}_2(g)
\]
On the other hand, Brusatin et al. (2004) stated that redox agents are not preferable to be used as foaming agents of lead silicate glass because they may interact with large amounts of the dissolved oxygen in the lead silicate or with PbO resulting in lacking of the oxidative conditions. Regarding the lack of oxidative condition Bernardo et al. (2010) stated that the oxygen present in the glass while softening may be insufficient to complete the oxidation reaction of redox agents, so they added Manganese Dioxide MnO₂ as “oxidation promoter” to provide extra oxygen. MnO₂ can decompose into Mn₂O₃, Mn₃O₄ or MnO along with oxygen. For the largest release of oxygen, MnO₂ will decompose to MnO and oxygen as shown in the following equation:

$$2\text{MnO}_2 \rightarrow 2\text{MnO} + \text{O}_2$$

When using SiC as foaming agent MnO₂ can participate in the oxidation reaction to release CO₂ as follows (Bernardo et al., 2010):

$$\text{SiC} + 4\text{MnO}_2 \rightarrow \text{SiO}_2 + \text{CO}_2 + 4\text{MnO}$$

Because MnO₂ is not the only source of oxygen that takes part in the oxidation reaction of SiC, then the amount of MnO₂ needed can be significantly lower than the predicted amount as per the aforementioned reaction. Bernardo et al. (2007a) used MnO₂/SiC ratios of 1:5 and 1:3, and Bernardo et al. (2010) used a ratio of 1:3. It should be noted, however, that the research carried out to investigate the combination of MnO₂ and SiC as foaming agent was in the area of foam glass production from waste soda-lime glass. The adoption of this combination was not investigated to produce foam glass from CRT glass. However, Méar et al. (2006c) used a combination of SiC and Magnesium Oxide MgO at MgO/SiC ratio of 0.6 as a foaming agent to produce foam glass from CRT funnel and panel glass.

Using redox agents results in the formation of metal lead. This has been confirmed in various studies while using redox agents such as SiC and TiN (Yot and Méar, 2009; Méar et al., 2005a; Méar et al., 2005b). Guo et al. (2010a) stated that the precipitation and distribution of Pb micro-crystals reinforces the glass foam and provides higher mechanical strength.

### 2.3.2 Foam Glass Properties

The most important properties of the produced foam glass are: density, thermal conductivity and mechanical strength. Figure 2.6 shows the range of
properties for foams in comparison with solids, while Table 2.2 shows the range of the properties of some selected commercial foam glass available in the market.

![Image](image.png)

**Figure 2.6:** The range of properties for foams (Gibson and Ashby, 1999)

**Table 2.2:** Properties of some selected commercial foam glass

<table>
<thead>
<tr>
<th>Property</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.1-0.3 g/cm³</td>
</tr>
<tr>
<td>Porosity</td>
<td>85-95%</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>0.04-0.08 W/m.K</td>
</tr>
<tr>
<td>Compressive Strength</td>
<td>0.4 – 6 MPa</td>
</tr>
</tbody>
</table>

Source: (Scarinci et al., 2006)

The relative density of foam glass ($\rho_{rel}$) is the ratio between its bulk density including pores ($\rho_b$) to the powder density ($\rho$) which is the density of the solid that constitutes the walls of the cells. It has been proved that compressive strength of foam glass increases with the increase of the relative density (Gibson and Ashby, 1999).
Also Brusatin et al. (2004) confirmed that the compressive strength of all foams usually increases with the increase of the foam bulk density.

In certain cases, however, the known trend of increasing the compressive strength with increasing the foam density is inversed. This can be attributed to the thickness of the struts of the cells. Sometimes more dense foams have larger cells with thicker struts. These thicker struts have larger voids that decrease the struts resistance and thus decrease the compressive strength of the foam as shown in Figure 2.7 (Brusatin et al., 2004). This usually happens due to the coalescence phenomenon in which the cellular structure is coarsened due to dissolving of smaller pores with larger ones (Bernardo et al., 2007a).

![Figure 2.7: Variation of compressive strength and density of glass foams with the strut thickness of cells (Brusatin et al., 2004)](image)

The compressive strength of foam glass was found to be inversely proportional with square root of the cell size (Morgan et al., 1981). Figure 2.8 shows the plotting of the compressive strength of foam glass produced from soda-lime glass with Silicon Carbide SiC as foaming agent versus the square root of the pore size.
Thermal conductivity is another important property for foam glass. Foam glasses that are commercially available in the market have a range of thermal conductivity between 0.04-0.08 W/m.K as previously presented in Table 2.2. A material can be classified as insulating material if its thermal conductivity is below 0.25 W/m.K (Méar et al., 2005a). Thus, the very low values of thermal conductivity of foam glass makes it used extensively in the applications of thermal insulation. Méar et al. (2007) investigated the relationship between the thermal conductivity and the porosity of the foam glass produced from CRT funnel and panel glass with SiC and TiN as foaming agent. They concluded that increasing the porosity results in a linear decrease in the thermal conductivity as shown in Figure 2.9.
Abdel Alim (2009) also found that there is an inverse relationship between the thermal conductivity and the porosity of the foam glass produced from soda-lime glass with sodium silicate as foaming agent. The lowest thermal conductivity of 0.053 W/m.K was achieved at 91% porosity, while the highest thermal conductivity of 0.092 W/m.K was achieved at 76% porosity. The percentage of porosity is simply calculated by using the following equation (Méar et al., 2007):

\[
\text{% Porosity} = (1 - \rho_{rel}) \times 100
\]  

(2.1)

where \(\rho_{rel}\) is the relative density=\(\rho_b/\rho\)

The equation shows that porosity percentage is inversely proportional to the relative density. Thus, it can be concluded that increasing the relative density of foam glass results to increase its thermal conductivity.

### 2.3.3 Compressive stress model for open and closed cells

Gibson and Ashby (1999) proposed a model for the compressive stress of foam materials. In their model the cells can be either open or closed cells. Figure 2.10 shows the cubic cell model for open and closed cells.

![Cubic cell model for open and closed cells](image)

Figure 2.10: Cubic cell model for open and closed cells (Gibson and Ashby, 1999)

The crushing/compressive strength of brittle foams in this model is expressed as follows:

\[
\frac{\sigma_{cr}}{\sigma_{bs}} = 0.2(\phi \rho_{rel})^{1.5} + (1 - \phi)\rho_{rel}
\]

(2.2)

where \(\sigma_{cr}\) is the crushing/compressive strength of foam, \(\sigma_{bs}\) is the bending strength of the utilized glass and \(\rho_{rel}\) is relative density of the foam. In a closed-cell foam, \(\phi\) is the fraction of the solid contained in the cell edges and the remaining fraction (1-\(\phi\)) is in
the faces. For closed-cell foams, $\phi=0$ while $\phi=1$ for open-cell foams. The bending strength of glass can be selected as 70 MPa (Bernardo et al., 2005). The experimental results of the compressive strength along the relative density of the foam glass prepared from different mixtures of panel, funnel and neck CRT glass with 5 wt.% CaCO$_3$ as foaming agent were plotted and compared to the model as shown in Figure 2.11. The foam glass samples whose results are shown in the figure were found to have open-cell morphology by using Scanning Electron Microscope (SEM). However, their compressive strength values were much larger than those predicted by the model for open-cell foam glass (Bernardo et al., 2005; Brusatin et al., 2004).

Figure 2.11: Comparison between the experimental results of foam glass prepared from CRT glass with Gibson and Ashby model (Bernardo et al., 2005).

Bernardo et al. (2007a) plotted the compressive strength versus the relative density of the foam glass produced from soda-lime glass with SiC and MnO$_2$ additives as foaming agent against Gibson and Ashby model as shown in Figure 2.12. Most of the results existed in the region between $\phi=0.8$ and 0.90 which means that the mechanical behavior of the samples is similar to that of open-cell foams.
Figure 2.12: Comparison between the experimental results of foam glass prepared from soda-lime glass with Gibson and Ashby model (Bernardo et al, 2007a).

2.4 Parameters Affecting the Properties of Foam Glass

The properties of the produced foam glass from glass powder depend on many parameters. These parameters include: the heating rate used to reach the desired sintering temperature, the cooling rate of the sample after finishing the sintering process, the amount and type of the foaming agents used, the holding or soaking time which is the duration that the sample stays in the furnace at the desired sintering temperature, the sintering temperature as well as the particle size of the used glass powder.

2.4.1 Heating & cooling rate

The heating rate is an important factor in the process of producing foam glass. Heating rates in the range of 5-10 °C/min are usually convenient. High heating rates (e.g. 40 °C/min) can cause large cracks due to the non-uniform temperature distribution in the sample. Thus, slower heating rates should be adopted for large samples. On the other hand, slow heating rates should also be avoided because prolonged isothermal heating at high temperatures can cause gas generation before the sintering of the glass powder so gases escape before causing the foaming effect (Scarinci et al., 2006).
Pokorny et al. (2011) investigated the effect of three heating rates (50, 100 and 150 °C/hr) on the foam glass produced from soda-lime glass with dolomite as foaming agent. They found that lower heating rates result in lower volumetric expansion due to the escape of CO₂ from the samples and that higher heating rates result in foams with larger pores.

Research has been also carried out to investigate the effect of heating rate on the produced foam glass from CRT. Bernardo and Albertini (2006) investigated the effect of three heating rates (5, 10 and 20 °C/min) with CaCO₃ as foaming agent on the morphology of the foam glass produced from CRT panel glass. They found that the size of the cells significantly decreases with increasing the heating rate which contradicts the findings of Pokorny et al. (2011). This might be attributed to studying different heating rate ranges. Bernardo and Albertini (2006) also found that slow heating rate results in non-homogeneous foams which contain large pores surrounded by small cells and that fine microstructure can be accomplished through fast heating. Fast heating rate resulted in higher compressive strength associated with higher bulk density compared to slow heating rates. Guo et al. (2010a) produced high compressive strength foam glass from CRT funnel glass in the range of 12- 24 MPa by using a heating rate of 5 °C/min and SiC as a foaming agent. The same heating rate was also adopted by Fernandes et al. (2013) to produce foam glass from CRT panel and funnel glass with egg shell that contains 95 wt.% CaCO₃ as foaming agent. The produced foam glass had compressive strength in the range of 1- 6 MPa. Guo et al., (2010b) studied the effect of heating rate on the compressive strength of the foam glass produced by SiC foaming agent from CRT lead-silicate glass. They found that increasing the heating rate results in gradual decrease in the compressive strength. They contributed the higher compressive strength at lower heating rate to the fact that CO₂ has enough time to escape from the samples resulting in more dense samples.

Direct insertion of the CRT waste glass mixed with the foaming agent in the desired sintering temperature has been also adopted in producing foam glass (Méar et al., 2006c; Méar et al., 2007; Bernardo et al., 2005). Bernardo and Albertini (2006) found that the direct insertion of CRT panel glass with 5 wt. % CaCO₃ and holding time of 15 minutes at 725 °C results in foam glass with similar properties of the fast heating of 20 °C/min. The density and thermal conductivity of the produced foam glass with the heating rate of 20 °C/min was 0.25 g/cm³ and 0.060 W/m.K while 0.27 g/cm³ and 0.068 W/m.K for direct insertion. The microstructure of both of the
produced foams was also similar with about 100 μm diameter pores surrounded by 10 μm diameter pores with very thin separation as shown in Figure 2.13. The figure shows, however, that many pores existed in the separating walls of the main pores in the case of the heating rate of 20 °C/min which may be responsible for the slight decrease of the thermal conductivity from 0.068 W/m.K for direct insertion to 0.060 W/m.K in the case of 20 °C/min heating rate (Bernardo and Albertini, 2006).

Figure 2.13: Morphology of foam glass sintered at 725 °C and holding time 15 minute prepared by a) Heating rate 20 °C/min b) Direct insertion (Bernardo and Albertini, 2006).

The cooling rate is another important factor. Drastic cooling to a temperature slightly higher than the annealing range is used to freeze the evolution of the microstructure. Then the foam glass should be slowly cooled to provide some sort of annealing that eliminates any residual stresses (Scarinci et al., 2006; Bernardo and Albertini, 2006). Bernardo and Albertini (2006) rapidly cooled the foam glass produced from CRT panel glass at a rate higher than 10 °C/min to 600 °C then slowly cooled it at a rate of approximately 1 °C/min to 500 °C. Abdel Alim (2009) adopted a similar methodology by severely cooling the foam glass produced from soda-lime glass at a rate of 40 °C/min to 600 °C, then slowly cooling it to 500 °C at a rate of
1°C/min. Guo et al., (2010a) produced foam glass with high compressive strength from CRT lead-silicate glass by using a constant cooling rate of 0.5 °C/min. Guo et al. (2010b) studied the effect of cooling rate on the bending strength of the foam glass produced from CRT. They found that the bending strength decreases from 2 MPa to 1 MPa by increasing the cooling rate from 1 °C/min to 3 °C/min. They attributed that to the insulating behavior of foam glass which leads to large temperature difference between the internal and external parts while being cooled. Such temperature difference results in internal cracks that decrease the foam strength.

### 2.4.2 Amount of foaming agent

Changing the amount of the added foaming agent results in changing the properties of the produced foam glass. Figure 2.14 shows the variation of the compressive and bending strength of foam glass produced from CRT lead-silicate glass as a function of SiC wt% at a sintering temperature of 840–850 °C and holding time of 30 minutes.

![Figure 2.14: The variation of the mechanical strength With different SiC content (Guo et al., 2010a)](image)

The high compressive strength at low SiC content can be attributed to the low gas release rate which results in more dense foam, while the high compressive strength at high SiC content can be attributed to the increased amount of the generated Pb as a result of the chemical reaction between PbO and SiC. Increasing the content of redox agents such as SiC results in increasing the amount of the generated metal lead content (Méar et al., 2005a; Méar et al.2005b; Yot and Méar, 2009). The
presence of the heavy metal of Pb in the crystal phase gives higher mechanical properties (Guo et al., 2010a).

Méar et al. (2006 b) investigated the effect of three amounts of SiC (1 wt%, 5 wt% and 9 wt%) on the pore size and homogeneity of the foam glass produced from CRT funnel glass. They found that increasing the content of SiC results in increasing the pore size from 50 μm with homogeneous distribution to 100-300 μm with heterogeneous distribution as shown in Figure 2.15. The figure shows the morphology of the foam glass produced at sintering temperature of 850 °C and holding time of 60 minutes with three weight percentages of SiC; 1%, 5% and 9%. Fernandes et al. (2013) used a different foaming agent (egg shell containing 95 wt% CaCO₃) to produce foam glass from CRT funnel and panel glass, and also reached the same conclusion that increasing the dosage of foaming agent results in larger pore size.

![Figure 2.15 Morphology of foam glass with different content of SiC: a) 1 wt% b) 5 wt% c) 9 wt% (Méar et al., 2006 b)](image)

Regarding the relationship between the density of the produced foam glass from CRT and the amount of the added foaming agent, Bernardo and Albertini (2006) showed that increasing the amount of CaCO₃ leads to decreasing the density of the foam glass produced from CRT panel glass. Also Fernandes et al. (2013) found that increasing the content of the foaming agent (egg shell containing 95 wt% CaCO₃) results in decreasing the foam density produced from CRT funnel and panel glass as shown in Figure 2.16. The figure shows the relationship between the density and the amount of the foaming agent at a sintering temperature of 700 °C and 15 minutes holding time. Bernardo et al. (2007a) showed a similar trend for the foam glass prepared from soda-lime glass prepared by SiC as foaming agent. However, further increase of the amount of added SiC beyond 12.5 wt% resulted in an increase of the density due to the coalescence phenomenon.
2.4.3 Holding time

Bernardo and Albertini (2006) studied the effect of holding time on the microstructure of the foam glass produced from CRT panel glass with CaCO₃ as foaming agent. They found that increasing the holding time results in larger pores as shown in Figure 2.17. The figure shows the morphology of the produced foam glass with 3 wt% CaCO₃ at 725 °C and heating rate of 10 °C/min at four different holding times; 5, 10, 15, 30 minutes.
It can be noticed from Fig. 2.17 that the sample with the least holding time (i.e. 5 minutes) has the finest and most homogenous structure. This made the sample have the highest compressive strength (2.5 MPa) with the highest foam glass bulk density (around 0.39 g/cm³).

The research carried out by Méar et al. (2006b) confirms the findings of Bernardo and Albertini (2006). Méar et al. (2006b) used different foaming agents (SiC and TiN) and longer holding times, but also found that increasing the holding time for the foam glass produced from CRT funnel glass results in heterogeneous structure with larger pores as shown in Figure 2.18. The figure shows the morphology of the produced foam glass with 5wt% SiC at 850°C at three different holding times; 30, 60, 90 minutes.
Generally increasing the holding time results in decreasing the foam density due to the generation of larger pores, however after a certain holding time the density starts to increase due to the coalescence phenomenon (Scarinci et al., 2006).

### 2.4.4 Sintering temperature

Méar et al. (2006b) investigated the effect of sintering temperature on the micro-structure of the foam glass produced from CRT funnel glass with SiC as foaming agent. They found that increasing the sintering temperature results in increasing the pore size as shown in Figure 2.19. The figure shows the morphology of the produced foam glass with 5 wt% SiC and holding time of 90 minutes at three different temperatures; 750 °C, 850 °C and 950 °C. Similar results were obtained at the same conditions with 4 wt% TiN (Méar et al., 2006b).

This finding is confirmed by the research carried out by Fernandes et al. (2013) who used a different foaming agent (egg shell containing 95 wt% CaCO₃) and
lower sintering temperatures (600 °C and 700 °C), and also concluded that increasing the temperature results in larger pore size as shown in Figure 2.20. The figure shows the morphology of the produced foam glass from CRT panel glass with 3wt% foaming agent and holding time of 15 minutes at temperatures of 600 °C and 700 °C.

![Figure 2.20: Morphology of foam glass at sintering temperature: a) 600 °C b) 700 °C (Fernandes et al., 2013)](image)

The effect of sintering temperature on the density and compressive strength of the foam glass produced from CRT funnel and panel glass with 3 wt% egg shell containing 95 wt% CaCO₃ as foaming agent and holding time of 15 minutes is presented in Figure 2.21. Generally the less dense samples have lower compressive strength with some exceptions. These exceptions can be attributed to coalescence phenomenon that affects the microstructure of the struts between the pores (Fernandes et al., 2013).

![Figure 2.21: The variation of a) density b) compressive strength with sintering temperature (Fernandes et al., 2013)](image)
The density variation with sintering temperature of the foam glass prepared from CRT panel glass by the novel technique of making the sintering process under vacuum innovated by Chen et al. (2011) is presented in Figure 2.22. The figure shows the density variation with the sintering temperature for the foam glass prepared from CRT panel glass with 3wt% CaCO$_3$ foaming agent and holding time of 30 minutes under different vacuum pressures.

![Figure 2.22: Effect of sintering temperature on relative density under various pressures (Chen et al., 2011)](image)

It can be noticed that the density of the prepared foam from CRT panel glass generally decreases with the increase of the sintering temperature till a certain temperature then starts to increase. Figure 2.23 shows the morphology of the produced foam glass from soda-lime glass at different sintering temperatures. The coalescence phenomenon was clear at the temperature of 900 °C as marked by the two circles in Figure 2.23 (d).
Guo et al. (2010a) found that the best mechanical strength of the foam glass produced from lead silicate CRT glass with 5 wt % SiC is achieved at a sintering temperature of 780 °C. They attributed this to the fact that at this temperature the reaction between PbO and SiC that starts at 600 °C is intensified resulting in generation of lead that exists in crystal phase. The precipitation and distribution of Pb micro-crystals provides higher mechanical strength because it reinforces the produced foam. It should be noted, however, that further increase in the sintering temperature leads to generation of more metal lead as shown in Figure 2.24. The figure shows the reduced metal lead content Pb (0) as wt% of the unreduced lead Pb (+II) that was initially present in the glass before foaming versus the sintering temperature for SiC and TiC content of 5wt% and holding time of 60 minutes. As shown in the figure, by increasing the temperature to around 950 °C, 40% wt. of the lead initially present in the glass is reduced to lead metal. However, the mechanical strength would be expected to be reduced at this high temperature due the coalescence phenomenon as previously explained.
2.5 Measuring Compressive Strength

2.5.1 Stress-strain curve of foam glass

The compressive stress-strain curve of elastic-brittle foams as described by Gibson and Ashby (1999) is presented Figure 2.25.

Figure 2.25: Compressive stress-strain curve for elastic-brittle foams (Gibson and Ashby, 1999).

The figure shows three different regions in the stress-strain compression curve of elastic-brittle foams (Gibson and Ashby, 1999):
1. **Linear Elasticity:** This happens during the first loading of the foam glass.

2. **Brittle Crushing Plateau:** This is an approximately constant stress plateau in which the cells in the foam are crushed by brittle fracture in irrecoverable manner.

3. **Densification:** This happens when further compression is applied to the foam. In this region the stress-strain curve shows a steeply rising stress. The reason behind this behavior is because further compression of the foam results in packing the fragments of the crushed cell walls on each other leading to compressing the material of the walls themselves.

   The average stress of the brittle crushing plateau is considered as the compressive strength as represented by $\sigma^*_{cr}$ in Figure 2.25 (Gibson and Ashby, 1999; Ebaretonbofa and Evans, 2002).

   Abdel Alim (2009) compared the compression stress-strain curve of the foam glass prepared from soda-lime glass with that of the elastic brittle foam. Under the conditions stated in Figure 2.26, the first two regions (i.e. the linear elasticity and the plateau of brittle crushing) existed. However, the densification region was represented by a decreased stress rather than by a steep rising stress. The reason behind the decreased stress was attributed to the very fragile and brittle behavior of glass and to the critical flaws in the foam samples that existed in the form of tiny strength-decreasing pores. The decreased stress plateau was of approximately equal stress because the fragments of the crushed cells were the carrier of the load until the complete failure takes place. The highest compressive stress of the brittle crushing plateau was considered as the compressive or crushing stress of the sample as shown in Figure 2.26.
Figure 2.26: Compression stress-strain curve for foam glass prepared from soda-lime glass (Abdel Alim, 2009)

The foam glass samples prepared by Tulyaganov et al. (2006) from soda-lime glass and aluminosilicate glass powder with SiC as foaming agent exhibited a similar behavior as shown in Figure 2.27. The compressive strength was also considered as the highest stress in the brittle crushing plateau.

Figure 2.27: Compression stress-strain curve for different samples of foam glass prepared from soda-lime glass, aluminosilicate glass powder and SiC as foaming agent (Tulyaganov et al., 2006)

On the other hand, Abdel Alim (2009) found that increasing the particle size and keeping all other parameters constant, not only increases the bulk density as well
as the compressive strength, but also gives a completely different behavior for the compression stress-strain curve as shown in Figure 2.28. The curve behavior shifted gradually to that of solid brittle glass. The compressive strength of the samples with stress-strain behavior as shown in Figure 2.28 b) and c) is simply the stress at which the samples suffer from catastrophic failure as stated by ASTM 552 (2012).

![Figure 2.28 Compression stress-strain curve for foam glass with different particle size prepared from soda-lime glass with 12wt% sodium silicate at sintering temperature of 850 °C , holding time 30 minutes (Abdel Alim, 2009)]
The compression stress-strain curve of the foam glass produced from CRT funnel and panel glass with SiC and TiN as foaming agent by Méar et al. (2007) had a similar behavior of that presented in Figure 2.28 (c). As shown in Figure 2.29 such compression stress-strain curve can be divided into three regions (Méar et al., 2007):

- **Region I**: In this region the sample shows linear elasticity behavior.
- **Region II**: This region is represented by the discontinuity in the curve. This discontinuity is due to the fracture of the weakest individual elements in the sample. This fracture leads to redistribute the compression load on the stronger parts.
- **Region III**: At this region the sample suffers a catastrophic failure.

**Figure 2.29**: Compression stress-strain curve for foam glass prepared from CRT panel and funnel glass with SiC and TiN as foaming agent (Méar et al., 2007)

### 2.5.2 Sample size and cross head speed

The size of the foam glass sample for the compression test is defined by ASTM C522 (2012) “Standard Specification for Cellular Glass Thermal Insulation”. The standard states that the sample should have a minimum size of 200 mm x 200 mm with nominal thickness (from 38 mm to 178 mm). Such large dimensions might be practical in the commercial scale, but they are not convenient in the lab scale (Abdel Alim, 2009). Literature shows that much smaller samples are used as listed in Table 2.3.

ASTM C165 (2012) “Standard Test Method for Measuring Compressive Properties of Thermal Insulations” specifies the range of the cross head speeds that should be adopted in the compression test of thermal insulating materials. The range
should be from 0.25 to 12.7 mm/min for each 25.4 mm of specimen thickness. Table 2.3 also lists the adopted cross head speeds in literature.

Table 2.3: Size of compression test samples and the adopted cross head speeds

<table>
<thead>
<tr>
<th>Reference</th>
<th>Glass waste</th>
<th>Sample Size (mm)</th>
<th>Cross head speed (mm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Méar et al. (2007)</td>
<td>Funnel &amp; Panel CRT</td>
<td>5x5x 12.5</td>
<td>2</td>
</tr>
<tr>
<td>Bernardo et al. (2006)</td>
<td>Panel CRT</td>
<td>15x15x10</td>
<td>2</td>
</tr>
<tr>
<td>Guo et al. (2010a)</td>
<td>CRT</td>
<td>5x5x12.5</td>
<td>2</td>
</tr>
<tr>
<td>Bernardo and Albertini (2006)</td>
<td>Panel CRT</td>
<td>15x15x10</td>
<td>2</td>
</tr>
<tr>
<td>Fernandes et al. (2013)</td>
<td>Funnel &amp; Panel CRT</td>
<td>30x30x30</td>
<td>0.5</td>
</tr>
<tr>
<td>Bernardo et al. (2005)</td>
<td>CRT</td>
<td>15x15x6</td>
<td>0.5</td>
</tr>
<tr>
<td>Bernardo et al. (2010)</td>
<td>Soda-lime</td>
<td>8x8x3</td>
<td>1</td>
</tr>
<tr>
<td>Abdel Alim (2009)</td>
<td>Soda-lime</td>
<td>20x20x20</td>
<td>2</td>
</tr>
<tr>
<td>Tulyaganov et al. (2006)</td>
<td>Soda-lime</td>
<td>30x30x30</td>
<td>0.5</td>
</tr>
</tbody>
</table>

2.6 Leaching Of Lead Silicate Glass

Several testing procedures exist to test the leachability of heavy metals. These testing procedures include the shake extraction procedure of ASTM D3987 (2012) and the Toxicity Characteristic Leaching Procedure TCLP as well as the EP procedure that were both developed by the US Environmental Protection Agency USEPA. It should be noticed, however, that the landfill leachate can’t be duplicated by using any testing procedure (Eisenberg et al., 1986). One of the main differences between EP, TCLP and ASTM D3987 is that the leaching medium used in both EP and TCLP is acidic while it is neutral (distilled water of pH=7) in ASTM D3987. Comparing the leachate results for the metals including lead from fly ash by using these three tests showed that the leaching results of EP and TCLP are significantly higher than ASTM D3987 (Egemen and Yurteri, 1996; Baba and Türkman 2001; Baba and Kaya, 2004). Also the research carried out by Chang et al. (2001) showed that generally the leachable metal content resulting from different wastes obtained by using of EP and TCLP is higher than ASTM D3987. Jang and Townsend (2003) investigated the lead leaching from CRT glass by using TCLP (acidic leaching solution of pH 4.93). The obtained results were compared with those obtained by using actual landfill leachate from 11 landfills having an average pH of 7.6 as the leaching solution to simulate actual landfill conditions. The comparison showed that the results are significantly different. The average leaching lead content was 413 mg/l and 4.06 mg/l for TCLP and MSW leachate medium, respectively. They contributed this significant increase in
the leaching lead content when using TCLP to the acidity of the leaching medium. It should be noted however that the CRT glass samples used in this research was not representative of an entire CRT because the aim of the research was to compare the results of lead leaching from TCLP with that of actual landfill conditions rather than studying the toxicity characteristics of CRT. Egemen and Yurteri (1996) investigated the metal leaching from fly ash using the three methods and compared the results with actual leachate collected from fly ash landfills. They concluded that although the three tests result in higher leaching values than those under actual field conditions, the metal leachate results for fly ash by using ASTM D3987 gives the most close results to actual values in landfills. The variability of replicate results is another important aspect in the leaching tests. Eisenberg et al. (1986) stated that the shake extraction procedure of ASTM D3987 has a low variability of replicate data.

Regarding the leachate values for lead glass like the CRT glass, literature shows that the values are usually higher than the US regulatory limit of 5 mg/l (Townsend et al., 1999; Musson et al., 2000; Yot and Méar, 2011). Musson et al. (2000) showed that out of 30 tested color CRTs only 9 CRTs had values lower than 5 mg/l. The 30 tested color CRTs had an average value of 22.2 mg/l. Table 2.4 shows the lead leachate values for the 30 CRTs tested in accordance with TCLP.
Table 2.4: Lead leachate values for 30 CRTs

<table>
<thead>
<tr>
<th>CRT Manufacturer</th>
<th>Manufacturing year</th>
<th>Tube Manufacturer</th>
<th>Leachable lead concentration (mg/l)</th>
<th>Weighted Average*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acer</td>
<td>93</td>
<td>Panasonic</td>
<td>9.5 347.3 &lt;1.0 57.2</td>
<td></td>
</tr>
<tr>
<td>Elite</td>
<td>92</td>
<td>Chunghwa</td>
<td>9.7 81.2 &lt;1.0 19.3</td>
<td></td>
</tr>
<tr>
<td>Emerson</td>
<td>84</td>
<td>Goldstar</td>
<td>6.5 6.6 &lt;1.0 1.5</td>
<td></td>
</tr>
<tr>
<td>Gateway</td>
<td>93</td>
<td>Toshiba</td>
<td>9.0 9.2 &lt;1.0 3.2</td>
<td></td>
</tr>
<tr>
<td>Gateway</td>
<td>92</td>
<td>Toshiba</td>
<td>12.8 174.5 &lt;1.0 54.1</td>
<td></td>
</tr>
<tr>
<td>IBM</td>
<td>87</td>
<td>Matsushita</td>
<td>9.5 38.4 &lt;1.0 9.4</td>
<td></td>
</tr>
<tr>
<td>IBM</td>
<td>89</td>
<td>Panasonic</td>
<td>9.5 142.9 &lt;1.0 41.5</td>
<td></td>
</tr>
<tr>
<td>Imtec</td>
<td>89</td>
<td>Samsung</td>
<td>8.2 200.6 &lt;1.0 60.8</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>97</td>
<td>Toshiba</td>
<td>10.1 103.0 &lt;1.0 21.3</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>97</td>
<td>Kch</td>
<td>12.7 49.4 &lt;1.0 15.4</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>98</td>
<td>Samsung</td>
<td>7.0 25.7 &lt;1.0 6.1</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>98</td>
<td>Chunghwa</td>
<td>10.9 7.8 &lt;1.0 2.3</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>97</td>
<td>Toshiba</td>
<td>8.4 34.9 &lt;1.0 9.1</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>98</td>
<td>Samsung</td>
<td>7.1 7.1 &lt;1.0 2.2</td>
<td></td>
</tr>
<tr>
<td>Memorex</td>
<td>97</td>
<td>Chunghwa</td>
<td>8.3 35.3 &lt;1.0 10.6</td>
<td></td>
</tr>
<tr>
<td>NEC</td>
<td>87</td>
<td>NEC</td>
<td>11.3 50.3 &lt;1.0 10.7</td>
<td></td>
</tr>
<tr>
<td>Orion</td>
<td>96</td>
<td>Orion</td>
<td>9.1 132.5 &lt;1.0 33.1</td>
<td></td>
</tr>
<tr>
<td>Panasonic</td>
<td>84</td>
<td>Matsushita</td>
<td>22.4 11.8 &lt;1.0 3.5</td>
<td></td>
</tr>
<tr>
<td>Quasar</td>
<td>84</td>
<td>Quasar</td>
<td>13.6 182.4 &lt;1.0 43.5</td>
<td></td>
</tr>
<tr>
<td>Seiko</td>
<td>87</td>
<td>NEC</td>
<td>9.1 100.0 8.0 26.6</td>
<td></td>
</tr>
<tr>
<td>Sharp</td>
<td>94</td>
<td>Sharp</td>
<td>8.7 16.4 &lt;1.0 4.4</td>
<td></td>
</tr>
<tr>
<td>Sharp</td>
<td>84</td>
<td>Sharp</td>
<td>7.9 6.0 &lt;1.0 1.5</td>
<td></td>
</tr>
<tr>
<td>Tandy</td>
<td>85</td>
<td>Sharp</td>
<td>17.6 116.1 &lt;1.0 35.2</td>
<td></td>
</tr>
<tr>
<td>Techmedia</td>
<td>95</td>
<td>Samsung</td>
<td>&lt;1.0 20.1 &lt;1.0 6.9</td>
<td></td>
</tr>
<tr>
<td>Ttx</td>
<td>91</td>
<td>Chunghwa</td>
<td>7.5 10.0 &lt;1.0 2.8</td>
<td></td>
</tr>
<tr>
<td>Zenith</td>
<td>94</td>
<td>Zenith</td>
<td>18.3 198.8 &lt;1.0 54.5</td>
<td></td>
</tr>
<tr>
<td>Zenith</td>
<td>94</td>
<td>Zenith</td>
<td>15.8 7.1 &lt;1.0 1.6</td>
<td></td>
</tr>
<tr>
<td>Zenith</td>
<td>77</td>
<td>Zenith</td>
<td>&lt;1.0 97.7 &lt;1.0 21.9</td>
<td></td>
</tr>
<tr>
<td>Zenith</td>
<td>85</td>
<td>Toshiba</td>
<td>7.5 92.1 &lt;1.0 21.5</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>10.1 90.3 &lt;1.0 22.2</td>
<td></td>
</tr>
</tbody>
</table>

*Weighted average was calculated based on the percentage of glass weight in each CRT component.
Source: (Musson et al., 2000)

It is interesting to notice that the average leachable lead concentration of the funnel is significantly higher than the neck despite the fact that the lead content in the funnel is lower than in the neck. Musson et al. (2000) attributed this to the presence of the frit seal, which has a lead content of 85% (Méar et al., 2006a), in the funnel parts that showed higher leachable lead concentration than the neck parts. To confirm this justification they carried out the leachate test for two funnel parts with and without the
frit seal and compared the results. They found that the leachable lead concentrations for funnel parts that contain the frit seal are 492 and 575 mg/l while only 10.8 and 13.3 mg/l for those without it. This justifies the very high variability of the results shown in table 2.4 where two funnel parts manufactured by the same manufacturer in the same year showed leachable lead concentration of 7 and 200 mg/l. Thus, Musson et al. (2000) stated that if the frit seal were included in all tested CRTs none of the 30 color CRTs would have leachable lead content below the regulatory limit.

While the literature that investigates the leaching of lead from lead glass is available (Townsend et al., 1999; Musson et al., 2000; Yamashita et al. 2010; Yot and Méar, 2011), the literature investigating the lead leaching from the foam glass produced from lead glass is rare. Bernardo et al (2005) found that the lead concentration in the leaching test for the foam glass prepared from CRT (65.7% panel + 34.3% Pb-glass) and 5% CaCO₃ as foaming agent is less than 0.02 mg/l. The research carried out by Yot and Méar (2011) seems to be the only available in-depth research in this area. However, the lead leaching results of this research seem unreasonable. Thus, a thorough analysis of the obtained results would be beneficial.

Yot and Méar (2011) investigated the lead leaching of the foam glass produced from CRT funnel glass by using either 5wt% SiC or 4wt% TiN as foaming agent at a sintering temperature of 850 °C and holding time of 60 minutes. The overall lead leachate results and the composition of the samples along with their porosity percentage are presented in Table 2.5. The leaching test was carried out in accordance with AFNOR X 31-210 which is a testing procedure released by the French Association of Normalization. This test is similar to ASTM D3987 in terms of the used leaching medium since both of them use distilled water (pH=7).

Table 2.5: Samples composition, their porosity and their lead leachate value

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of the sample</th>
<th>Funnel Glass (F)</th>
<th>Panel Glass (P)</th>
<th>SiC (S)</th>
<th>TiN (T)</th>
<th>Porosity %</th>
<th>Lead leachate (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Glass</td>
<td>100%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>NA</td>
<td>13</td>
</tr>
<tr>
<td>F5S</td>
<td>Foam glass</td>
<td>95%</td>
<td>5%</td>
<td>-</td>
<td>84%</td>
<td>86.1%</td>
<td>2.1</td>
</tr>
<tr>
<td>F4T</td>
<td>Foam glass</td>
<td>96%</td>
<td>-</td>
<td>4%</td>
<td>-</td>
<td>67.9%</td>
<td>111.3</td>
</tr>
<tr>
<td>PF5S</td>
<td>Foam glass</td>
<td>31.7%</td>
<td>63.3%</td>
<td>5%</td>
<td>-</td>
<td>46.5%</td>
<td>3.1</td>
</tr>
<tr>
<td>PF4T</td>
<td>Foam glass</td>
<td>32%</td>
<td>64%</td>
<td>4%</td>
<td>-</td>
<td>67.9%</td>
<td>5</td>
</tr>
</tbody>
</table>

Source: (Yot and Méar, 2011)
The results show that while the leachable lead concentration in the funnel glass (F) was found to be 13 mg/l, the value changed to 2.1 and 111.3 mg/l for the foam glass produced by using SiC (F5S) and TiN (F4T), respectively. The higher lead leaching values associated with using TiN rather than SiC can be attributed to two reasons as noted by the authors. Firstly, using TiN as a foaming agent results in increasing the porosity percentage in comparison with SiC which provides larger surface area. Secondly, the amount of the generated metal lead when using TiN is higher than when using SiC. The latter reason is illustrated in Figure 2.30 that shows the generated metal lead content in the case of using 4% TiN and 5% SiC at 850 °C and holding time of 60 minutes (i.e. the same conditions used to produce the studied foams). The results presented in this figure are confirmed by other studies (Méar et al., 2005a; Méar et al., 2005b). The aforementioned two reasons could result in a slight increase of the lead leaching values, but they may not justify such significant increase from only 2.1 mg/l (F5S) to 111.3 mg/l (F4T) especially because the increase in the porosity percentage, 2.1%, and the metal lead content, less than 1.0%, are not that significant as shown in Table 2.5 and Figure 2.30, respectively. Further investigation of the results shows that using TiN rather than SiC results only in just a slight increase in the lead leachate results (less than 2 mg/l) in the case of PF4T and PF5S even when the porosity percentage difference is significant (more than 20%) as shown in Table 2.5.

![Figure 2.30: Metal lead content in wt% of unreduced lead initially present before foaming vs. the foaming agent content (Yot and Méar, 2009)](image-url)
It’s interesting also to notice that the lead leaching results of the foam glass produced by using SiC in the case of the funnel glass only (F5S), 2.1 mg/l, is lower than when the glass is mixed with panel glass while using the same amount and type of foaming agent (PF5S), 3.1 mg/l. This seems to be unreasonable result since the panel glass of CRT hardly contains any lead, as previously shown in Table 1.3, which means that the lead concentration in the glass used to prepare (F5S) is considerably higher than (PF5S). What makes this result even more unreasonable is that F5S has a significant higher porosity percentage (84%) in comparison with PF5S (46.5%).

The results of the lead leachate include one more unexpected result. The lead leaching from the funnel glass sample (F) was 13 mg/l which is significantly higher than the lead leachate of the foam glass prepared by using funnel glass with SiC (F5S) which was only 2.1 mg/l. This result is unexpected because, as shown in Figure.2.30, using redox agents such as SiC or TiN results in generation of metal lead. This metal lead is generated on the surface of the foam glass pores in the form of lead bubbles/droplets as shown in Figures 2.31 and 2.32. Thus, it would be expected that these foams would have higher lead leaching results than the leaching results of the funnel glass. This is typically the case of F4T which has lead leaching value of 111.3 mg/l.

![Figure 2.31: Small lead bubbles generated on the surface of the pores of the foam glass (Méar et al. 2006b)](image)
The surface area certainly can affect the leaching results. However, its effect can’t be included in the justification of the different lead leaching results of (F) and (F5S). This is because although Yot and Méar (2011) stated that the foam glass samples such as (F5S) used in the leaching test were ground and sieved to particle size below 4mm, the particle size of the funnel glass (F) used in the leaching test was not clearly stated. However, the CRT glass powder used to prepare the foam glass might have the same particle size of that used in the leaching test of the CRT glass (i.e. less than 65 μm). This is significantly lower than the 4 mm F5S particles which can increase the lead leaching results of F in comparison F5S due to the larger surface area. However, interpreting the results in this way excludes the effect of the increased surface area of the foam glass F5S due to porosity.

Yot and Méar (2011) stated that the presented leachate result for each sample is the average of three repeated experiments with a relative standard deviation of less than 0.2%. On the other hand, the aforementioned discussion suggests that the results may suffer from high variability which led to such unreasonable results. The high variability of the lead leaching results from CRT glass can be attributed to the possibility of the presence of the frit seal in some parts of the funnel glass used to prepare the samples as proved by the research carried out by Musson et al. (2000). Yot and Méar (2011) did not state the method used to divide the CRT glass to separate the funnel from the panel in order to get the funnel glass used in their research. There are several methods that can be used for this purpose (Musson et al., 2000; Lee et al., 2001; Geskin et al., 2002; Herat, 2008). These methods can generally
be classified as physical and chemical methods. Using physical methods such as diamond saw or electric wire heating can’t remove the frit seal adhered to the funnel glass, while chemical methods can remove the entire frit seal (Lee et al., 2001). If one of the physical methods was applied in their research, then the high variability of the lead leachate results could be justified.

Yot and Méar (2009) found that increasing the sintering temperature, the foaming agent content or the holding time would generally result in increase in the metal lead content generated at the surface of the pores of the foam glass in the case of using redox agents. This suggests that increasing any of these parameters would result in increasing the leachable lead concentration of the produced foam glass. On the other hand, this is not applicable to neutralization agents such as CaCO₃, because they don’t result in generation of metal lead since the foaming gas CO₂ is released by thermal decomposition as previously stated.

The present research aims at adopting an open-recycling system to produce foam glass from the grinding and polishing sludge of lead crystal. The effect of sintering temperature and holding time on the properties of the produced foam glass will be studied. SiC and granite powder will be added to enhance the properties of the produced foam glass. The effect of their amounts on the properties of the produced foam glass will be investigated. The properties of the produced foam glass that will be investigated in this research include; density, total porosity percentage, compressive strength, and thermal conductivity. In addition, the lead leachate of the sludge as well as the produced foam glass will be investigated.
CHAPTER 3
EXPERIMENTAL PROCEDURE

The aim of this chapter is to present the experimental procedures used in this study. The chapter is divided into four parts. The first part presents the tests carried out for the raw material (sludge) provided by ASFOUR Crystal. The second part presents the experimental matrix adopted to study the effect of several parameters on the properties of the produced foam glass. The third part describes the experimental method used to prepare the foam glass. The fourth part presents the tests carried out for the produced foam glass.

3.1 Characteristics of Raw Material

3.1.1 Chemical analysis

The chemical analysis of the sludge was provided by ASFOUR Crystal and was carried out by using Wavelength Dispersive X-ray spectroscopy (WDX).

3.1.2 Particle size analysis

The particle size of the sludge was analyzed in accordance with ASTM D422 (2007) “Particle-Size Analysis of Soils”. The sludge was dried for 10 hours then 200 g was used in the sieve analysis. Table 3.1 presents the number of the used set of sieves along with their diameter while Figure 3.1 shows the used set of sieves.

Table 3.1: Sieves used in the particle size analysis of the sludge

<table>
<thead>
<tr>
<th>Sieve Number</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2.36 mm</td>
</tr>
<tr>
<td>16</td>
<td>1.18 mm</td>
</tr>
<tr>
<td>30</td>
<td>600 μm</td>
</tr>
<tr>
<td>50</td>
<td>300 μm</td>
</tr>
<tr>
<td>100</td>
<td>150 μm</td>
</tr>
<tr>
<td>200</td>
<td>75 μm</td>
</tr>
</tbody>
</table>
Figure 3.1: Used set of sieves in the particle size analysis of the sludge

The mass of each empty sieve was recorded. These six sieves were stacked in a descending order (sieve #200 at bottom and sieve #4 at top). Then a pan was installed below sieve #200 after recording its mass. The sieve stack was placed into mechanical shaker as shown in Figure 3.2 for 10 minutes. Then the mass retained in each sieve and in the pan was recorded. The analysis was carried out four times and the average mean diameter as well as the average median diameter of the sludge powder was calculated.

Figure 3.2: The set of sieves with the pan installed in the mechanical shaker
3.1.3 Powder density measurement

The density of the sludge was measured in accordance with ASTM D854 (2010) “Specific Gravity of Soil Solids by Water Pycnometer”. Distilled water was added to 500 ml flask and the mass of the flask filled with water was recorded as \( m_1 \). A mass of 50 g of the dried sludge \( m_2 \) was added to empty flask and distilled water was added till the mark of 500 ml, then the mass of the flask with the dried sludge and water was recorded as \( m_3 \). The volume of the powder in cm\(^3\) was calculated as follows:

\[
V = m_1 - (m_3 - m_2)
\]  

(3.1)

Then the density of the powder was calculated by dividing \( m_2 \) (50 g) by the calculated volume. The deairing process in the test to remove the entrapped air was carried out by using vacuum pump for 30 minutes. The test was repeated three times and the average value was calculated. The powder density of the additives was also measured using the same procedure.

The powder density of the sludge with different wt.% SiC or wt.% granite was calculated by using the measured density of the powders and applying the rule of mixtures (German, 2008):

\[
\frac{1}{\rho} = \frac{M_x}{\rho_x} + \frac{M_y}{\rho_y}
\]  

(3.2)

Where: \( \rho \) is the density of the powder mixture

\( M_x \) and \( M_y \) are the mass fractions of the powders

\( \rho_x \) and \( \rho_y \) are the densities of the powders

3.1.4 Leaching test

The leaching test was carried out in accordance with ASTM D3987 (2012) “Standard Practice for Shake Extraction of Solid Waste with Water”. Before carrying the leaching test, the moisture content in the sludge was measured. A sample of 70 g was dried at 104 °C for 10 hr. Then the mass of the sample was recorded after drying. The solid content (S) was calculated by using the following simple equation:

\[
S = \frac{A}{B}
\]  

(3.3)

Where:

\( A \) = mass of sample after drying, g

\( B \) = original mass of sample, g

\( S \) = solid content
A sample of 70 g of the sludge along with 1400 ml of distilled water was added in 2 liter container leaving adequate headspace for mixing as required by the standard. The mechanism shown in Figure 3.3 was assembled to simulate the agitation equipment required by the standard that mixes the sample in an end-over-end fashion as shown in Figure 3.4. The simovert shown in Figure 3.5 was used to adjust the rpm to 29 rpm. The sample was agitated for 18 hours.

Figure 3.3: Plan view of the assembled mechanism used for the shake extraction
After agitation the sample was filtered through a coarse filter paper then through 0.45-μm cellulose nitrate membrane filter by using a vacuum pump as shown in Figure 3.6.
The sample was filtered 5 times through the 0.45-μm membrane filter until no visible solid particles were separated by the filter. Figure 3.7 shows the five consecutive filters used in this process.

After this filtration process the color of the sample changed and became transparent as shown in Figure 3.8.
Figure 3.8: The sample before filtration (on the left) and after filtration (on the right)

The pH meter shown in Figure 3.9 was calibrated by buffer solutions of pH 4 and 7. Then the pH of the extract was measured immediately after the filtration. The Atomic Absorption Spectrometer shown in Figure 3.10 was calibrated by using solutions of known lead concentration (2.5, 5 and 10 mg/l) before measuring the lead concentration in the extract.

Figure 3.9: the pH-meter used to measure the pH
The test was repeated three times and in each time the pH value and the lead concentration were measured and the average value was calculated.

### 3.2 Foam Glass Preparation Procedure

The sludge coming from the plant included agglomerated parts. Thus, the rotary mixer with metallic blades shown in Figure 3.11 was used to obtain the sludge powder.
The sludge powder was then dried at the drying oven shown in Figure 3.12 for 10 hr at 104 °C.

![Drying oven and its temperature control unit](image)

**Figure 3.12: Drying oven and its temperature control unit**

In the case of using any additives the rotary mixer shown in Figure 3.13 was used for 15 minutes to ensure a good mixing between the sludge powder and the additives.

![Rotary mixer to mix the sludge powder with additives](image)

**Figure 3.13: Rotary mixer to mix the sludge powder with additives**

A cylindrical mould of 11 cm diameter was then filled with 500 g of the powder and was dry pressed at 5 ton by using the hydraulic press shown in Figure
3.14. The hydraulic press was calibrated by using a proving ring. The obtained pressed sample is shown in Figure 3.15.

Figure 3.14: The hydraulic press and the mould used in sample preparation

Figure 3.15: The pressed sample before sintering

After that the pressed samples were inserted into the electric oven shown in Figure 3.16 for sintering.
Although there is a temperature control unit that is used to adjust the required sintering temperature, the heating rate of the oven is not controlled. Figure 3.17 shows the heating rate of the oven. As shown in the figure the heating rate at the first hour is about 5 °C/min. However, the heating rate after the first hour decreases to have an average of 1.3 °C/min.

After reaching the desired sintering temperature the samples stayed in the sintering oven for the required holding time. Then they were severely cooled at a rate
of approximately 20 °C/min to 600 °C. The aim of this severe cooling is to stop the microstructure evolution. The samples were then cooled slowly with an average rate of 0.5 °C/min as shown in Figure 3.18 to provide some sort of annealing for the produced foam glass. A sample of the produced foam glass is shown in Figure 3.19.

![Figure 3.18: Slow cooling rate of foam glass](image)

![Figure 3.19: A sample of the produced foam glass](image)

The foam glass samples were carefully cut with high precession to the desired dimensions using the bench-type circular saw shown in Figure 3.20. Some samples suffered from irregular large cavities. The samples selected for testing were carefully chosen to avoid such flaws.
Cube samples with average size of 20 mm were used in the compression test while the selected dimensions of the samples for measuring the thermal conductivity were 100*30*30 mm. These samples are shown in Figures 3.21 and 3.22 respectively.
3.3 Experimental Matrix

The experimental matrix shown in Table 3.2 was adopted to investigate the effect of the heating method, sintering temperature, holding time and the amount of additives (SiC and granite powder) on the properties of the produced foam glass. All the samples presented in the experimental matrix were prepared using the heating rate of the available oven except for sample#4 that was directly inserted at 800 °C.

Table 3.2: Experimental matrix

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Sintering Temperature (°C)</th>
<th>Holding time (min)</th>
<th>wt.% SiC powder</th>
<th>wt.% granite powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>800 (direct insertion)</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>850</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>750</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>750</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>750</td>
<td>40</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>750</td>
<td>30</td>
<td>2%</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>750</td>
<td>30</td>
<td>4%</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>750</td>
<td>30</td>
<td>6%</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>750</td>
<td>30</td>
<td>8%</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>750</td>
<td>30</td>
<td>-</td>
<td>2%</td>
</tr>
<tr>
<td>14</td>
<td>750</td>
<td>30</td>
<td>-</td>
<td>4%</td>
</tr>
<tr>
<td>15</td>
<td>750</td>
<td>30</td>
<td>-</td>
<td>6%</td>
</tr>
<tr>
<td>16</td>
<td>750</td>
<td>30</td>
<td>-</td>
<td>8%</td>
</tr>
</tbody>
</table>
• Samples# 1,2,3,5 were prepared to investigate the effect of sintering temperature.
• Samples# 4,5 were prepared to investigate the effect of heating method.
• Samples# 2,6,7,8 were prepared to investigate the effect of holding time.
• Samples# 9,10,11,12 were prepared to investigate the effect of the amount of SiC.
• Samples# 13,14,15,16 were prepared to investigate the effect of the amount of granite powder.

3.4 Testing of the Produced Foam Glass

3.4.1 Compression test

The compression tests were carried by using screw driven universal testing machine of type Instron 3382 - 100 kN load cell as shown in Figure 3.23.

Figure 3.23: The universal testing machine used in the compression test

Cube samples with average size of 20 mm were tested with a cross head speed of 2 mm/min. The samples were compressed till catastrophic failure occurred as shown in Figure 3.24. Four samples of each sample-type stated in the experimental matrix were tested and the average compressive strength was calculated.
3.4.2 Bulk density measurement

The envelope dimensions of the samples were geometrically measured to calculate the volume (including pores). The bulk density of the produced foam glass was measured by dividing the mass of the samples by their measured volume. The bulk density of four samples of each sample-type stated in the experimental matrix was measured and the average value was calculated.

3.4.3 Thermal conductivity measurement

The thermal conductivity of the samples was measured at the Housing and Building National Research Center in accordance with ASTM D5334 (2008) “Determination of Thermal Conductivity of Soil and Soft Rock by Thermal Needle Probe Procedure”. The size of the samples was 100*30*30 mm and they were measured at a temperature of 24 °C.

3.4.4 Leaching test

The leaching test of the foam glass sample#2 was carried out three times using the same procedure stated in section 3.1.4.
CHAPTER 4

RESULTS AND DISCUSSION

In this chapter the experimental results are presented and discussed. This includes the physical properties of the powders, the effect of sintering temperature and holding time as well as the effect of silicon carbide and granite powder additives on the physical and mechanical properties of the produced foam glass. Also the leaching test results of the sludge powder and foam glass are presented.

4.1 Physical Properties of Powders

The analysis of the chemical composition of the sludge is presented in Table 4.1. The sludge is mainly composed of SiO$_2$ and PbO representing 40.55 wt.% and 35.28 wt., respectively. This is quite similar to the chemical analysis of the CRT neck as presented by Bernardo et al. (2007b) in which the SiO$_2$ and PbO represented 38 wt.% and 35wt.% respectively.

Table 4.1: Chemical composition of the sludge

<table>
<thead>
<tr>
<th>Composition</th>
<th>wt.%</th>
<th>Composition</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>1.03</td>
<td>Sb$_2$O$_3$</td>
<td>0.47</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>40.55</td>
<td>La$_2$O$_3$</td>
<td>0.60</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>5.38</td>
<td>CeO$_2$</td>
<td>1.45</td>
</tr>
<tr>
<td>CaO</td>
<td>5.32</td>
<td>PbO</td>
<td>35.28</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>8.33</td>
<td>F</td>
<td>0.44</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The solid content of the sludge was found to be 0.8 which means that the moisture content in the sludge was 0.2. The results of the sieve analysis of the dried sludge are presented in Table 4.2 and Figure 4.1. The average mean diameter of the four tests is 111.25 µm and the average median diameter (at 50% passing) is 108.5 µm. Appendix A includes the experimental data of the sieve analysis.
Table 4.2: Particle size of the sludge powder from sieve analysis tests

<table>
<thead>
<tr>
<th>Tests</th>
<th>16% passing</th>
<th>50% passing</th>
<th>84% passing</th>
<th>Mean diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test I</td>
<td>82</td>
<td>110</td>
<td>148</td>
<td>113.33</td>
</tr>
<tr>
<td>Test II</td>
<td>80</td>
<td>108</td>
<td>145</td>
<td>111.00</td>
</tr>
<tr>
<td>Test III</td>
<td>80</td>
<td>108</td>
<td>143</td>
<td>110.33</td>
</tr>
<tr>
<td>Test IV</td>
<td>80</td>
<td>108</td>
<td>143</td>
<td>110.33</td>
</tr>
<tr>
<td>Average</td>
<td>108.5</td>
<td></td>
<td></td>
<td>111.25</td>
</tr>
<tr>
<td>STDEV</td>
<td>1.0</td>
<td></td>
<td></td>
<td>1.42</td>
</tr>
</tbody>
</table>

Figure 4.1: Particle-size distribution of sludge using sieve analysis

The experimental results of the powder density of the sludge, SiC and granite powders are shown in Table 4.3. The average values of three tests for each powder are 3.16, 3.28 and 2.79 g/cm$^3$ respectively with maximum standard deviation of 0.062.

Table 4.3: The results of measured powder density ($\rho$)

<table>
<thead>
<tr>
<th>Powder</th>
<th>Test</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>Sludge</td>
<td>3.23</td>
<td>3.13</td>
<td>3.13</td>
</tr>
<tr>
<td>SiC</td>
<td>3.21</td>
<td>3.33</td>
<td>3.3</td>
</tr>
<tr>
<td>Granite</td>
<td>2.78</td>
<td>2.78</td>
<td>2.81</td>
</tr>
</tbody>
</table>
4.2 The Effect of Low Heating Rate vs. Direct Insertion

The heating rate of the oven was previously discussed and presented in Figure 3.17. Such heating rate is considered as low heating rate since it is less than 5 °C/min (Scarinci et al., 2006). Table 4.4 shows the results of the bulk density and calculated porosity for the foam glass produced by this low heating rate and by direct insertion. The bulk density of the foam glass produced by using the low heating rate is significantly higher by 177% compared to direct insertion. As previously discussed in chapter 2 low heating rate results in prolonged isothermal heating which can cause gas generation to take place before the sintering temperature of the foam glass. This makes the gases escape before the full foaming effect takes place (Scarinci et al., 2006) which results in foam glass with higher bulk density and lower porosity.

Table 4.4: The effect of heating method on the foam glass density and porosity

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating method</th>
<th>Test</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>STDEV</th>
<th>% Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Low heating rate</td>
<td>I</td>
<td>0.561</td>
<td>0.009</td>
<td>82.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>0.554</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>III</td>
<td>0.551</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV</td>
<td>0.538</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Direct insertion</td>
<td>I</td>
<td>0.182</td>
<td>0.010</td>
<td>93.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>0.189</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>III</td>
<td>0.193</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV</td>
<td>0.205</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The higher bulk density of foam glass is usually associated with higher compressive strength as previously discussed. Figure 4.2 shows the compressive stress-strain curve for the foam glass produced by the low heating rate and the direct insertion method. The linear elasticity region followed by the brittle crushing plateau region is evident. These two regions are then followed by a region of approximately equal decreased stress which is similar to the behavior of the foam glass produced from soda-lime glass prepared by Abdel Alim (2009). The brittle crushing plateau is relatively narrow in the case of the low heating rate. The compressive strength is considered as the highest compressive stress of the brittle crushing plateau as represented by the red circle in the figure.
Figure 4.2: Compressive stress-strain curve for the foam glass prepared by low heating rate and direct insertion

The compressive strength of the foam glass produced by the low heating rate is higher by 260% compared to the direct insertion method as shown in Table 4.5 and Figure 4.3

Table 4.5: The effect of heating method on the foam glass compressive strength

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating method</th>
<th>Test</th>
<th>Compressive strength (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Low heating rate</td>
<td>I</td>
<td>1.03</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>1.20</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>III</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Direct insertion</td>
<td>I</td>
<td>0.28</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II</td>
<td>0.32</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>III</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.3: The effect of low heating rate and direct insertion on the foam glass properties

The aforementioned results show that low heating rate results in higher bulk density while direct insertion results in lower compressive strength. The low heating rate was chosen as the heating methodology throughout this research and the effect of the sintering temperature, holding time as well as SiC and granite powder additives on the properties of the produced foam glass will be investigated.

4.3 The Effect of Sintering Temperature on the Foam Glass Properties

The effect of sintering temperature on the foam glass produced from the sludge powder without any additives at holding time of 30 min was investigated. Foam glass was successfully produced at temperatures of 700, 750 and 800 °C while at a higher temperature of 850 °C the foam was seriously cracked. The sludge contains the foaming agent of calcium carbonate (CaCO$_3$) due to the added lime stone during the sedimentation process.

The results of bulk density and calculated porosity are shown in Table 4.6 and Figure 4.4. As the sintering temperature increased from 700 to 750 °C, the bulk density decreased by 44%, consequently the porosity increased by 16%. Further increase of the sintering temperature from 750 to 800 °C leads to an increase in bulk density by 10% and reduction in porosity by 2%. This can be attributed to the coalescence phenomenon in which the cellular structure is coarsened due to dissolving of smaller pores with larger ones resulting in foam glass with higher...
density and lower compressive strength (Bernardo et al., 2007a; Brusatin et al., 2004). Similar trend was observed for the foam glass prepared from panel glass by Fernandes et al. (2013) when the sintering temperature increased beyond 725 °C.

Table 4.6: The variation of bulk density and porosity with sintering temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temp. (°C)</th>
<th>Test</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>STDEV</th>
<th>% of Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>1</td>
<td>700</td>
<td>0.776</td>
<td>0.821</td>
<td>0.890</td>
<td>0.949</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>0.462</td>
<td>0.465</td>
<td>0.471</td>
<td>0.543</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>0.561</td>
<td>0.554</td>
<td>0.551</td>
<td>0.538</td>
</tr>
</tbody>
</table>

Figure 4.4: The variation of bulk density and porosity with sintering temperature

Figure 4.5 shows the compressive stress-strain curves at the studied sintering temperatures. The curves exhibit a similar behavior to the compressive stress-strain curves of the foam glass prepared by Tulyaganov et al. (2006) as previously presented in Figure 2.27. It can be noticed that as the sintering temperature increases the brittle crushing plateau becomes narrower.
The effect of sintering temperature on the compressive strength is shown in Table 4.7 and Figure 4.6. It is clear that the compressive strength of the foam glass significantly decreased from 4.45 to 1.19 MPa with a reduction of 73% as the sintering temperature increased from 700 to 800 °C.

Table 4.7: The variation of compressive strength with sintering temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temp. (°C)</th>
<th>Test</th>
<th>Compressive strength (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>1</td>
<td>700</td>
<td>4.37</td>
<td>4.39</td>
<td>4.52</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>2.15</td>
<td>2.16</td>
<td>2.17</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>1.03</td>
<td>1.20</td>
<td>1.20</td>
</tr>
</tbody>
</table>
The variation of thermal conductivity with sintering temperature is presented in Table 4.8 and Figure 4.7. The thermal conductivity decreased from 0.089 W/m.K to 0.051 W/m.K due to the increased porosity as the temperature increased from 700 to 750 °C. Further increase in temperature leads to increase the thermal conductivity to 0.071 W/m.K due to the decreased porosity associated with the coalescence phenomenon.

Table 4.8: The variation of thermal conductivity with sintering temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering Temperature (°C)</th>
<th>Thermal conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>0.089</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>0.051</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>0.071</td>
</tr>
</tbody>
</table>
Thermal conductivity (W/mK) 

Sintering temperature (°C) 

Figure 4.7: The variation of thermal conductivity with sintering temperature

The properties of the foam glass produced at 750 °C are comparable to that of the commercial foam glass (Scarinci et al., 2006). However, the foam glass produced at sintering temperature of 700 °C had a significantly higher density compared to commercial foam glass. Increasing the temperature to 800 °C increased the energy consumption and lead to deterioration in the foam glass properties (increased density, reduced compressive strength and increased thermal conductivity) due to the coalescence phenomenon. Therefore, 750 °C was chosen as the sintering temperature while investigating the effect of holding time and additives.

4.4 The Effect of Holding Time on the Foam Glass Properties

The effect of holding time on the bulk density of the foam glass produced from sludge at sintering temperature of 750 °C are shown in Table 4.9 and Figure 4.8. The obtained bulk density and porosity are in the range of 0.479-0.573 g/cm³ and 81.9-84.8% respectively within the holding time range 10 - 40 min. In general the foam bulk density decreases and the porosity increases as the holding time increases. This can be attributed to the generation of larger pores as the holding time increases as demonstrated by Bernardo and Albertini (2006) and Méar et al. (2006b).

Slight changes in the bulk density occur as the holding time increases from 10 to 20 min and from 30 to 40 min. However, a significant reduction of 13% in the bulk density is evident as the holding time increases from 20 to 30 min.
Table 4.9: The variation of bulk density and porosity with holding time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Holding time (min)</th>
<th>Test</th>
<th>( \rho_b ) (g/cm³)</th>
<th>STDEV</th>
<th>% of Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>0.546</td>
<td>0.573</td>
<td>0.586</td>
<td>0.586</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>0.542</td>
<td>0.549</td>
<td>0.567</td>
<td>0.573</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.462</td>
<td>0.465</td>
<td>0.471</td>
<td>0.543</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>0.453</td>
<td>0.473</td>
<td>0.490</td>
<td>0.499</td>
</tr>
</tbody>
</table>

Figure 4.8: The variation of bulk density and porosity with holding time

Figure 4.9 shows the compressive stress-strain curves at different holding times. The curves have the three regions of linear elasticity, brittle crushing plateau as well as the region of approximately equal decreased stress. At holding time of 10 min. and 20 min. the brittle crushing plateau region is quite narrow, it starts to be wider as the holding time increases to 30 and 40 min.
The variation of the compressive strength with the holding time is shown in Table 4.10 and Figure 4.10. The compressive strength decreased as the holding time increased. The compressive strength dropped from 2.86 MPa to 2.31 MPa as the holding time increased from 10 to 40 min. These results are in agreement with the results of Bernardo and Albertini (2006) in which the highest compressive strength and bulk density were achieved with the least amount of holding time.

Table 4.10: The variation of compressive strength with holding time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Holding time (min)</th>
<th>Test</th>
<th>Compressive strength (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>2.91</td>
<td>2.84</td>
<td>2.84</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>2.94</td>
<td>2.78</td>
<td>2.52</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>2.15</td>
<td>2.16</td>
<td>2.17</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>2.2</td>
<td>2.23</td>
<td>2.32</td>
</tr>
</tbody>
</table>
The effect of holding time on the foam glass thermal conductivity is shown in Table 4.11 and Figure 4.11. The thermal conductivity is in the range of 0.051-0.083 W/m.K. In general the thermal conductivity decreased with increasing the holding time which can be attributed to the increased foam glass porosity.

Table 4.11: The variation of thermal conductivity with holding time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Holding time (min)</th>
<th>Thermal conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>10</td>
<td>0.067</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>0.083</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>0.051</td>
</tr>
<tr>
<td>8</td>
<td>40</td>
<td>0.058</td>
</tr>
</tbody>
</table>
Increasing the holding time to 30 minutes resulted in a lighter foam glass with reduced thermal conductivity. On the other hand, the compressive strength was reduced, but its value is still within the range of the commercial foam glass (Scarinci et al., 2006). Further increase of the holding time to 40 min showed insignificant changes in the foam glass properties while increasing the energy consumption. Thus, the holding time of 30 min was selected for the purpose of energy saving while investigating the effect of SiC and granite powder additives.

4.5 The Effect of Silicon Carbide Additive on the Foam Glass Properties

The effect of wt.% silicon carbide (SiC) as foaming agent on the bulk density and porosity of the produced foam glass at sintering temperature of 750 °C and holding time of 30 min. is presented in Table 4.12 and Figure 4.12. Also, the calculated powder density of the sludge with different wt.% SiC is shown in Table 4.12.

The addition of 2% of SiC to the sludge leads to produce foam glass with a bulk density lower than that produced without any SiC by 31 % and increases the porosity by 6%. A reduction of 9% in the bulk density is evident as the SiC content increases from 2% to 6%. Adding 8% SiC results in a significant decrease of about 47% in the bulk density compared to the foam glass produced without any SiC. A similar trend was observed while increasing the foaming agent content in previous studies (Fernandes et al., 2013; Bernardo and Albertini, 2006). The reduction in the
bulk density as shown in Figure 4.12 can be attributed to the generation of larger pores as the amount of wt.% SiC increases as demonstrated by Bernardo et al. (2007a) and Méar et al. (2006b).

Table 4.12: The variation of bulk density and porosity with SiC content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% SiC</th>
<th>Test</th>
<th>ρb (g/cm³)</th>
<th>STDEV</th>
<th>ρ (g/cm³)</th>
<th>% of Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.462</td>
<td>0.465</td>
<td>0.471</td>
<td>0.543</td>
<td>0.485</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.312</td>
<td>0.340</td>
<td>0.342</td>
<td>0.343</td>
<td>0.334</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.311</td>
<td>0.312</td>
<td>0.325</td>
<td>0.326</td>
<td>0.319</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.281</td>
<td>0.309</td>
<td>0.310</td>
<td>0.318</td>
<td>0.305</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>0.241</td>
<td>0.255</td>
<td>0.260</td>
<td>0.270</td>
<td>0.256</td>
</tr>
</tbody>
</table>

The compressive stress-strain curves with different wt.% of SiC are shown in Figure 4.13. The figure shows the three different regions that occur during the compression of elastic-brittle foams as previously discussed.
The effect of SiC content on the compressive strength is presented in Table 4.13 and Figure 4.14. The addition of 2% of SiC reduces the compressive strength from 2.21 to 1.44 MPa by 35%. Further increase of SiC from 2 to 4% leads to drop the compressive strength from 1.44 to 1.07 by 26%. However, insignificant reduction in the compressive strength is evident at SiC greater than 4%.

Table 4.13: The variation of compressive strength with SiC content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% SiC</th>
<th>Test</th>
<th>Compressive strength (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>I,II,III,IV</td>
<td>2.15, 2.16, 2.17, 2.35</td>
<td>2.21, 0.095</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>I,II,III,IV</td>
<td>1.39, 1.42, 1.47, 1.49</td>
<td>1.44, 0.046</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>I,II,III,IV</td>
<td>0.98, 1.0, 1.06, 1.25</td>
<td>1.07, 0.123</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>I,II,III,IV</td>
<td>0.86, 0.99, 1.05, 1.11</td>
<td>1.00, 0.107</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>I,II,III,IV</td>
<td>0.79, 0.89, 0.94, 0.95</td>
<td>0.89, 0.073</td>
</tr>
</tbody>
</table>
The effect of SiC content on the thermal conductivity is shown in Table 4.14 and Figure 4.15. The measured thermal conductivity is in the range of 0.039-0.058 W/m.K. In general, the thermal conductivity tends to decrease as the percentage content of SiC increases. This can be attributed to the increase of porosity.

Table 4.14: The variation of thermal conductivity with SiC content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% SiC</th>
<th>Thermal conductivity (W/m.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.051</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>0.046</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>0.058</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>0.047</td>
</tr>
<tr>
<td>12</td>
<td>8</td>
<td>0.039</td>
</tr>
</tbody>
</table>
The addition of SiC from 2 to 8% produces a foam glass with a bulk density 0.256-0.334 g/cm$^3$, compressive strength 0.89-1.44 MPa, thermal conductivity 0.039-0.058 W/m.K and porosity 89.4-91.9%. Adding SiC reduced the density and thermal conductivity of the produced foam glass which is considered as an advantage for insulating foam glass. On the other hand, it resulted in a decrease in the compressive strength, but its values are still within the range of the commercial foam glass (Scarinci et al., 2006).

4.6 The Effect of Granite Additive on the Foam Glass Properties

Adding granite powder to the sludge in order to enhance the compressive strength of the produced foam glass was investigated. The variation of bulk density and porosity of the produced foam glass with the additive of granite powder at sintering temperature of 750 °C and holding time of 30 min. are shown in Table 4.15 and Figure 4.16. Adding 2wt.% of granite powder resulted in increase in the bulk density by 9% compared to the foam glass prepared from the sludge without any additives. As the wt.% granite increased from 2 to 8%, the bulk density increased from 0.529 to 0.747 g/cm$^3$ by 41% while the porosity decreased from 83.2 to 76.1%.
Table 4.15: The variation of bulk density and porosity with granite content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% granite</th>
<th>Test</th>
<th>ρb (g/cm³)</th>
<th>STDEV</th>
<th>ρ (g/cm³)</th>
<th>% of Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
<td>IV</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0.462</td>
<td>0.465</td>
<td>0.471</td>
<td>0.543</td>
<td>0.485</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.038</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>0.503</td>
<td>0.516</td>
<td>0.541</td>
<td>0.556</td>
<td>0.529</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.024</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>0.538</td>
<td>0.540</td>
<td>0.591</td>
<td>0.648</td>
<td>0.579</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.052</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0.610</td>
<td>0.633</td>
<td>0.657</td>
<td>0.658</td>
<td>0.640</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.023</td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>0.725</td>
<td>0.749</td>
<td>0.751</td>
<td>0.762</td>
<td>0.747</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.016</td>
</tr>
</tbody>
</table>

Figure 4.16: The variation of bulk density and porosity with granite content

The compressive stress-strain curves with different wt.% of granite are shown in Figure 4.17. While the linear elasticity as well as the region of approximately equal decreased stress are clear, the brittle crushing plateau is not noticeable. This is quite similar to the compressive stress-strain curve behavior of Abdel Alim (2009) shown in Figure 2.28 (b).
Figure 4.17: Compressive stress-strain curves at different wt.% granite

The presence of granite content increases the compressive strength of the foam glass as shown in Table 4.16 and Figure 4.18. The compressive strength increased from 2.43 to 5.09 MPa by 109% as the wt% granite increased from 2 to 8%.

Table 4.16: The variation of compressive strength with granite content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt.% granite</th>
<th>Test</th>
<th>Compressive strength (MPa)</th>
<th>STDEV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>2.15</td>
<td>2.16</td>
<td>2.17</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>2.12</td>
<td>2.33</td>
<td>2.41</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>2.77</td>
<td>2.89</td>
<td>3.43</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>3.82</td>
<td>4.05</td>
<td>4.2</td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>4.63</td>
<td>4.83</td>
<td>5.36</td>
</tr>
</tbody>
</table>
The introduction of granite powder to the sludge by wt. 2% increases the thermal conductivity from 0.051 to 0.071 W/m.K by 28% as shown in Table 4.19 and Figure 4.18. Further increase in granite content increases the thermal conductivity up to 0.135 W/m. K at wt. 8% granite because of the reduced porosity.

Table 4.17: The variation of thermal conductivity with granite content

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt. % granite</th>
<th>Thermal conductivity (W/m. K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.051</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>0.074</td>
</tr>
<tr>
<td>14</td>
<td>4</td>
<td>0.071</td>
</tr>
<tr>
<td>15</td>
<td>6</td>
<td>0.085</td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>0.135</td>
</tr>
</tbody>
</table>
The addition of granite from 2 to 8% produces a foam glass with a bulk density 0.529-0.747 g/cm$^3$, compressive strength 2.43-5.09 MPa, thermal conductivity 0.074-0.135 W/m.K and porosity 76.1-83.2%. Adding granite resulted in a substantial increase in the compressive strength of the produced foam glass. Also the density and thermal conductivity increased. The increase in the thermal conductivity is considered as a disadvantage in foam glass because it means deterioration in its thermal insulating properties. Usually commercial foam glass has a range of thermal conductivity between 0.04 and 0.08 W/m. K (Scarinci et al., 2006). However, since the thermal conductivity values are still lower than 0.25 W/m. K, the produced foam can still be considered as insulating material (Méar et al., 2005a).

### 4.7 Compressive Strength-Relative Density Relationship

The relative density results of the tested foam glass samples produced by adopting the low heating rate and their compressive strength are presented in Table 4.18.
Table 4.18: The variation of compressive strength with relative density

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Relative density, $\rho_{rel}$</th>
<th>Compressive strength, MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.272</td>
<td>4.45</td>
</tr>
<tr>
<td>2</td>
<td>0.154</td>
<td>2.21</td>
</tr>
<tr>
<td>3</td>
<td>0.174</td>
<td>1.19</td>
</tr>
<tr>
<td>6</td>
<td>0.181</td>
<td>2.86</td>
</tr>
<tr>
<td>7</td>
<td>0.176</td>
<td>2.63</td>
</tr>
<tr>
<td>8</td>
<td>0.152</td>
<td>2.31</td>
</tr>
<tr>
<td>9</td>
<td>0.106</td>
<td>1.44</td>
</tr>
<tr>
<td>10</td>
<td>0.101</td>
<td>1.07</td>
</tr>
<tr>
<td>11</td>
<td>0.096</td>
<td>1.00</td>
</tr>
<tr>
<td>12</td>
<td>0.081</td>
<td>0.89</td>
</tr>
<tr>
<td>13</td>
<td>0.168</td>
<td>2.43</td>
</tr>
<tr>
<td>14</td>
<td>0.184</td>
<td>3.26</td>
</tr>
<tr>
<td>15</td>
<td>0.204</td>
<td>4.09</td>
</tr>
<tr>
<td>16</td>
<td>0.239</td>
<td>5.09</td>
</tr>
</tbody>
</table>

The compressive strength of each tested sample was plotted against its relative density as shown in Figure 4.20. The numbers in the graph represent the samples’ numbers previously presented in the experimental matrix. Gibson and Ashby model (1999) with different values of $\phi$ was also plotted.

![Graph showing compressive strength vs. relative density](image)

Figure 4.20: Compressive strength vs. relative density of the samples along with Gibson and Ashby model

97
The foam glass prepared from the sludge without any additives at different holding times and sintering temperatures matched the curve of $\phi=0.85$ expect for sample#3. The deviation of this sample can be attributed to the coalescence phenomenon that occurred as the sintering temperature increased to 800 °C as previously illustrated.

The addition of SiC resulted in decreasing the foam density associated with a decrease in the compressive strength. Thus, the samples with different wt.% of SiC were grouped together in the lower left corner of the graph between $\phi=0.85$ and 0.90. This is quite close to the results of the foam glass produced from soda-lime glass with SiC as foaming agent by Bernardo et al (2007a) in terms of the obtained values of $\phi$, compressive strength and relative density as previously presented in Figure 2.12.

The addition of granite powder resulted in a gradual increase in the foam density associated with a gradual increase in the compressive strength. Also a gradual decrease in the value of $\phi$ from 0.85 to 0.75 was evident which indicates that more fraction of the solid became contained in the faces of the cells.

### 4.8 Leaching Test Results

The results of the leaching tests for the sludge powder are presented in Table 4.19 which shows an average values of 9.44 and 7.532 mg/l for pH and Pb concentration, respectively.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>pH</th>
<th>Pb concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9.2</td>
<td>6.715</td>
</tr>
<tr>
<td>II</td>
<td>9.80</td>
<td>8.483</td>
</tr>
<tr>
<td>III</td>
<td>9.31</td>
<td>7.397</td>
</tr>
<tr>
<td>Average</td>
<td>9.44</td>
<td>7.532</td>
</tr>
</tbody>
</table>

Since the average measured lead concentration in the leachate of the sludge is higher than 5 mg/l, this solid waste is considered hazardous based on the US legislations as previously presented in Table 1.9.

The results of leaching tests for the produced foam glass at sintering temperature of 750 °C and holding time of 30 min (sample#2) are shown in Table 4.20. The results show that the average measured values of pH and Pb concentration
are 10.55 and 0.018 mg/l respectively. The results illustrate that the Pb concentration in the leachate of the produced foam glass is very small compared with the maximum allowable concentration of 5 mg/l.

Table 4.20: Measured pH value and Pb concentration of the leachate of foam glass sample#2

<table>
<thead>
<tr>
<th>Test No.</th>
<th>pH</th>
<th>Pb concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
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<td>0.026</td>
</tr>
<tr>
<td>II</td>
<td>10.45</td>
<td>0.010</td>
</tr>
<tr>
<td>III</td>
<td>10.51</td>
<td>0.019</td>
</tr>
<tr>
<td>Average</td>
<td>10.55</td>
<td>0.018</td>
</tr>
</tbody>
</table>

This significant reduction in Pb concentration can be attributed to the reduced surface area of the tested foam glass in comparison with the sludge powder that has an average particle size of about 110 µm. Moreover, the lead in the tested foam glass was encapsulated which significantly reduced the amount of Pb released during the leaching test. This result is in agreement with the leaching test results of the foam glass prepared from CRT glass (65.7% panel + 34.3% Pb-glass) with 5% CaCO3 as foaming agent by Bernardo et al (2005) in which the value of Pb concentration was less than 0.02 mg/l.
CHAPTER 5
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The grinding and polishing sludge resulting from the lead crystal glass industry represents an environmental challenge. The sludge used in this study has an average mean particle size of 111.25 µm and is mainly composed of SiO$_2$ and PbO representing 40.55 wt.% and 35.28 wt.%, respectively. The leaching test of the sludge showed that it is considered as hazardous waste since its leachate contains lead concentration of more than 5 mg/l. Foam glass production from this sludge was proved to be a promising cleaner production technique. Such innovative technique leads to produce foam glass that is completely safe in terms of lead leaching and that does not require special landfills at the end of its life. This was confirmed by the leaching test of the produced foam glass which showed a negligible lead concentration of less than 0.02 mg/l. Moreover, the open-recycling system presented in this research is an environmental sustainable alternative to directing the sludge to landfills in terms of resources conservation. Applying this open-recycling system on an industrial scale will not only result in eliminating the costs associated with sludge landfilling in hazardous landfills, but also it will provide a free raw material to a secondary industry that depends on the sludge of the lead crystal glass plants.

The sintering temperature, holding time as well as SiC and granite powder additives were proved to substantially affect the properties of the produced foam glass. The heating method (i.e. direct insertion or low heating rate) was also proved to have a significant effect. At 800 °C and holding time of 30 minutes, the low heating rate adopted in this study was found to result in higher bulk density of 0.531 g/cm$^3$ associated with higher compressive strength of 1.19 MPa compared to direct insertion which was found to result in bulk density of 0.192 g/cm$^3$ and compressive strength of 0.33 MPa.

The investigated sintering temperature range was from 700 to 800 °C with holding time of 30 min. Increasing the sintering temperature beyond this range
resulted in severe cracks in the produced foam glass. The coalescence phenomenon manifested in higher bulk density and lower compressive strength was observed at 800 °C. Thus, temperatures of 800 °C or higher should be avoided because it results in deterioration of the foam glass properties while increasing the energy consumption. The foam glass produced at 700 °C had a substantial high bulk density of 0.859 g/cm³ compared to commercial foam glass. Increasing the sintering temperature to 750 °C resulted in foam glass with comparable properties to that of the commercial foam glass available in the market. The foam glass produced at 750 °C had bulk density of 0.485 g/cm³, porosity of 84.6%, compressive strength of 2.21 MPa and thermal conductivity of 0.051 W/m. K. The relationship between compressive strength and relative density for both the foam glass prepared at sintering temperature of 700 and 750 °C matched Gibson and Ashby model with \( \phi = 0.85 \) while it shifted to the open-cell foam glass of \( \phi = 1.0 \) at 800 °C because of the coalescence phenomenon.

The effect of holding time was investigated at 10, 20, 30 and 40 min while maintaining the sintering temperature at 750 °C. The change in the properties of the produced foam glass from 10 to 20 min. and from 30 to 40 min was insignificant, while significant change was evident when the holding time was increased from 20 to 30 min. Generally, increasing the holding time led to reduce the bulk density, compressive strength and thermal conductivity. The properties of the produced foam glass at all the holding times were comparable to commercial foam glass, however the bulk density at 10 and 20 min had a relatively higher value of 0.586 and 0.573 g/cm³ respectively. The relationship between compressive strength and relative density for all the investigated holding times matched Gibson and Ashby model with \( \phi = 0.85 \).

The effect of adding 2wt.%, 4wt.%, 6w.% and 8wt.% of SiC while maintaining the sintering temperature at 750 °C and the holding time at 30 min was investigated. As the amount of SiC increased, the bulk density, thermal conductivity and compressive strength decreased. The foam glass prepared with 8wt.% SiC represents the lightest foam glass produced and the one with the lowest thermal conductivity throughout this study (while adopting the low heating rate method). It has a bulk density of 0.256 g/cm³, porosity of 91.9% and thermal conductivity of 0.039 W/m. K. Although the compressive strength of this sample also represents the
lowest compressive strength, but its value of 0.95 MPa is still comparable to the commercial foam glass available in the market. The relationship between compressive strength and relative density of the produced foam glass with different SiC content matched Gibson and Ashby model with $\phi$ in the range of 0.85-0.90.

The effect of adding 2wt.%, 4wt.%, 6w.% and 8wt.% of granite powder while maintaining the sintering temperature at 750 °C and holding time at 30 min was investigated. Granite powder worked as a compressive strength enhancing material. As the content of granite powder increased, the compressive strength substantially increased to reach to the highest value obtained throughout this study at 8wt.% with a value of 5.09 MPa. This value is more than the double of the compressive strength of the foam glass produced at the same sintering temperature and holding time without any additives. On the other hand, adding granite powder led to reduce the foam porosity to 76.1% and significantly increase its bulk density and thermal conductivity to reach to 0.747 g/cm$^3$ and 0.135 W/m·K, respectively. Such values are higher than those of commercial foam glass, however the material can still be considered as insulating material. Using Gibson and Ashby model shows that as the amount of granite powder increased the samples shifted gradually to the closed-cell foam. At 8wt.% the foam glass had $\phi$ value of around 0.75.

It can be concluded that while the foam glass produced by adding SiC is suitable to the applications that need very low thermal conductivity, the foam glass produced by adding granite powder is suitable to the applications where compressive strength is of more importance.

5.2 Recommendations for Future Work

- Study the morphology of the produced foam glass by using Scanning Electron Microscope SEM which can provide in-depth interpretation of the results.
- Make a cost-benefit analysis for applying this innovative cleaner production technique on industrial scale.
- Study other properties of the produced foam glass such flexural strength, water absorption and sound transmission loss.
• Investigate the effect of adding a mixture of SiC and granite powder with different percentages and ratios.
• Study the effect of sintering temperature, holding time and SiC and granite additives in the case of direct insertion.
• Investigate the effect of adding oxidation promoter like MnO₂ with SiC.
• Narrow the intervals of sintering temperatures between 700 and 800 °C when studying its effect on the produced foam glass.
• Investigate the effect of sintering temperature, holding time and SiC and granite additives on the lead leachate of the foam glass.
• Study how to eliminate the large cavities appeared in some samples.
References


### APPENDIX A: SIEVE ANALYSIS OF SLUDGE POWDER

#### Test number I

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<tr>
<th>Sieve Number</th>
<th>Diameter (mm)</th>
<th>Mass of empty sieve (g)</th>
<th>Mass of sieve &amp; powder retained (g)</th>
<th>Powder retained (g)</th>
<th>Percent retained</th>
<th>Percent pass</th>
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**Total weight (g)**: 200

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<th>Powder retained (g)</th>
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<th>Powder retained (g)</th>
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Test number IV

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<th>Powder retained (g)</th>
<th>Percent retained</th>
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Total weight (g) 200