

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

School of Energy Systems

Sustainability science

**UTILIZATION OF COAL COMBUSTION RESIDUES IN GLASS
MANUFACTURING PROCESS**

Lappeenranta, 2016

Professor: Mika Horttanainen

Assistant: Dr. Jouni Havukainen

0458639 Alexey Gavrilov

ABSTRACT

Lappeenranta University of Technology

Faculty of Technology

Sustainable Technology and Business in Environmental Technology

Alexey Gavrilov

Utilization of Coal Combustion Residues in Glass Manufacturing Process

2016

71 pages, 17 figures, 16 tables, 7 equations, 2 appendixes

Examiner: Professor Mika Horttanainen

Second Examiner: Dr. Jouni Havukainen

Keywords:

coal, glass, utilization

The focus of paper is to assess and evaluate new utilisation method of coals combustion residues in glass manufacturing process. Mathematical model of glass manufacturing material balance was used to find favourable proportion of normally used batch materials and coal ash. It was found that possible to substitute up to 20 % of batch with coal ash. On the world glass production scale there is a potential to save 8,4 million tons of silica sand, 6 million tons of dolomite, 3 million tons of clay and 0,2 million tons of lime borate. Furthermore, potential to utilize 2 % of coal combustion products with suggested method.

Acknowledgments

I would like to thank professor Mika Horttanainen for his thoughtful comments, patience, understanding and kindness. His attention to details, support and motivations helped to finish this thesis. He was not only a great supervisor, but also a great example of the teacher and the person.

Also I would like to thank Dr. Jouni Havukainen for his attention and responsiveness.

Finally, I would like to thank my family and wife for continuous encouragement and care.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS	6
1 INTRODUCTION	7
1.1 Background of coal combustion products	7
1.2 Problems in managing of coal combustion products	13
1.3 Importance of minerals in glass manufacturing	15
2 WAYS OF COAL ASH UTILIZATION	16
2.1 Zeolitic material.....	16
2.2 Cement and concrete products	17
2.2.1 Cement	17
2.2.2 Concrete	18
2.3 Fill or cover material	18
2.4 Stabilizator or solidificator	19
2.5 Road utilization.....	20
2.6 Construction material	21
2.7 Penetration obstacle	21
2.8 Alumosilicates microspheres	23
2.9 Magnetic balls.....	24
2.10 Ferrosilicon	24
2.11 Source of metals.....	25
2.12 Modern rates of ash utilization in China.....	25
2.13 Previous utilization of ash in glass manufacturing process	27
3 GLASS MANUFACTURING PROCESS	27
3.1 History of the glass	27
3.2 Glass demand.....	28
3.2.1 Flat Glass	28
3.2.2 Glass containers	29

3.2.3 Glass Fibre.....	29
3.3 The structure of the glass	29
3.4 The composition and properties of glasses	29
3.3 Raw materials used in glass melting	30
3.3 Production.....	34
3.4 Iron in the glass.....	36
4 MARKET ANALYSIS OF GLASS RAW MATERIAL.....	38
4.1 Silica sand	38
4.2 Alumina	40
4.3 Dolomite.....	40
4.4 Calcium borate.....	41
5 MODEL	43
5.1 Description of the model	43
5.2 Algorithm of calculation	44
5.3 Mixing batch with ash.....	51
6 DATA ANALYSIS	56
7 CONCLUSION.....	59
REFERENCES	60
Appendix 1	65
Appendix 2.....	69

LIST OF ABBREVIATIONS

CCP - coal combustion products

WCA - World Coal Association

STM - simple transform manufactures

ELB - elaborate transform manufacturing

FBC – fluidized-bed combustion

FGB – flue gas desulfurization

PFA – pulverized fuel ash

BA – bottom ash

FBA - furnace bottom ash

FGD – fuel gas desulphurization gypsum

ASPM - aluminosilicates microspheres

BMT - billion metric tons

ACAA – American coal ash association

SW - severe weather

AMD - acid mine drainages

1 INTRODUCTION

Coal has currently a very significant impact on the environment as fossil fuel by producing many combustion products. Ash as well, as small amount of unburned solid products, referred as char, are the end product of coal combustion. Coal use in energy production leads to combustion products which have to be managed. Combustion products include also some unburned coal referred as char. Presently, there a lot of practices of ash utilization, but they do not cover all volume of the ash issue.

Coal is the essential fuel representing 30.1% of total energy consumption and 40 % of electricity generation. Coal combustion has several environmental impacts, which depend on the type of incineration technologies. Major of them are land and water use, contaminant pollution, production of waste and health of people. (WCA, 2016)

Observations by Cheng (2013) suggest that coal fly ash has a decent feature for transformation into glass. Moreover, he described the creation of material for lightweight aggregates or elements for engineering purposes using this idea.

It is of interest to discover the possibility how to create a model of glass manufacturing using fly ash. Additionally, it is desirable to calculate influence from this type of utilization on environmental and, likewise, economic efficiency.

Objectives of the thesis are creation of the model for material balance of glass manufacturing process, estimation of environmental and economical impact of new alternative, study of previous approaches to coal combustion products and glass production. Likewise, complications of glass manufacturing process will be shown. Finally, new problems which addition of fly ash brings will be examined.

1.1 BACKGROUND OF COAL COMBUSTION PRODUCTS

Before studying the problems of coal combustion products there is a very important question “What is a coal?”.

All plants absorb solar energy and release it during a decay process, but under proper conditions decay process stops and those energy stays in a coal. On our planet coal formation period was roughly 330 million years ago. Due to tectonic movements plants were buried under the surface of the earth and high temperatures and pressure were

applied to them. Subsequently, plants were transformed into peat and then into coal, since physical and chemical properties have changed. (WCA, 2016)

Coalification process is a noteworthy process, which transform peat into anthracite. Moreover, coalification reflects a physical and chemical properties of resulted coal. If more plant material was transformed into carbon, then rank of coal is higher. Major factors of coal quality are vegetation, submerged length, temperature and pressure and period of occurrences. (WCA, 2016)

There are two major types of coal: low rank coals (47% of world reserves) and hard coal (53% of world reserves). At the first place peat is converted into lignite (17% of world reserves). Lignite has low carbon content, high moisture content and mostly brown color (sometimes dark black). Those properties make lignite less desirable coal type and useful mainly only for power generation. Millions years of physical and chemical influence transform lignite into “sub-bituminous” coal (30% of world reserves). Organic content of those coal type is significantly higher and that makes it useful for power generation, cement manufacture and industry. Subsequent transformations lead to creation of “bituminous” coal (52% of world reserves) and finally most desirable and precious type of coal is anthracite (1% of world reserves). “Bituminous” coal is subdivided into thermal “steal coal” for power generation, cement manufacture and industrial use and metallurgical “cocking coal” for manufacture of iron and steel. Finally, anthracite is used as local/industrial including smokeless fuel. Those hierarchy of coals is shown in the Figure 1. (WCA, 2016)

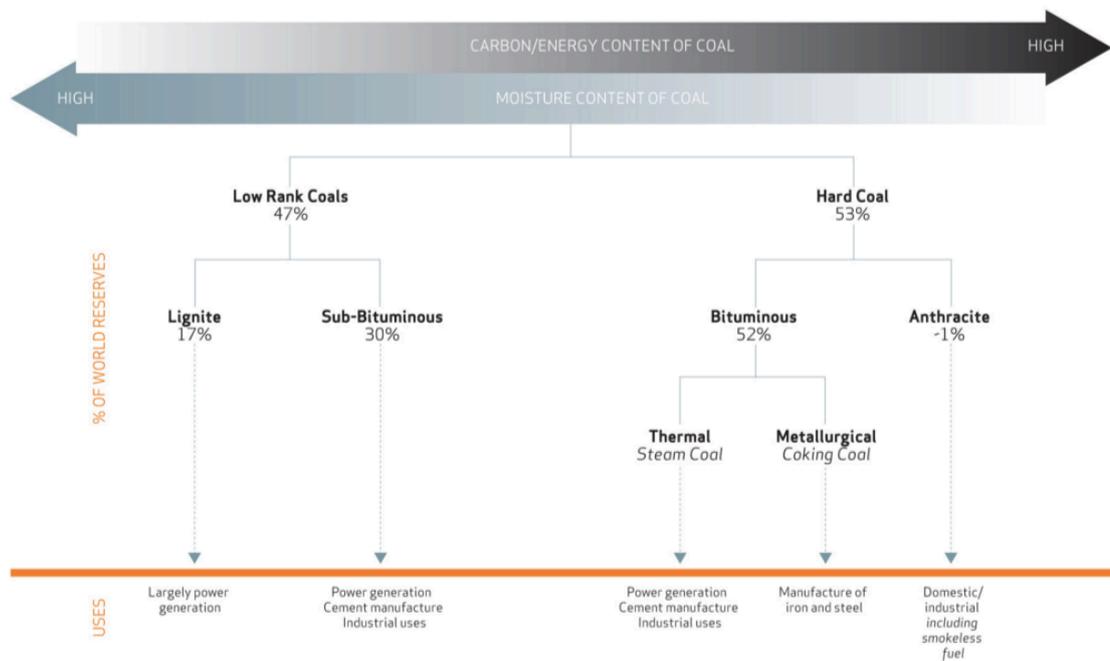


Figure 1. Types of coal

Source: WCA, 2016

Coal consists of organic and mineral substances. A carbon-rich organic component is the carrier of useful properties. However, the mineral components only degrade the quality of coal as fuel. The more minerals there are in coal, so less organic material and, consequently, the lower the calorific value is. If the ash content, is the mass of the mineral residue after the combustion of coal, expressed by a percentage of burnt mass, is more than a certain limit, the coal becomes "useless fossil" unfit for industrial use. The limit for ash content varies according to the use of coal and the ash content also varies between coalfields. For energy, this is usually no more than 40-45%. (Kiselstein. 2002)

Some mineral components of lower the quality coal, even with allowable ash content. There are a lot of examples. Contained in coals, the mineral pyrite (FeS_2), decomposing at high temperatures, forms a gaseous oxide of sulfur, which when interacting with water vapor occurs sulphurous acid, which destroys equipment of thermal power plants. The portion of the sulfur oxides, from flue gases emitted into the atmosphere, becoming one of the most serious pollutants of the natural environment. Calcium carbonates affect the melting point of the ash and slag that has to be considered when designing boilers. (Kiselstein. 2002)

The combustion of the coal mineral components is converted into ash and slag, which had been stockpiled as a waste product of energy production in the ash ponds.

Fabricated mountains of mineral material from the standpoint of ecology is very alarming. Despite the usual measures taken, with all the ensuing consequences for the population and the natural environment. Infiltrating through them of an atmospheric precipitation and industrial water dissolved mineral compounds, polluting the groundwater. (Kiselstein. 2002)

The process of coal combustion in thermal power plants occur at high temperatures from 1500 to 1800°C, depending on coal quality and combustion method. At these temperatures, the mineral components of coals disintegrate or melt. The ash and slag is composed of quartz grains and clay minerals, particles of vitreous material similar to volcanic glass, the particles of newly formed minerals mullite ($3\text{Al}_2\text{O}_3\text{-SiO}_2$), magnetite, ferrosilicon and others are present, and particles of unburned coal, especially a lot when burning anthracite. (Kiselstein, Oaks, Szpirglas. 1993)

Ash is a fine-grained material. About a third of the grains has a particle size of 1 to 5 mm, the rest is a few tenths of a millimetre, including about 20% with size of hundredths millimetre. A significant portion of the grains has the form of bubbles, which are formed during the cooling of the melt drops in suspension in the flue gas. The Characteristics of different ash vary at different thermal power plants, since they depend on characteristics of the mineral components of coal, method of preparation of fuel for burning, incineration technology, flue gas cleaning system ashes and the method of transportation of ash in ash dumps. (Panteleev, Larina, Melentiev. 1986)

Extracting of fossil fuels, producing energy from them and landfilling the combustion residues causes a significant impact on environment. For this reason, waste-free technologies are very important and necessary to prevent destruction of our ecosystem.

Burning of coal produces considerable amount of combustion products, which appear as amorphous inorganic oxides after thermal transformation so called inert material - ash plus small amount of solid products of incomplete combustion called char.

According to Heidrich, Feuerborn and Weir (2013) in 2010, the production of coal combustion products was around 780 Million metric tonnes (Mt) globally, as shown in Table 1.

Moreover, Japan and Europe have the highest utilization rates of coal combustion products: 96,4 % and 90,9 % accordingly. The biggest CCPs utilization per person is in Australia 0,27 Mt/person and China 0,20 Mt/person. The highest production rate of CCPs per person is in Australia 0,60 Mt/person and China 0,29 Mt/person.

Table 1. Estimated Annual Production, Utilization Rates by Country 2010

Source: Heidrich, Feuerborn and Weir, 2013

Country/Region	CCPs Production (Mt)	CCPs Utilization (Mt)	Utilization Rate %	CCPs Production/person (Mt)	CCPs Utilization/person (Mt)
China	395,0	265,0	67,1	0,29	0,20
Unites States of America	118,0	49,7	42.1	0,37	0,16
India	105,0	14,5	13,8	0,09	0,01
Europe (EU15)	52,6	47,8	90.9	0,11	0,10
Middle East & Africa	32,2	3,4	10,6	0,02	0,01
Russian Federation	26,6	5,0	18,8	0,19	0,04
Japan	11,1	10,7	96,4	0,09	0,08
Australia	13,1	6,0	45,8	0,60	0,27
Canada	6,8	2,3	33,8	0,20	0,07
Total	777,1	415,5	53,5		

Coal is currently the most widespread fossil fuel. According to World Coal Association there are 1052 billions tonnes of coal reserves in different countries and this amount will be sufficient for 134 years with the remain usage. Coal is the essential fuel representing 30.1% of total energy consumption and 40 % of electricity generation. Total global production of coal is 7823 Mt annually and the main producers are China 45,5 %, USA 11,5 % and India 7,8 %. (WCA, 2013)

According to World Wide Coal Combustion Product (CCP) Network the most coal burning countries in 2013 were China (395 Mt/a), U.S.A (118 Mt/a) and India (105 Mt/a).

To make terminology of coal combustion products more clear it was suggested by World Wide Coal Combustion Products Network (WWCCPN) Associations across the globe to create 'draft' definitions, which are provided in the following Table 2. (Heidrich, Feuerborn and Weir, 2013)

Table 2. Draft global definitions for coal combustion products

Source: Heidrich, Feuerborn and Weir, 2013

Term	Definition
Coal Combustion Products	Coal combustion products (CCPs) include fly ash, bottom ash, boiler slag, fluidized-bed combustion (FBC) ash, or flue gas desulfurization (FGD) material produced primarily from the combustion of coal or the cleaning of the stack gases. The term coal ash is used interchangeable for the different ash types..
Fly ash	The finer ash produced in a coal-fired power station, which is collected using electro-static precipitators. Sometimes spelt as 'fly ash'. This is also known as Pulverized Fuel Ash (PFA) in some countries. About 85+% of the ash produced is fly ash.
Bottom ash	The coarse ash that falls to the bottom of a furnace. The molten ash adheres to the boiler tubes, eventually falling to the base of the furnace. In many furnaces there is a water system that rapidly cools this ash, so-called 'wet bottomed' ash. Usually <15% of the ash produced is bottom ash (BA), in some countries also known as furnace bottom ash (FBA)
Cenospheres	Hollow ash particles that form in the furnace gas stream. Sometime these particles will contain smaller ash spheres. They float on water and are usually collected from lagoons, where ash/water disposal systems are being used. Only 1 to 2% of the ash produced are cenospheres and with the reduction in ash/water transportation, fewer are collected/available
Conditioned ash	Where fly ash is mixed with a proportion of water (10 to 20% by dry mass typically) in order that it can be transported in normal tipping vehicles without problems with dust for sale or disposal or interim stockpile.
Flue Gas De-Sulfurisation	Where a source of Calcium is injected into the furnace gas stream to remove sulfur compounds. In wet systems a slurry with ground limestone is sprayed in gas stream. After decomposition of the limestone the sulfur reacts with lime and after oxidization forms calcium sulfate. This flue gas desulphurization gypsum (FGD) is used in the gypsum industry as replacement for natural gypsum.

1.2 PROBLEMS IN MANAGING OF COAL COMBUSTION PRODUCTS

There are several ways to treat CCP: Non-Beneficial, Simple transform manufactures (STM) and Elaborate transform manufacturing (ELB). (Weir, 2011). The major differences between them are value of end products and difficulty of procession. They are shown in the Figure 1.

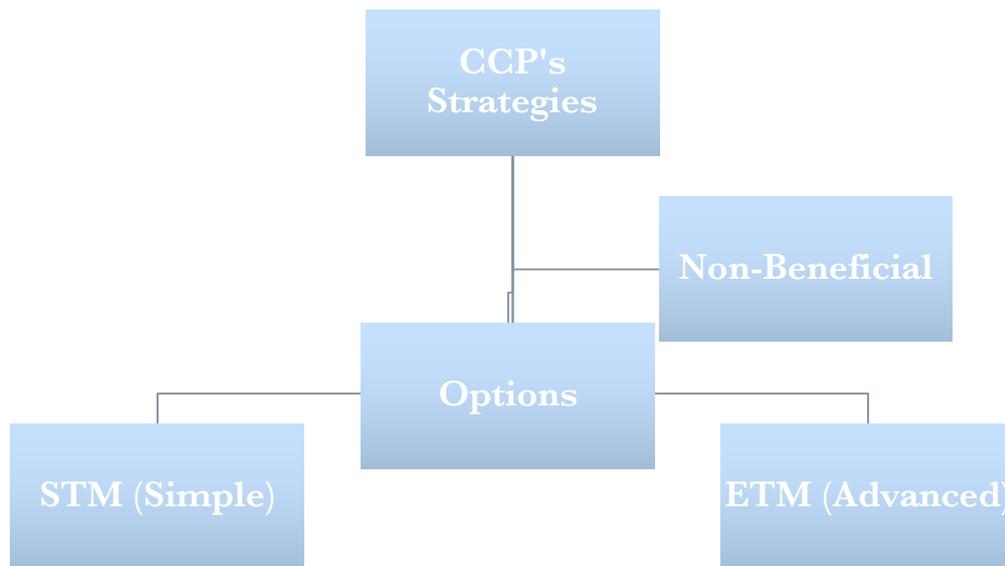


Figure 2. Coal combustion products utilization STM vs. ETM strategies (Heidrich, 2005)

One of ELB's types is producing glass melts by mixing batch (sand, clay, lime borate and dolomite) with fly ash. Glass mostly consists of Silica (SiO_2) - basic raw material (sand) with vitrifying function. Calcium (Ca) provides stability to the glass against attacks of atmospheric agents. Magnesium (MgO) ensures the resistance to the glass in order to it support abrupt changes of temperatures, as well as increases the mechanical resistance. Alumina (Al_2O_3) increase the mechanical resistance, and Potassium oxide (K_2O). Components can vary considering future purpose of glass. (Chemical Composition, 2015).

Fly ash also has various components because of source of mining and type of coal (bituminous, sub-bituminous and lignite) (Barnes, 2010; Heidrich, Ward, & Grubba, 2007).

The information about ash composition is divided by 3 categories. There are bituminous, sub-bituminous and lignite coal types. Also, approximate content of most significant chemical elements and loss on ignition are presented. Wide variation of

percentages is also mention and shown in Table 3. (Heidrich, Feuerborn and Weir, 2013)

Table 3. Composition of ash (Heidrich, Feuerborn and Weir, 2013)

Element	Bituminous	Sub-bituminous	Lignite
SiO	20-60	40-60	15-45
AlO	5-35	20-30	10-25
FeO	10-40	4-10	4-15
CaO	1-12	5-30	15-40
MgO	0-5	1-6	3-10
SO	0-5	0-2	0-15
NaO	0-4	0-2	0-6
KO	0-15	0-3	0-5
LOI	0-15	0-3	0-5

There are a lot of obvious benefits from using fly ash instead of storing. The cost of landfilling becomes higher by cause of taxes, which government introduces to make waste disposal less economically viable, and an enormous amount of space is also needed. Land can always be used more effectively than just for disposal of waste. Due to rains some elements (Hg-mercury) can leach to the groundwater as well, but ash ponds, lined with layer of clay, prevent elements from entering groundwater. After all, all elements should remain in the landfill forever. This danger can be reduced by increasing the amount of utilized ash. (Kentucky Ash Education Site, 2015)

1.3 IMPORTANCE OF MINERALS IN GLASS MANUFACTURING

On the natural extraction stage of glass's life cycle minerals such as sand, clay, lime borate and dolomite are mined. All of this removals from the earth causes harm to our ecosystem. However, replacing some of this materials with fly ash will mitigate the need for them.

Sand is presently a vital and rather expensive material compared to other batch compounds expensive material. Additionally, not all types of sand are suitable for construction and manufacturing. Some countries even ban export of sand (China, Indonesia, Malaysia) (The Economist, 2009). People use more than 40 billion tons of sand and total industry of sand is 70 billion dollars globally (Beiser, 2015).

Moreover, during the sand excavation a lot of side materials are extracted too. According to Virgilio Panapanaan's (2015) lectures from basic course on environmental management and economics ecological rucksack is an amount of environmental resources (kg) (MI), that are needed in the production of the product – (minus) weight of the product. In addition, all the material flows taken from the nature that are used, but are not included in the product, are taken into account (mining wastes or used fuel). The lighter the rucksack, the fewer environmental resources have been consumed.

Ecological rucksack components are divided into five categories:

- Abiotic raw materials, like minerals and fossil fuels;
- Biotic raw materials, like farmed animals and plants as well as wild animals and fishes; Soil movements from agriculture and forestry;
- Water when it used in the processes (irrigation);
- Air when it is used actively (e.g. chemical synthesis);

Information on these categories are collected and saved separately. As it shown in Table 4 ecological rucksack of sand is 1:0.86, where 0.86 stand for a rucksack factor and 1 stand for a rucksack value. To put it simply, to produce 1 kilogram of sand 0.86 kilogram of natural resources are used during the process. (Charles j. Kibert. 2002). Also there is another mathematical explanation of ecological rucksack definition.

$$ER = MI - W_{(product)} \quad (1)$$

$$MI = SUM(Mi * Ri) \quad (2)$$

“W” is the weight of the product, “Mi” is the weight of the material in kilograms, “Ri” is the rucksack factor. Rucksack factor is a quantity in kilograms of material moved from nature to create 1 kilogram of resource.

Table 4. Ecological Rucksack of selected materials
Source: Policy instruments for a sustainable built environment 2002

Material	Ecological Rucksack
Oil	1:0,1
Sand	1:0,86
Natural Stone	1:1,2
Coal	1:5
Gold	1:350 000

Therefore, it is hard to underestimate the value of that mineral. If it will be possible to decrease sand consumption, we will be able to make our planet more sustainable.

2 WAYS OF COAL ASH UTILIZATION

Fortunately, there have been a lot of studies towards ash utilization due to high importance of that problem. It will show variety of methods and prove uniqueness of new utilization method, which proposed in that paper.

2.1 ZEOLITIC MATERIAL

Production of zeolitic material grounded on the metakaolin-type compound existing in the fly ash was proposed by University of Antioquia in 1989. Zeilitic material could be produced from reaction of metakaolin or similar compounds with sodium hydroxide. The zeolitic material produced has decent adsorption characteristics (70-80% of ability to absorb), almost the same as commercial zeolite 13X, consequently it is possible to use it as an adsorbent of heavy metals from industrial wastewater, as a catalyst in selective catalytic reduction of NO-emissions in air pollution control of the flue gases or

as a support to make diverse types of catalysts. For their studies scientists used fly ash from Amaga coal (Colombia). Kaoline is a major compound of mineral material in the coal. Method contains treatment of ash with sodium hydroxide (NaOH) at diverse volumes and numerous attempts and temperatures of crystallization. Kaolinite in the coal combustion ash mineral substance is converted into zeolitic material. In the issue with Amaga coal a faujasite type material can be also produced. Content of a faujasite type material is 50-75%. There is an amorphous part contained in the fly ash, which is converted into crystalline outcome: zeolite X and zeoplite P (hydroxysodalite) could additionally be produced. Reaction conditions could be change to achieve higher selectivity of the synthesis. (Fanor Mondragon, Fabio Rincon, Ligia Sierra and others. 1989).

2.2 CEMENT AND CONCRETE PRODUCTS

Next application of ash will be an additive to cement and concrete products, which considered as supreme method of utilization with devastating amount of information accessible. In 1996, 49% of all reused ash were on the account of that application in the U.S.A. (ACAA. 1996). Comprehensive examination has been conducted on that type of utilization and the characteristics that it has. Usage of fly ash as a part of Portland cement has several advantages on the subsequent concrete. Those advantages will be presented underneath. (Barry E Scheetz and Russell Earle. 1998).

Ash materials serve as a replacement of sand used as aggregate of concrete and mortar. At sufficiently high lime content, that can be used instead of cement. (Kiselstein. 2002)

2.2.1 CEMENT

Specific density of cement is increased due to smaller fly ash particles compared to previous compounds, which consequently decrease capture of air into a concrete. Reduced air capture in a concrete has a negative influence on the original freeze-thaw durability. (Xu A. 1977)

Project cost is reduced due to lower necessity of Portland cement compounds. (Halstead WJ. 1986)

Calcium hydroxide ($\text{Ca}(\text{OH})_2$) become stable by reacting with fly ash and consequently resistance of cement to corrosion and entrance of corrosive fluids is increased. The

reaction produces calcium silicate hydrate (Ca-Si-H). The initial calcium hydroxide (Ca(OH)_2) was dissolvable, while the calcium silicate hydrate (Ca-Si-H) is fewer dissolvable in the fly ash material, thus decreasing the probability of calcium hydroxide (Ca(OH)_2) to escape from the concrete. (Halstead WJ. 1986)

The liquid request of the cement will be mostly decreased by usage of the fly ash as a part in Portland cement. Normally 150-250 L/m³ of water (15-25% of whole mixture) are required for Portland cement. Because of the oiling abilities of the fly ash water content could be lowered and consequently drying period of concrete decreasing and more required situation is made. Moreover, usefulness of the cement enhanced as well. Normally 15-20 L/m³ of water request is decreased by adding of the fly ash to the Portland cement. (Owens PL. 1976)

2.2.2 CONCRETE

Proper quantities of added fly ash will eventually outcome in an increased strength of Portland concrete. Otherwise, if enlarged time of strength development is not taken into account project postponement might happen. Moreover, outcome characteristics of concrete may vary due to different content and consistency of the used fly ash. (Halstead WJ. 1986)

Moreover, fewer dissolvability of calcium silicate hydrate (Ca-Si-H) results in reduced penetrability of the concrete by filling of capillary voids with reaction products. (Halstead WJ. 1986)

The slag porous aggregates are calcined at temperatures of 1050-1250°C, at which the slag granules swell. Porous fillers are necessary components in the production of light concrete (with lower density), and are used for heat and sound insulation. (Kiselstein. 2002)

2.3 FILL OR COVER MATERIAL

Second by popularity method of fly ash utilization is use as structural fill or cover material. Such way of utilizations seems to be a very logical solution for fly ash disposal and reuse. In the U.S.A, 2.5 million tons or approximately 15 % of entire fly ash utilization were on the account of the studied method in 1996. (ACAA. 1996). The fly ash could be used as a filling substance for walls, bridge supports or retaining

constructions. (Meyers JJ, Pichumani R, Kapples BS. 1976). Moreover, ash could be used to fill forsaken rock mines or as an isolation material for solid waste landfills. Crucial fly ash characteristics to be used as cover or fill material are density, tightening ability, squeeze force and penetrability. (Lamb DW. 1973). The small size of the fly ash particle is a very important characteristic of the fly ash due to several advantages: faster physical strengthening, more compactly compressed bulk, more chemically responsive (due to enlarged space for reaction to happen). Supporting machinery to achieve strengthening and solidity are pulsated, air-tired or steel wheeled drums. (Meyers JJ, Pichumani R, Kapples BS. 1976). If the capable of lifting of ground to be enclosed is small, the density of the fly ash is very significant. The density of normal soil is 1600-2000 Kg/m³ while the density of fly ash is 1100-1500 Kg/m³. That makes fly ash lighter compared to soil. The lesser density is explained by the attendance of aluminosilicates microspheres (ASMP) in the portion of fly ash. Excessive settlement and avalanche are fended off as a result of lighter weight put on as a cover material. Penetrability of fly ash is significant in the case when segregation abilities of fly ash are used. For example, at landfills, where infiltration of contamination leakages into the ground is unacceptable. Penetrability value of 10⁽⁻⁶⁾ cm/sec could be achieved with the addition of calcium oxide (CaO) to a fly ash mix, which brings improved attachment of the internal elements. Moreover, addition of well-atomized fly ash fulfills more hollow spaces, which creates more solid masses of ash mix and consequently decrease leakages tracks. (Gehring D. 1990)

2.4 STABILIZATOR OR SOLIDIFICATOR

According to American Coal Ash Association roughly 1.7 million tons of the fly ash were recycled as stabilizator and solidificator of dangerous waste in 1996 in the U.S.A. (ACAA. 1996). Stabilization is reached by covering the thrash with layers of ash, while solidification is achieved by drying the liquid waste into the solid. Advantages of such method are described in the Table 5 below. (Barry E Scheetz and Russell Earle. 1998)

Table 5. Advantages of solidification and stabilization

Source: Barry E Scheetz and Russell Earle. 1998

Stabilization	Solidification
Decrease the dissolvability and flexibility of dangerous chemicals by closing them in a impervious layer.	Creates a robust, tough solid construction trash mass.
Amphoteric metals leak fewer as a result of alters pH level of waste .	Hydration characteristics alike to properties of Portland concrete.
Penetrability of the trash is decreased due to adjusted pH level.	Makes transportation and treatment of liquid wastes (sludge) easier by improving durability of waste.

2.5 ROAD UTILIZATION

Next application of fly ash will be utilization as asphalt in the building of roads and related constructions. The fly ash was used in mound ground balancing, the main lower layer of coating, as a bulk filler, the bitumen supplement for road asphalt and as inorganic filler for bituminous cement. In the U.S.A. in 1996, approximately 900 thousand tons or 5.5% of the whole fly ash production were utilized in those methods. (ACAA. 1996). As a ground balancer the fly ash has several advantages. In areas, where road materials are limited, fly ash could be supplied from the nearest coal-fired plant. Convenient transportation and sufficient characteristics have made the fly ash as ground balancer a very economically viable option. Transversal strength is a vital ability for ground balancer fly ash recycle and it usually matches or surpasses the strength of soils normally applied for mounds. (Twin Cities Testing and Engineering Laboratory. 1970). (Lin YK. 1971). Those characteristics are the result of self-hardening abilities of fly ash more appropriate for ashes from fluidized-bed combustion (FBC) plants. The ground balancing with the fly ash may brings unpleasant outcomes due to chill vulnerability of the fly ash. In the icy climate and unprotected to the cold environment, the fly ash has to be steadied with a lime blend to chemically fasten the whole mix. Another option could be to place the fly ash underneath the domestic depth of freezing. (Meyers JJ, Pichumani R, Kapples BS. 1976).

2.6 CONSTRUCTION MATERIAL

Subsequent type of the fly ash reuse as a component in the production of lightweight building goods seems to be a very viable method with a noteworthy amount of advantages. Typically use of the fly ash decrease expenditures of producer on transportation charges of outcome item delivery, in contrast with heavy item, while heaviness is an issue. It is noteworthy even more when blocks are transported. Fly ash brick compares to clay-fired one weight 30% less, allowing to deliver more blocks per cargo, consequently decreasing transportation expenditures and enhancing incomes.

Moreover, there are plenty of cheap accessible fly ash for purchase, simultaneously block's qualities are remaining the same or even higher. (Reidelbach JA. 1970)

University of West Virginia manufactured blocks made of 74% fly ash, 23% slag and 3% Na_2SiO_3 during an examination. Chemical structure of outcome blocks was comparable to clay-fired blocks. Moreover, during the ASTM C 216 Standard for SW (severe weather) test fly ash blocks surpassed or match each criteria. (Reidelbach JA. 1970).

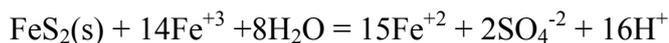
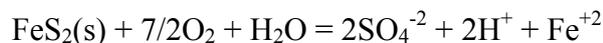
Moreover, the fly ash could be also recycled during a production of lightweight tiling goods into firm covering tiles. Resulted tiles have low weight compared to the clay ones and simultaneously offering a highest fireproof level and that makes them a brilliant substitution for cedar thatch in zones with extreme inflame ability. (Barry E Scheetz and Russell Earle. 1998)

In the United States of America this method is not widely used and responsible only for 0.5% recycled fly ash in 1996. (ACAA. 1996). But there is a tremendous potential since recycle rates in this zone are low.

2.7 PENETRATION OBSTACLE

The last application of the fly ash utilization to mention is penetration obstacle and charging of old empty mines. There are two ways how fly ash will reduce consequences of acid mine drainages (AMD): deactivating of AMD and avoiding reaction among liquid and mineral pyrite (FeS_2). AMD happens in zones where coal was excavated and some pyrite minerals are left. Pyrite material is in reaction with liquid and air. The

natural dumps accommodate pyrite mineral that reacts with germs, air and water. AMD is an outcome of following reactions. (Kimmel W. 1983)



In the first reaction pyrite (FeS_2) reacts with oxygen (O_2) and water (H_2O) into sulphuric acid ions (SO_4) with chemical valence “- 2”, hydrogen (H) and iron (Fe) with chemical valence “2”. In the second reaction iron (Fe) with chemical valence “2” reacts with hydrogen (H_2), oxygen (O_2) and microorganism called “Thiobacillus” to oxidize and transform into Fe with chemical valence “3” and water (H_2O). Acid mine drainage (AMD) happens after two last chemical reactions, where iron (Fe) with chemical valence “3” is decreased by pyrite(FeS_2) mineral and even more iron (Fe) with chemical valence “2” is created. (Barry E Scheetz and Russell Earle. 1998)

There a lot of motives to treat excavations abysses. First motive is where the groundwater crosses the excavation residues AMD should be controlled. Second is the fly ash mixture offers backing to zones, where mine columns are destroying, which begin a soil dropping on the earth. Last motive is fly ash mixture in mine to prevent ignition. (Barry E Scheetz and Russell Earle. 1998)

As a conclusion for that method of utilization let’s examine the real-life experience of mine filling with fly ash mixture in Las Vegas, Nevada. During a construction of the new road, roughly 770 meter of 1.5-meter width buried water duct was forsaken. (Gehring D. 1988). That duct had to be demolished due to the risk of failure with an intensive traffic of fresh road. Injection of fly ash mixture was considered as less money-loosing option. The blend of fly ash, sand, water and pebble was injected into the duct with approximate 180 meters breaks. Favourable fly ash: concrete proportion 2.2:1.0 thus significantly decreased the expenditures of the work due to use of the fly ash more than concrete. Moreover, such proportion made it easier to extract the mixture to the duct. Overall, similar utilization methods are great in terms of money saving due to lesser quantity of concrete used during the process plus problem of the fly ash utilization is solved as well. (Barry E Scheetz and Russell Earle. 1998)

2.8 ALUMOSILICATES MICROSPHERES

The most original and perhaps the most valuable components of ash is hollow aluminosilicates microspheres (ASPM). They are hollow, almost perfect form silicate beads with a smooth surface, with diameters from 10 to several hundred micrometers, with an average of about 100 microns. Wall thickness from 2 to 10 μm , the melting temperature of 1400-1500°C, the density of 580— 690 kg/m³. (Kiselstein. 2002)

The formation of microspheres is as follows. At high temperatures silicate mineral material coal and melted in a gas stream of products of combustion is crushed into very fine drops. Gas inclusions in the mineral particles expand when heated and inflate individual drops of the melt. Those drops, in which the internal gas pressure is balanced by surface tension forces to form hollow beads. In other drops, there is a gap (internal pressure greater than surface tension forces), or they are just silicate beads, solid or porous (surface tension greater than the internal pressure). The ASPM content in ash and slag materials is typically a few tenths of a percent, however, their production on large thermal power plants in Russia may reach several thousand tons per year.

The value of ASPM is determined by the fact that they are perfect fillers. To make many plastic products and ceramics required properties, for example to reduce the density (weight) of the products, improving the thermal, electrical and sound insulating properties, in their composition are introduced manufactured by industrial methods of glass microspheres. This is a complex process. So why not to use ready-made microspheres — MOA of ash from coal-fired power stations? It is estimated that the cost of such microspheres in ten and more times lower than that of the microspheres obtained by industrial methods. (Kiselstein. 2002)

Polymeric materials with microspheres (so-called spheroplastic) are used in the manufacture of a variety of watercraft (boats, signal buoys, blocks of buoyancy, life jackets, etc.), furniture, radio transparent heat-insulating screens for electronic equipment, insulation of heating mains, road-marking thermoplastics, etc. ASPM successfully applied in the cement composition in the manufacture of light concretes and heat-insulating refractory concretes. This is not a complete list of features of application of ASPM. (Kiselstein. 2002)

It is important to note that unlike the other components of the hollow microspheres is comparatively easy to stand out from the ash. Due to their low density, they float to the surface water hydraulic structures (ponds, canals recycled water) and can be collected by any means, including by the simplest means. (Kiselstein. 2002)

ASPM are in great demand. However, ready to acquire their firms require a high degree of purification from material impurities. In addition, many technologies are only used microspheres of a particular size (diameter). All this requires appropriate industrial base. The high cost of prepared similarly ASPM in the world markets of mineral raw materials ensures the economic efficiency of enterprises according to their "production". (Kiselstein. 2002)

2.9 MAGNETIC BALLS

Iron in coal is contained mainly in the composition of the minerals pyrite (FeS_2) and siderite (FeCO_3). A significant amount is in the form of iron compounds. The combustion of coal occurs thermochemical conversion of all these compounds in the mineral magnetite (Fe_3O_4). While in the melted, floured and suspended in a stream of flue gas condition, the magnetite drops take the form of balls. The magnetite balls sizes range from 20 to 100 μm . They are magnetic (magnetite — ferromagnet). Their content in the ash from 3 to 16%, and yearly "production", approximate calculations, for power plants of the Russian Federation in the tens of thousands of tons. On the technology of extracting magnetite microspheres from fly ash of coal power plants granted patents. Possible areas of use magnetite microspheres is so-called heavy-mineral processing, production of dyes, filler "heavy" concrete, capable of screening electromagnetic radiation, powder metallurgy, natural alloy of iron ore concentrates. (Panteleev, Larina, Melentiev. 1986)

2.10 FERROSILICON

With the deficiency of air and the presence of unburned coal particles in the molten slag is formed ferrosilicon — an alloy of iron with silicon. The ratio between Fe and Si is variable, and therefore the chemical formula of the compound is usually written Fe_nSi_m . Pellets of molten ferrosilicon have a rounded irregular shape; the size — from a few to tens of millimeters. In supervision, the ratio of iron and silicon ferrosilicon density ranges from 5,500 to 7,000 kg/m^3 (two times higher than that of magnetite).

This is a strong ferromagnet. The production of ferrosilicon in the composition of ash materials, for example, at Novocherkasskaya GRES is more than 2000 t/year.

(Yudovich, Katniss. 1985)

Ferrosilicon is used in the smelting of iron and steel. It's specially produced for these purposes, however, the process (electro thermal smelting of iron and silicon) is very energy intensive. Therefore, technology to replace industrial ferrosilicon is extracted from ash-and-slag materials was developed. Ferrosilicon has a very high corrosion resistance in environment of acid and alkali, therefore, used in the manufacture of parts of equipment operating in aggressive environments. With its high density, ferrosilicon and magnetite, can be used in mineral processing, in the "heavy" concrete, protecting from electromagnetic and radioactive radiation, as well as in powder metallurgy.

(Kiselstein. 2002)

2.11 SOURCE OF METALS

Ash and slag can be a valuable source of metals. The metals in coal are composed of various minerals and organometallic compounds. The combustion of coal, much of it flows to ash. Developed technology for extraction of ash and slag materials of aluminum oxide as raw materials for subsequent production of metallic aluminum.

From the ashes of coals in industrial scale are extracted germanium and uranium. It is considered promising for the extraction of gallium, lead, zinc, molybdenum, selenium, gold, silver, rhenium, rare earths. (Kiselstein, Oaks, Szpirglas. 1993)

2.12 MODERN RATES OF ASH UTILIZATION IN CHINA

According to Harris D. (2014) Uneven development of the China creates imbalance in fly ash utilization. In the developed regions (Yangtze, Pearl River Delta and Bohai Rim) fly ash utilization could be 100%, while in the western parts those numbers are lesser, even lower than 30%. Currently fly ash in China used as:

- Construction material, for example, bricks, expanded-clay, ash cement or concrete.
- Road construction, for example, body of road cover material or concrete mixture.
- Building plans, for example, concrete mixture.

- Agricultural, for example, fertilized or soil enricher.
- Fill material for mines
- Extraction of precious metals

Share of those methods is presented in the Chart 1.

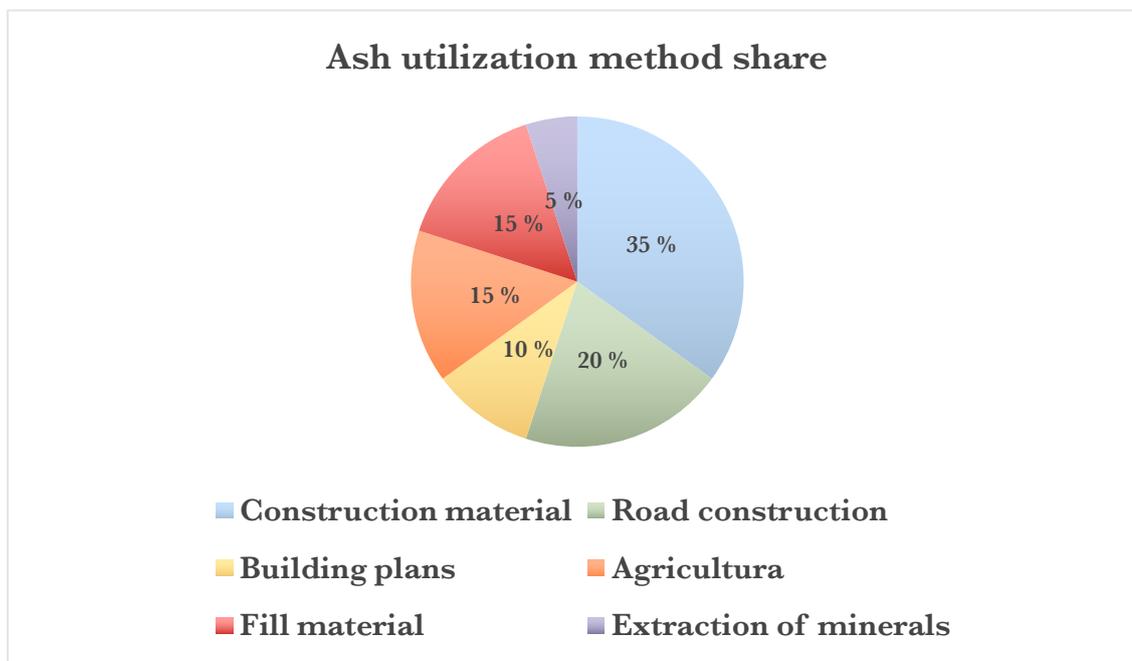


Chart 1. Ash utilization methods share in China.

Source: Harris D. 2014.

To make it clear further fly ash production and utilization statistics in China is presented in Table 6. It could be mentioned that utilization ratio of fly ash is slightly increasing, however, production rate is faster compared to utilization rate.

Table 6. Statistics on fly ash production and utilization

Source: Harris D. 2014.

Year	Fly ash production (million tons)	Fly ash utilization (million tons)	Ratio
2006	352	232	66
2007	388	260	67
2008	395	265	67
2009	405	271	67
2010	417	280	67

2011	428	287	67
2012	440	294	67

2.13 PREVIOUS UTILIZATION OF ASH IN GLASS MANUFACTURING PROCESS

It is possible to produce glass-ceramic products by using melt technology and a heat treatment process. Fly ash has a great feature for transformation into a glass. Creation of one of the melilite group minerals - gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) occur at temperatures beyond 700 C due to crystallization of fly ash. Hexagonal shape construction glass-ceramics form with hole scopes around 20-80 mm. Mechanical and physical properties are optimal if incinerator fly ash-based glass-ceramics material is sintered and heat treated at 950 C for 2 hours. This substantial has a respectable prospective to production lightweight aggregates or elements for engineering claims. These method creates stable glass from the ash waste. Disadvantages of this method is energy intensity. (Cheng, 2013)

3 GLASS MANUFACTURING PROCESS

3.1 HISTORY OF THE GLASS

In the glassy state can be transformed substances of different nature. This melts some of the pure oxides and their mixtures in countless ways, and the molten salt is halide, nitrate, etc. Glasses are easily formed by aqueous solutions of many salts and mixtures thereof. In the last decade became known metallic glass, obtained especially by rapid cooling of alloys of different metals. Thus, in the glassy state can be substances of different chemical types, with different types of chemical bonds, for example, covalent, ionic, metallic and a variety of physico-chemical properties.

For the first time humanity became acquainted with natural glass-like substance is obsidian in prehistoric times. Artificial material like glass for the first time openly in Egypt CA. 4000 BC for millennia, people using various additives, has achieved greater diversity of classes and varieties of glasses. Until the XIX century glass is used mainly in the manufacture of objects of utilitarian purpose and art glass. In Russia formation of

the science of glass and glassmaking industrial connected with the names of M. V. Lomonosov and D. I. Mendeleev. Lomonosov was the first in the world practice of glassmaking drew serious attention to the relationship of the properties of glasses and their chemical composition. The merit of Mendeleev is anticipating polymeric structure of SiO₂ and developed by their ideas about the chemical nature of the glass, which he considered in the overall context of the development of such fundamental concepts of chemical science as definite-indefinite compound, solution, alloy, etc. (Feltz. 1986)

3.2 GLASS DEMAND

3.2.1 FLAT GLASS

Global demand in flat glass is estimated to be roughly 11.5 billion square meters with a total cost of 112 billion U.S. dollars. Hence, global demand in flat glass increased approximately by 8.5 percent since previous years. That growth is driven by increased building rates in established countries of Europe and North America, where flat glass is used. However, developing countries with their “leader” China will remain the fastest emerging market of flat glass. (Freedonia. 2016)

Approximately 40 % of flat glass is used in the construction industry, but also flat glass demand will be increased in manufacturing of displays and high technological devices. Moreover, in the manufacturing of solar panes demand of flat glass will be increased due to significant investments into alternative sources of energy. 130 million square meters of flat glass was used in solar panels in 2013 and that number predicted to doubled in 2018. Also, growth of flat glass demand in motor vehicles industry due to boosted investments in developed countries. (Freedonia. 2016)

East part of the world is responsible for roughly 50 % of global request in flat glass in terms of quantity. Thailand, Indonesia, India, Vietnam, Japan and China are biggest developing markets for flat glass in the Asian region. China remains leaderships here as well with approximately 60 % of region demand. (Freedonia. 2016)

Eastern part of Europe will suppress Western part, since automobile industry is expected to develop. Glass manufacturers moving their production to developing countries. Consequently, investments and item yields in North/Central America, Africa and Asian areas eventually should overwhelm Europe and North America. China is responsible for half of the global flat glass production. There are around 430 glass

production lines active globally and roughly 240 of them are situated in China. (Freedonia. 2016)

3.2.2 GLASS CONTAINERS

Glass containers are expected to increase their share as well, however with lower rates. Glass containers are considered as premium segment and used as marketing tool. (Freedonia. 2008)

3.2.3 GLASS FIBRE

Production of glass fibre in U.S. in 2009 was 3,6 billion tonnes and assesses at 6.2 billion U.S. dollars. Reinforced plastic sector will support glass textile fibre development. Glass wool will increase on slower rates due to the problems in single-unit housing. Nevertheless, material and technological improvements will support overall glass fibre sector and improve costs and implementation properties of the product. (Jushi Group. 2014)

Glass fibre is responsible for 90% of fortifications in composite materials in the world. Glass fibers are used in wind turbines, cars, pipes and other application, where corrosion resistance is important. World market is expected to grow up 45 billion U.S. dollars. (Jushi Group. 2014)

3.3 THE STRUCTURE OF THE GLASS

Radiographs of quartz glass is best interpreted within a model of continuous chaotic mesh of tetrahedroid SiO_4 (silicon atom surrounded by four oxygen atoms), and reflect the short-range order in the glass structure. X-ray and neutron diffraction studies have shown that the presence of an irregular grid is confirmed with regard to the structure of single-component glasses. In defect-free silica glass there are only bridging oxygen atoms. For glasses containing two or more components characterized by chemical heterogeneity. However, coordination of silicon atoms relative to oxygen, the continuity of silicon oxide tetrahedral mesh is broken due to the partial ruptures of the relations Si-O-Si linking the tetrahedroid together. (Feltz. 1986)

3.4 THE COMPOSITION AND PROPERTIES OF GLASSES

The chemical composition of the inorganic glass is divided into elementary, chalcogenide and oxide. The base oxide glass is glass-forming oxide. Among the glass-forming oxides are SiO_2 , B_2O_3 , GeO_2 , P_2O_5 . The most widespread is silicate glass (based on SiO_2) due to its high chemical resistance, and the cheapness and availability of raw materials. To impart certain physical properties to the composition of silicate glasses introduce oxides of different metals (most commonly alkaline and alkaline earth). (Feltz. 1986)

Physico-chemical properties of the glass depend on its composition and the degree of processing. The lowest density ($\sim 2.3 \text{ g/cm}^3$) quartz is glass consisting only of silicon oxide. The heaviest lead glass containing much lead oxide (80%), have a density of about 8 g/cm^3 . (Feltz. 1986)

The tensile strength of glass in tension is small (8.107 N/m^2) and increases with rising content of SiO_2 and CaO . Alkaline oxides reduce the strength of the glass. The glass resists compression much better than tension, and ultimate strength in compression and tension can vary considerably. (Feltz. 1986)

The glass is very fragile material; the smallest have boroplumbic fragility of glass. Quartz glass is fragile when heated to a temperature of $\sim 400^\circ\text{C}$, further heating the glass gradually softens and becomes a viscous liquid. The transition of glass from a solid to a liquid is not characterized by any definite melting point. With proper cooling of liquid glass this process occurs in the opposite direction also without crystallization (deamortization). (Feltz. 1986)

3.3 RAW MATERIALS USED IN GLASS MELTING

The raw materials used for the production of glass, conventionally divided into two groups: main and auxiliary.

The main raw materials include substances that are introduced into the glass melt of acid, alkali and alkaline earth oxides; they form the basis of glass and determine its basic physical and chemical properties.

The auxiliary raw materials include substances that contribute to the acceleration of glass melting, improve the quality of the glass, change the glass properties is the melting accelerators, oxidizing and reducing agents, suppressors, dyes and discolouring.

In glassmaking are used as natural (silica sand, dolomite, nepheline, feldspar, limestone) and synthetic materials – soda, potash, minium and litharge, dyes, etc.

To raw materials to meet a number of requirements concerning the constancy of the chemical and grain composition, homogeneity, humidity and the content of undesirable impurities. Fluctuations in the chemical composition of the raw material adversely affects the uniformity of the glass, therefore, in such cases it is necessary to adjust the composition of the charge.

High demands are placed on raw materials for permissible content of harmful impurities, mainly oxides painted. Iron oxides contained in the sand and other raw materials, deteriorate the transparency of glass and give it an unpleasant yellow-green colour. Depending on the types of glass are different allowable limits of the content of iron oxides in the raw materials.

A significant role is played also by the constancy of the grain composition of the charge, e.g., charge, consisting of rounded grains of sand, are more prone to delamination than the charge, consisting of a plate of an acute-angled grains.

The quality of raw materials (chemical and granulometric composition, impurities, etc.) is regulated by relevant standards and technical conditions, which are periodically reviewed and refined. (Ilya Melnikov. 2013)

3.1 Acidic oxides

The basic material for the introduction of silicon dioxide is quartz sand (however, there are also quartzite and rock crystal, generally in the production of optical and quartz glass). The sand quality is evaluated by their chemical and grain compositions. The main requirement: high content of silica and low content of colouring impurities. In the production of lead crystal apply of enriched quartz Sands premium grade with a content of 0.01 to 0.02% iron oxides.

The boron oxide is widely used in the manufacture of chemical glassware, heat-resistant and of a number of specialty glasses and fiberglass. The starting materials for introducing boron anhydride – boric acid and borax, based on the composition of the glass is inserted together with brown oxide of sodium.

Introduction in the glass composition is insignificant amounts of boron oxide (up to 2%) contributes to the alleviation of melting and refining glass, reduces boiling temperature,

to improve the physico-chemical data of glass. For introduction of boron oxide is used boric acid, borax and calcium borate. (Ilya Melnikov. 2013)

3.2 Alkaline oxides

Along with silica, the oxide of sodium is one of the most important parts of the glass. Sodium oxide glass formation accelerates and lowers the temperature of melting glass, facilitates the process of clarification. In the glass composition oxide of sodium is introduced by means of soda ash and sodium sulphate. Soda ash is sodium carbonate anhydrous, or soda, and crystal soda. In the melting crystal soda is not used because it contains too much water; in the manufacture of glass use mainly soda ash. Sodium sulfate is the sodium salt of sulfuric acid; there are two types of sulfate – natural and artificial. In glassmaking used mainly natural sodium sulfate.

The main materials to put in the glass of sodium oxide are sodium carbonate (soda), sulphate and sodium nitrate (saltpeter). Sodium sulfate is used in the production of high quality glass in small amounts as an accelerator of cooking and clarifier. The introduction of sodium oxide using sulfate when cooking crystal and colored glass is not desirable due to the formation of intensively coloured sulphides of metals.

Potassium oxide affects many properties of glass similar to the sodium oxide, but it has its own peculiarities, for example, potassium oxide increases the viscosity of the glass, particularly in the area of the forming. Oxide of potassium improves the colour of the glass, gives the product a better appearance, so it is often used instead of sodium oxide in the production of high quality, especially crystal glasses. A small Supplement is sometimes used in the production of sheet glass.

As raw materials for the introduction of potassium oxide is used mainly potash.

Distinguish crystalline potash and calcined. In the manufacture of glass used mainly calcined potash; for the introduction of potassium oxide is also used potassium nitrate (nitrate) as an oxidizing agent for the introduction of potassium oxide. (Ilya Melnikov. 2013)

3.3 Alkaline earth oxides

For introduction of calcium oxide in the glass is most often used limestone, chalk, marble less.

Calcium oxide, accelerating the reaction of lime concrete, to facilitate cooking and lighting, improves workability properties of glass increases its chemical resistance. Calcium oxide is introduced, usually via a carbonate; for the introduction of calcium oxide in the glass compositions of high quality is recommended the use of calcium borate.

Magnesium oxide is introduced into the composition of glass mainly through the dolomite, sometimes using dolomitic limestone or magnesite. Dolomite is a double salt of calcium carbonate and magnesium, thus its application in the composition of the glass are simultaneously injected oxides of calcium and magnesium, which is very valuable in the manufacture of window and polished glass. Natural dolomite always contains impurities of silica, alumina and iron. Constancy of composition and minimal content of harmful impurities – iron compounds – is of great importance for the production of high quality glass products.

Alkaline earth oxides are part of most industrial glasses. They give glasses valuable physical and chemical properties – increased thermal and chemical stability, increase mechanical strength. (Ilya Melnikov. 2013)

3.4 Aluminum Oxide

Aluminum oxide is introduced into the glass composition from a technical alumina, feldspars and pegmatites. Additive in the compositions of the sodium-calcium-silicate glass of aluminium oxide lowers the expansion coefficient of the glass, increases chemical resistance, improves the mechanical and thermal strength. Technical alumina is produced by chemical processing of aluminum-containing glass. It is a product of high purity, contains little by-products. Feldspars according to their chemical composition are classified in potassium, calcium and sodium, respectively called the orthoclase, and albite anitepam; feldspars, consisting of mixtures of albite and anortite are called plagioclase. The chemical composition of the feldspars is variable. In pure feldspars, the content of alumina is 30%. Pegmatites represent a natural mixture of feldspar and quartz. In glass melting is usually used ground-enriched pegmatite. (Ilya Melnikov. 2013)

3.5 Barium oxide

A small amount of barium oxide accelerates the glass solidification, improves the workability properties of glass, especially when mechanized molding. Glass laced with barium oxide glass, increase the refractive index and density of the glass. To put in the glass is a barium oxide are the most suitable raw material is barium carbonate, may also be used nitrates and sulfates. (Ilya Melnikov. 2013)

3.6 Lead oxide

The lead oxide is the main component of the crystal, determining their high optical properties. The main materials for introduction into the glass is lead oxide, minium, and yellow lead. During decomposition oxide emits oxygen, which helps to lighten the glass and maintain an oxidising environment. The use of lead-containing raw materials – the minimum content of dye impurities. (Ilya Melnikov. 2013)

3.7 Zinc oxide

Adding zinc oxide to the molten glass lowers the coefficient of thermal expansion of the glass, increases the refractive index and chemical stability of glass; zinc oxide is an essential component of selenium ruby glass. (Ilya Melnikov. 2013)

3.3 PRODUCTION

Raw material for the manufacture of glass are quartz sand is SiO_2 , soda ash Na_2CO_3 , potash K_2CO_3 , CaCO_3 limestone, dolomite $\text{CaCO}_3 \cdot \text{MgCO}_3$, sodium sulfate Na_2SO_4 , $\text{Na}_2\text{B}_4\text{O}_7$ borax, boric acid H_3BO_3 , minium Pb_3O_4 , feldspar $\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{K}_2\text{O}$, etc. Raw materials are ground, weighed in the desired ratios and mixed thoroughly. The mixture usually contains glass shards remaining from the previous cooking, and, depending on the purpose of the further use of glass, oxidizing agents, dyes, decolourizers, brighteners, suppressors, reducing agents and oxidizing agents, boiling accelerators, or other additives. Dyes give the glass the desired color. During melting in a glass weight add oxides of metals. For example, iron will make the material transparent bluish-green or yellow, manganese — yellow or brown, chrome — grassy-green, uranium — yellowish-green (so-called uranium glass), cobalt blue (cobalt glass), colloidal silver — yellow, copper — red. The thus obtained charge is loaded into glass fiber oven. After that, the mixture is melted at a high temperature. The glass is cooked by exposing the mixture of raw materials at temperatures of 1200 to 1600°C for a long time — from 12 to 96 h. During heating, the mixture melts, volatile components (H_2O , CO_2 , SO_3) are

removed, and the remaining chemically react with each other, resulting in a homogeneous glass melt, which is the production of sheet glass or glass products. Glassy state of the material is obtained only by rapid cooling of glass. In the case of slow cooling begins partial crystallization, the glass loses its transparency due to violation of homogeneity, and the molded products have low mechanical strength.

During cooling of the melt greatly changes the viscosity of the glass. For any glass on the chart temperature dependence of viscosity there are two characteristic points corresponding to temperature T_f and the fluidity of the glass transition point T_g . At temperatures above T_f , the glass exhibits the properties of fluidity, typical of the liquid state. The viscosity of the various glasses at the temperature T_f is approximately the same and equal to 108 Pa. The glass transition temperature T_g , below which clearly shows the fragility of the glass corresponds to a viscosity of about 1012 PA. The temperature interval between T_g and T_f is called the softening interval in which the glass has plastic properties. For most engineering silicate glasses $T_g = 400-600 C^0$ and $C_f = 700-900 C^0$, i.e. the softening interval of several hundred degrees. The wider the interval softening, the manufacturability of the glass, as in this case, it is easier to form products. Fabricated glass product is subjected to annealing to eliminate encountered in uneven cooling of the tension. (Feltz. 1986)

If in ancient times melting of the glass was carried out in clay pots with a depth and a diameter of 5-7 cm, at the present time for the production of optical, artistic and other types of glass of special composition used fire clay pots of large dimensions, accommodating from 200 to 1400 kg of the charge. In one furnace can be maintained from 6 to 20 pots, pot furnaces used to produce relatively small amounts of glass with an accurately constant composition. In large-scale production used tank furnaces. Large masses of glass are boiled in continuous tank furnaces. This mode allows the flow of necessary chemical reactions, resulting in the raw material mixture acquires the properties of glass. A constant level of molten glass in the bath is maintained by continuous feed of the charge on one end of the installation and extraction of the finished product at the same speed from the other end. In this mode, some glass furnaces operate up to five years. Large furnaces, sometimes containing several hundred tons of molten glass, fit for intensive mechanical production. (Feltz. 1986)

3.4 IRON IN THE GLASS

High demands are placed on raw materials for permissible content of harmful impurities mainly of coated oxides. The oxides of iron contained in sand and other raw materials, deteriorate the transparency of glass and give it an unpleasant yellow-green colour. Depending on the types of glass are different allowable limits of the content of iron oxides in the raw materials.

Natural dolomite always contains impurities of silica, alumina and iron. Constancy of composition and mineral content of harmful impurities - iron compounds - is of great importance for the production of high quality glass products.

In pure feldspars, the content of alumina is 30%; of harmful oxides are iron oxides.

Iron compounds depending on its type give different colours to the glass. The iron oxide colours the glass in blue-green; iron oxide gives yellow or brown, and mixed with charcoal and sulphur in orange; a mixture of oxide and oxide give the glass a green colour.

Decolourizers are introduced into a glass melt to eliminate unwanted blue-green or yellow-green glass that give it an iron compound present in raw materials.

The ferrous form of iron colours the glass ten times stronger than the oxide. For discoloration of glass during its formation will need to convert the ferrous form of iron into oxide. To do this, use of such raw material, which upon heating decompose with evolution of free oxygen. The presence of oxygen is a prerequisite for the successful course of the main reaction can be carried out.

As discolour apply the peroxide of arsenic, nitrate, sodium sulphate or cerium dioxide. Most often the length of chemical discoloration of glass are used with a combination of oxide of arsenic: arsenic trioxide when heated at relatively low temperature absorbs oxygen, turning into the pentoxide of nitrogen; then, at high temperatures close to the temperatures of the lightness of glass - pentoxide decomposes into terraces with evolution of free oxygen, which provides the reaction can be carried out. For discoloration of glass in this way just enter into the glass melt of 0.3 - 0.5 % of arsenic trioxide.

Nitrate decomposes to release oxygen at a temperature of 400 degrees Celsius; it is administered together with trioxide arsenic.

Arsenic compounds, because of their great toxicity is often replaced by the oxide of antimony.

As chemical decolourization used as oxides of cerium. The cerium dioxide decomposes at high temperature with evolution of oxygen. Cerium oxide is a highly effective discolour, besides its use eliminates the use of poisonous compounds of arsenic and antimony.

Physical discoloration is that the molten glass injected substances that colour the glass in colour, additional to the existing one, that is, superimposed one colour to another. Colour matching is conducted so as to reduce the colour intensity of the glass, with a decrease in the intensity of colour glasses will reduce the translucency of glass. As a physical decolourization used oxides of manganese, cobalt, Nickel, neodymium and erbium, elemental selenium.

Sands subjected to enrichment - extracted and removed by iron impurities, then dried and sieved; dolomite and limestone pre-crush and smash them.

Used in the glassmaking Sands usually treated: enrichment, drying and sifting. The enrichment process consists in the removal of sand, that is the removal of ferrous impurities or the reduction of their content to the required parameters. The inclusion of iron in the sand can be of various types: there are clay impurities, light and heavy impurities of ferrous materials, surface films, and clusters within quartz grains of sand.

Gravitational method of beneficiation of sand based on the separation of particulate minerals in an aqueous or air environment according to their specific weight.

Flotation method of preparation of sand consists in the separation of minerals, wetted and not wetted by water; vacuuming into the pulp bubbles of air minerals, which surface is not wetted, adhere to the bubble and float along with them up flatirons. Mineralized air bubbles float and carry away harmful impurities in the foam, which is then easily separated from the sand. For the formation of stable bubbles in the slurry injected reagents; reagents can be used, for example, sulphate soap. Flotation method of preparation of sand includes three processes: flotation, attritioning of film and rinse. Attire based on mutual friction of the grains of sand, in water; when rubbed together

film of iron hydroxides having lower hardness compared to quartz, scrubbed. The method of electromagnetic separation is based on the ability of various minerals in different ways to be attracted by a magnet. For preparation of sand by the method of electromagnetic separation in the glass industry used magnetic separators; to remove from the raw materials iron hardware apply disk, induction-roll and drum separators. Magnetic separation Sands are intended for the production of high-quality colourless glass, especially lead crystal. (Melnikov I. 2013)

4 MARKET ANALYSIS OF GLASS RAW MATERIAL

4.1 SILICA SAND

According to Freedonia's report on "World industrial silica sand" planet requirement in quartz (silica sand) is predicted to be increased by 5.6 percent per year to almost 290 million tonnes in 2018. Increasing speeds in building expenditures and industrial product worldwide are relied upon to drive development in vital silica sand-devouring businesses, including the glass, foundry, and building items divisions. Especially fast profits are anticipated for the pressure driven breaking market as horizontal drilling for shale oil and gas assets grows, to a great extent in North America. In any case, quicker profits in the general business sector will be compelled by continuous endeavors to join higher volumes of reused glass cullet in the production of glass containers. Moreover, expanded recovery of foundry sand is relied upon to point of confinement interest for mechanical sand utilized as a part of the generation of metal casting molds. (Freedonia. 2014)

China is likely to hold its position as the main world business sector for modern silica sand through 2018, representing more than 33% of worldwide interest. The nation's gigantic glass industry, the biggest around the world, will keep on reinforcing mechanical sand utilization for the generation of windows, electronic showcase screens, photovoltaic boards, and other level glass items. China's container glass industry will drive additional silica sand deals, bolstered by rising generation of glass containers, especially in the alcoholic beverage area. In India, foundry action will progress at a solid pace, impelling the creation of sand molds to produce car, machine device, wind turbine, and different sorts of metal castings. Indonesia is likewise anticipated to enroll solid development in modern sand deals through 2018, encouraged by quick advances

in the yield of glass items and metal castings, joined with expanded water powered breaking movement. (Freedonia. 2014)

Interest for silica sand in North America is estimate to ascend at a quicker yearly pace than all other territorial markets. Utilization picks up in the US and Canada will support provincial development, driven by extension in the nations' individual pressure driven cracking portions. Continuous quality in US oilfield action will support interest for sand prop pants, as will increments in the quantity of cracking stages per well. Utilization of silica sand in Western Europe is anticipated to enroll humbler yearly increases through 2018, however such development will stamp a bounce back from the decreases enlisted somewhere around 2008 and 2013. Recuperations in building development and assembling movement, incorporating a turnaround in level glass yield, will empower restored interest for modern sand in the area. (Freedonia. 2014)

The glass market is the main consumer of mechanical silica sand, representing 42 percent of world interest in 2013 or 120 million tonnes of sand. Glass containers production involves a little more than 33% of the business sector; flat glass and different glass items, for example, fiberglass represents the rest of worldwide interest. Silica sand suppliers are relied upon to profit by solid additions in development spending and assembling yield, which will help the generation of glass items utilized as a part of structures, engine vehicles, furniture, and apparatuses. (Freedonia. 2014)

In terms of economics according to Chinese website Alibaba.com price of quartz sand varies from 60 to 145 U.S. dollars per 1 tonne. Let's assume that median price of quartz sand in China is 100 U.S. dollars.

Price for silica sand has increased greatly in past years due to booming construction rates, fracking and glass manufacturing. Trend could be seen in the Figure 3.

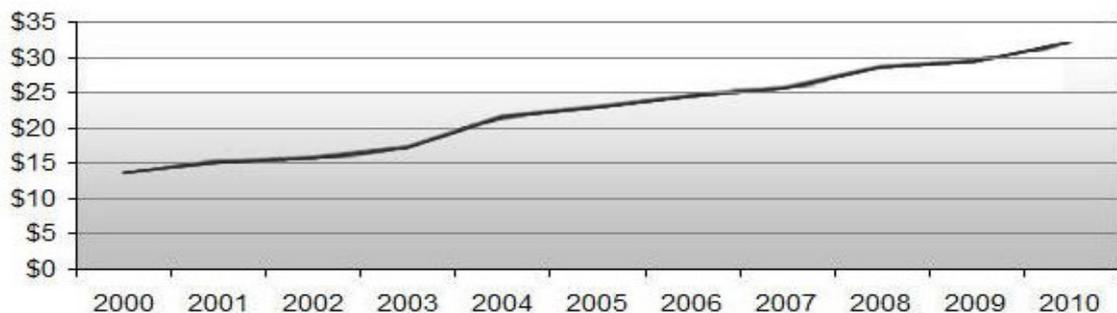


Figure 3. Historical commercial silica unit prices per ton.

Source: Mike Kapsch. 2016

4.2 ALUMINA

Global demand for alumina is approximately 82 million metric tons. Share of alumina consumption used for glass production is approximately 12 %. China is responsible for a half of the global growth. Also, china is a noteworthy aluminum manufacturer.

(Freedonia. 2013)

Increasing urbanization rates and financial progress in developing countries will assure request of alumina in construction sector. Without China, in most countries automobiles are responsible for alumina consumption more than building sector. (Freedonia. 2013)

Automobile sector will use more aluminum over a time due to shifting of production to China and low vehicle possession in emerging countries, which gives a significant space for expanding. (Freedonia. 2013)

Aluminum is also used for packing. Aluminum cans are popular due to high recycle rates. (Freedonia. 2013)

Average price of alumina on Chinese site Alibaba.com is 500-1000 \$ per tonne.

However, according to stock market prices from site finam.ru current price for alumina is approximately 1550 \$ per tonne. Price fluctuations during the 6-year period from 2008 until 2016 are presented in the Figure 4. Also, price lowering trend could be noticed.



Figure 4. Stock market price of alumina in dollars per tonne.

4.3 DOLOMITE

Global request for Dolomite is estimated to be approximate 440 thousand metric tonnes. (Global Industry Analysts. 2010.)

According to Chinese site Alibaba.com average price for dolomite is 100-200 \$ per tonne.

4.4 CALCIUM BORATE

U.S and Turkey are the global leaders of boron minerals. Global manufacture of boron minerals is approximately 4 million metric tonnes in 2010 (without U.S. manufacture). Data is presented in Table 6. (Marc A. Angulo, Robert D. Crangle, Jr. 2010)

Table 6. Production of boron minerals per country, thousand metric tonnes

Source: (Marc A. Angulo, Robert D. Crangle, Jr. 2010)

Country/Year	2006	2007	2008	2009	2010
Argentina	534	670	786	500	600
Chile	460	528	583	608	504
China	145	145	140	145	150
Russia	400	400	400	400	400
Turkey	1,819	2,128	2,139	1,800	2,000
Peru	191	234	350	187	293
Bolivia	39	64	56	86	97

For borates glass manufacturing sector is a main consumer. Glass responsible roughly for 60 percent of world borate demand. Boron is utilized as an added substance as a part of glass to diminish warm extension, enhance quality, chemical resistance, and solidness, and give resistance against vibration, high temperature, and thermal tremor. Boron is likewise utilized as a fluxing operators, decreasing the thickness of glass amid development to enhance production. Contingent upon the purpose and characteristic of the glass, borax, boric acid, colemanite, ulexite, and sodium borates are commonly utilized. Types of boron minerals are presented in the Table 7. Protection and material fiberglass are responsible for the biggest single utilization of borates around the world, at 45% of world utilization. End utilizes for fiberglass are erosion safe, heat-safe, and high-quality fabrics; protection; support; and sound ingestion. The addition of borates into fiberglass incredibly enhances quality, setting up an item that is solid, lightweight, and warm and chemically safe (Garrett, 1998). Borosilicate alludes to glass with boric oxide content somewhere around 5% and 30%. The boron in borosilicate gives numerous profitable properties to the glass, for example, expanded mechanical quality,

low coefficient of warm extension, and imperviousness to chemical aggression and thermal tremor. (Marc A. Angulo, Robert D. Crangle, Jr. 2010)

Table 7. Types of boron minerals

Source: Marc A. Angulo, Robert D. Crangle, Jr. 2010

Mineral	Chemical Composition	B ₂ O ₃ , weight percentage
Boracite	Mg ₃ B ₇ O ₁₃ Cl	62,2
Colemanite	Ca ₂ B ₆ O ₁₁ 5H ₂ O	50,8
Datolite	CaBSiO ₄ OH	24,9
Hydroboracite	CaMgB ₆ O ₁₁ 6H ₂ O	50,5
Kernite	Na ₂ B ₄ O ₇ 4H ₂ O	51,0
Priceite	CaB ₁₀ O ₁₉ 7H ₂ O	49,8
Proberite	NaCaB ₃ O ₉ 5H ₂ O	49,6
Sassolite	H ₃ BO ₃	56,3
Szaibelyite	MgBO ₂ OH	41,4
Tincal	Na ₂ B ₄ O ₇ 10H ₂ O	35,6
Tincalconite	Na ₂ B ₄ O ₇ 5H ₂ O	47,8
Ulexite	NaCaB ₅ O ₉ 8H ₂ O	43,0

China had more than 100 borate stores in 14 Provinces. Chinese boron assets are of low quality, averaging around 8.4% B₂O₃, in contrast with the Turkish and United States saves, which normal around 26% to 31% and 25% to 32% B₂O₃, correspondingly. Evident utilization of borate in China expanded by 7% every year somewhere around 2000 and 2009 powered by the glass and artistic commercial ventures, however household generation remained generally reliable amid this period. To keep up this abnormal state of utilization and moderate level of creation, China turned out to be more import dependent on borate items beginning from Russia, South America, Turkey, and the United States (Industrial Minerals. 2008a; Baylis. 2010).

The Chinese government was considering shutting a proviso that gives a 5% charge refund on the fare of amalgams in endeavors to shorten abuse of the discount. Some carbon steel plants included little measures of boron, almost 0.0005% by weight, to pass the steel off as an amalgam keeping in mind the end goal to gather the discount. This practice may have given these factories as much as a 20% valuing advantage on their items (Metal Bulletin. 2011).

Prices of boron minerals may vary a lot due to quality and source. In current paper Colemanite composition was used in the model. Thus, approximate price is 370-420 dollars according to Table 8. Moreover, quality and availability in China is very low and prices are much higher (20-30 \$ per kilogram according to Alibaba.com). Furthermore, addition of ash in batch will decrease calcium borate demand only for 1.4 percent.

Table 8. Borate mineral prices, dollars per metric ton

Source: (Marc A. Angulo, Robert D. Crangle, Jr. 2010)

Product	Price, December 31, 2008	Price, December 31, 2009	Price, December 31, 2010
Borax, decahydrate, Buenos Aires	560	520	520
Boric acid, Chile	950	800	735
Colemanite, Buenos Aires, 40% B ₂ O ₃	420-460	370-420	370-420
Ulexite, Buenos Aires, 40% B ₂ O ₃	390-410	350-380	350-380
Ulexite, granular, Chile, 40% B ₂ O ₃	500	400	400
Ulexite, Lima, 40% B ₂ O ₃	490-520	250-300	350-370

5 MODEL

5.1 DESCRIPTION OF THE MODEL

Aim of the model is to estimate the potential to utilize coal ash in glass manufacturing process. Model calculates the favourable proportion of normally used components and coal ash in glass manufacturing. That data will be used to estimate possible ash utilization rates and amount of saved natural resources.

For model creation MathCad software will be used as a main platform. MathCad software is an engineering calculation program, which helps significantly to solve difficult mathematical equations. In our case matrix method and Given-Find block will be used to estimate impact on glass material balance by using the ash as a part of batch. Software was kindly provided by Lappeenranta University of Technology.

Normal material balance of glass manufacturing (without ash) will be used to show the algorithm of calculation and also to display how many and which materials are used for glass production. Material balance itself shows what we had before chemical reaction and after, which is very important during an analysing of any engineering system to see what was lost during a process and what was converted into desired product successfully.

In that model such material balance will be imitated by using mathematical methods. To put it simply, there will be 2 matrixes: “C” contains information about the mineral composition of needed materials (sand, aluminium, dolomite and lime borate) and “M” contains information about the shares of needed materials to produce the desired glass. Those matrixes will be transformed into this resulting matrix by using an auxiliary function. With auxiliary function using these two matrix a preliminary result will be stored to matrix “M”. After an iteration process using “Given-Find” block in MatchCad last version of preliminary results will be presented in matrix “M”. Those preliminary results will be examined and checked by reverse calculation of preliminary outcome. Checking is obligatory because MathCAD software uses iteration method and results might be not very accurate.

That model will let us to model a glass manufacturing process without any real experiments, which are very complex to conduct in reality. Also scale of normal glass manufacturing and or model is deferent that’s why fraction digits and their variety will not be important to us because in reality sand is measured in tonnes instead of kilograms.

In addition, that model also could be used to calculate other material balances, for example, concrete manufacturing process. Only initial data will be changed: composition of desired product and batch’s compounds and their chemical composition.

5.2 ALGORITHM OF CALCULATION

At the beginning initial data with composition of different raw materials, their shares and desirable glass is needed. In our case we will use glass with a structure shown in Table 9. Glass mainly consists of silicone oxide (SiO_2), aluminium oxide (Al_2O_3), boron oxide (B_2O_3), calcium oxide (CaO) and sodium oxide (Na_2O). Also, in some types of glass magnesium oxide (MgO) and iron oxide (Fe_3O_4) are contained. Those percentages

may vary a lot. For our calculation approximate values were chosen. Borosilicate fibre glass composition was chosen and particularly E-class glass with highest properties. (Saint-Gobain Vetrotex. 2002)

Table 9. Chemical compounds percentages in a glass.

Source: Saint-Gobain Vetrotex. 2002

Chemical compound	SiO ₂ , %	Al ₂ O ₃ , %	B ₂ O ₃ , %	CaO, %	Na ₂ O, %
General	43-74	12-25.5	0-8.5	14-26	0-4
E-class	53-57	12-15	5-8.5	22-26	0-1
Desired	54,5	14,5	8,5	22	0,5

Next step will be to determine the shares of the materials, which will be used in the batch. In business as usual cases (without ash) current case sand, aluminium, lime borate and dolomite will be used. Components of those materials are presented in Table 10. As is seen from the table main source of silicone oxide (SiO₂) for a glass is a sand, where 99,48 % are silicone oxide (SiO₂). Aluminium is used because of its high aluminum oxide (Al₂O₃) content 99,20 %. For boron oxide (B₂O₃) lime borate is responsible with content of 56,50 %. Calcium oxide (CaO) is contained in lime borate and dolomite with 39,50 % and 50,87 % respectively. Loss on ignition (LOI) is high in lime borate and dolomite. Also, those chemical compositions are not for raw batch. They represent chemical composition of batch after thermal treatment, that's why loss on ignition is mentioned instead of combustible parts of the batch. Actually, LOI means that in the material, there are such volatile or carbon containing compounds which will be lost (volatilized) during heating in high temperature. These can be e.g. elemental carbon or carbonate compounds (but their composition is not determined). LOI is determined with a standard test where the material is heated and it tells the percentage change of the mass in the test. So, it is the property of the raw material. "I" in the table is used to represent the number of batch compound in matrix, which will be used further

Table 10. Components and percentages of batch, %

Component	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	Na ₂ O	Fe ₃ O ₄	LOI
Sand (i=0)	99,48	0,14	-	0,10	0,15	0,03	0,10
Aluminium (i=1)	0,30	99,20	-	0,10	-	0,10	0,30
Lime borate (i=2)	1,00	0,60	56,50	39,50	-	0,40	12,00
Dolomite (i=3)	1,44	0,50	-	50,87	-	0,50	46,69

Subsequent stage is creation of two matrixes “*C*” and “*M*”, where “*C*” is a matrix with batch compounds based on Table 10 and “*M*” us an unknown matrix, which represents the share of different raw materials in the batch and our aim is to solve that with the algorithm, and contains 1 column and 4 rows, one for each batch compound. As a result, we have 2 matrixes witch will be used to calculate material balance of glass manufacturing process.

Auxiliary function “*d*”, which tells the composition of the glass, meaning the share of each oxide in the ready glass metal, is needed for further calculation. In our case it will have 2 variables “*k*” and “*M*”, where “*k*” represents each component of a batch. This function finds total specific consumption of “*k*” oxide within batch, dimension is one kilogram of oxide per 100 kilograms of glass melts. Total specific consumption of “*k*” oxide within batch.

$$d(k, M) = \sum_{i=0}^3 (C_{i,k} * M_i) \left[\frac{\text{kilograms of oxide}}{100 \text{ kilograms of glass melts}} \right] \quad (1)$$

After finding an auxiliary function simultaneous equation could be solved using MathCad inner Given-Find block. Each equation will be a material balance for the certain glass component. Given block is shown in the Figure 5.

Given	
$d(0, M) = \text{SiO}_2$	SiO ₂ material balance
$d(1, M) = \text{Al}_2\text{O}_3$	Al ₂ O ₃ material balance
$d(2, M) = \text{B}_2\text{O}_3$	B ₂ O ₃ material balance
$d(3, M) = \text{CaO}$	CaO material balance

Figure 5. Given block

Preliminary results will be shown in Find block in the Figure 6. Dimension of outcome will be in kilograms of oxide per 100 kilograms of glass. As it shown to manufacture 100 kilograms of glass with given properties 54,139 kilograms of sand, 14,284 kilograms of aluminium, 18,28 kilograms of lime borate and 28,919 kilograms of dolomite are needed.

$$M := \text{Find}(M)$$

$$M = \begin{pmatrix} 54.139 \\ 14.284 \\ 18.28 \\ 28.919 \end{pmatrix} \begin{matrix} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \end{matrix}$$

Figure 6. Find block, $\frac{\text{kilograms of component}}{100 \text{ kilograms of glass melts}}$

Preliminary results (zero approximation) should be processed before final outcome. The first action will be a calculation of rated specific glass melts consumption in kilograms. It is an amount of materials required to produce 100 kilograms of glass regarding loss on ignition (LOI). Basically, we have to extract LOI from “k” and that gives “k” = 0...5. To estimate it equation 2 is needed. Specific glass melts consumption.

$$M_{sgm} = \sum_{k=0}^5 d(k, M) = 99.83 \text{ [kg]}(2)$$

Next step is multiplying each element with LOI share to find loss on ignition for each element of the batch. Results are in the Figure 7. LOI share is taken from the Table 10.

$$\begin{aligned} \text{loi_sand} &:= 54.139 \cdot 0.0010 = 0.054 \\ \text{loi_clay} &:= 14.284 \cdot 0.0030 = 0.043 \\ \text{loi_lime} &:= 18.28 \cdot 0.1200 = 2.194 \\ \text{loi_dolomite} &:= 28.919 \cdot 0.4669 = 13.502 \end{aligned}$$

Figure 7. Finding the loss on ignition for each element, [kg]

Now it is possible to calculate real consumption of each element of the batch taking into account loss on ignition. LOI for each element is subtracted from preliminary consumption of the minerals. Results are in the Figure 8.

$$\begin{aligned} \text{sand_real} &:= M_0 - \text{loi_sand} = 54.085 \\ \text{clay_real} &:= M_1 - \text{loi_clay} = 14.241 \\ \text{lime_real} &:= M_2 - \text{loi_lime} = 16.086 \\ \text{dolomite_real} &:= M_3 - \text{loi_dolomite} = 15.417 \end{aligned}$$

Figure 8. Real consumption of batch elements, [kg]

Real composition of manufactured glass is calculated by each compound divided by rated specific glass melts consumption and multiplying by 100 to show result in percentages. To check the correctness of calculation we put together percentages of compounds and result should be 100%. Calculation for each compound and check are shown in the Figure 9.

$$\begin{aligned} \text{SiO2_real} &:= 100 \cdot \frac{\text{SiO2}}{M_sgm} = 54.593 & \text{CaO_real} &:= 100 \cdot \frac{\text{CaO}}{M_sgm} = 22.038 \\ \text{Al2O3_real} &:= 100 \cdot \frac{\text{Al2O3}}{M_sgm} = 14.525 & \text{Na2O_real} &:= 100 \cdot \frac{d(4,M)}{M_sgm} = 0.081 \\ \text{B2O3_real} &:= 100 \cdot \frac{\text{B2O3}}{M_sgm} = 8.515 & \text{Fe3O4_real} &:= 100 \cdot \frac{d(5,M)}{M_sgm} = 0.249 \\ \text{SiO2_real} + \text{Al2O3_real} + \text{B2O3_real} + \text{CaO_real} + \text{Na2O_real} + \text{Fe3O4_real} &= 100 \end{aligned}$$

Figure 9. Real composition of manufactured glass and check, %

Further action will be a comparison of desired composition and a real one in the Table 11. For silicone oxide (SiO_2), aluminum oxide (Al_2O_3), boron oxide (B_2O_3) and calcium oxide (CaO) error is approximately 0,2 % which is acceptable for mathematical model. Otherwise, sodium oxide (Na_2O) and iron oxide (Fe_3O_4) errors are quite significant. To achieve desirable composition, more than 6 times of sodium oxide (Na_2O) are needed and iron oxide (Fe_3O_4) should be eliminated entirely. It will be shown in next parts of paper how those problems will be solved. Lack of sodium oxide (Na_2O) will be solved in part, where batch will be mixed with an ash, and iron influence on glass and treatment methods will be discussed in further parts as well. Moreover, regarding sodium oxide content in the batch it could be equal to 0 without significant impact on characteristics of the glass.

Table 11. Comparison of real and desired glass composition, %

Compound	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	Na ₂ O	Fe ₃ O ₄
Desired	54,500	14,500	8,500	22,000	0,500	0,000
Calculated	54,593	14,525	8,515	22,038	0,081	0,249
Relative difference	0,170	0,172	0,176	0,172	83,8	-

Specific consumption of batch components should be calculated again with taking into account that certain amount of mass is lost on ignition. Consequently, we have to divide each element of matrix “M” by real specific glass melts consumption and multiply it by 100 to get percentages. Result will show real amount on material needed for manufacturing of 100 kilograms of glass with taking into account loss on ignition. Dimension is kilogram of component per 100 kilogram of glass mass. Results are show in the figure 10.

$$M_0 := 100 \cdot \frac{\text{sand_real}}{M_sgm} = 54.178 \qquad M_2 := 100 \cdot \frac{\text{lime_real}}{M_sgm} = 16.113$$

$$M_1 := 100 \cdot \frac{\text{clay_real}}{M_sgm} = 14.266 \qquad M_3 := 100 \cdot \frac{\text{dolomite_real}}{M_sgm} = 15.443$$

$$M = \begin{pmatrix} 54.178 \\ 14.266 \\ 16.113 \\ 15.443 \end{pmatrix} \begin{matrix} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \end{matrix}$$

Figure 10. Specific consumption of batch components, $\frac{\text{kilograms of component}}{100 \text{ kilograms of glass melts}}$

Extra step will be to put results into table and calculate total real specific consumption of batch, which is needed to produce 100 kilograms of glass. Also, comparison with preliminary consumption will be done. As it seen from the Table 12 it would be needed a little more batch to adjust composition of glass to desired level.

Table 12. Specific consumption of batch and comparison, $\frac{\text{kilograms of component}}{100 \text{ kilograms of glass melts}}$

Component	Sand	Aluminium	Lime borate	Dolomite	Total
Real	54,178	14,266	16,113	15,443	100
Preliminary	54,139	14,284	18,280	28,919	115.622

To finish with calculations, we also should estimate amount of loss on ignition and its volume. This is very important to know how much of mass will be lost during the process to have a sufficient amount of batch to produce certain amount of glass. Rated specific LOI consumption in kilograms is calculated using auxiliary function “*d*” in equation 3. Rated specific LOI consumption.

$$M_{loi} = d(6, M) = 15.79 [kg] \quad (3)$$

After the correction of preliminary results amount of LOI will be changed as well. Rated specific LOI consumption will be divided by rated specific glass melts consumption to make an adjustment to real results. Dimension and outcome are shown in Equation 4. Specific LOI consumption.

$$M_{loi} = 100 * \frac{M_{loi}}{M_{sgm}} = 15.82 \left[\frac{kg}{100 \text{ kg of glass melt}} \right] \quad (4)$$

To calculate the volume of LOI we will need density of carbon dioxide (CO₂). Molar mass of carbon dioxide is 44 grams per mol, Avogadro’s number is 22,4 liters per mol. Density is equal to molar mass divided by Avogadro’s number. Calculation is shown in Equation 5. Density of carbon dioxide (CO₂).

$$CO_{2 \text{ density}} = \frac{44}{22.4} = 1.96 \left[\frac{kg}{m^3} \right] \quad (5)$$

Volume of LOI is equal to specific LOI consumption divided by density of carbon dioxide (CO₂). Calculation and dimension are shown in Equation 6. Volume of LOI.

$$V_{loi} = \frac{M_{loi}}{CO_{2 \text{ density}}} = 8.05 \left[\frac{m^3}{100 \text{ kg of glass melt}} \right] \quad (6)$$

In that part material balance calculation of glass manufacturing was made using MathCAD. Full calculation could be found in Appendix 1. As a result, we have a

working model of glass manufacturing process, which shows how much batch is needed, which compounds are used in batch and also composition of both batch and glass is adjustable. Loss on ignition is estimated and taken into account. Preliminary results go through checking methods to archive as relevant outcome as possible. The error of model is 0,2 % witch is acceptable for our purposes. In real life those errors do not have any influence on the resulting product due to the bigger scale, where you use tonnes of sand instead of kilograms in our case. The reason is that the measurement accuracy for the raw materials is worse than the calculation inaccuracy achieved. Other reason is that the variation in the compounds of raw materials is probably also larger than the calculation inaccuracy.

Further step will be to use the same model, but with adding of another compound to the batch and that would be an ash. We will see how addition of ash will change the outcome also advantages and disadvantages of ash mixing with batch will be analysed.

5.3 MIXING BATCH WITH ASH

There is a possibility to adjust certain MathCAD model to slightly different purpose, particularly, adding an ash to a batch. Composition of desired glass should remain the same and that will allow to compare normal batch and batch mixed with an ash.

Composition of glass shown in Table 6.

Otherwise composition of batch will be changed by adding one more compound – ash. Ash chemical composition is taken from literature and approximate percentages were used. (Barnes, 2010; Heidrich, Ward and Gurba, 2007). In our case properties of ash belongs to sub-bituminous coal. After modification of Table 10 by adding one more row with ash compounds. Result is shown in Table 13.

Table 13. Components and percentages of batch mixed with ash, %

Component	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	Na ₂ O	Fe ₃ O ₄	LOI
Sand (i=0)	99,48	0,14	-	0,10	0,15	0,03	0,10
Aluminium (i=1)	0,30	99,20	-	0,10	-	0,10	0,30
Lime borate (i=2)	1,00	0,60	56,50	39,50	-	0,40	12,00
Dolomite (i=3)	1,44	0,50	-	50,87	-	0,50	46,69
Ash (i=4)	50,00	20,00	-	20,00	2,00	5,00	3,00

Auxiliary function will also remain the same as shown in equation 1, but matrix “*M*” has to be changed by adding one more row due to additional compound in a batch. Furthermore, in Given-Find block one more material balance will be required, specifically, sodium oxide (Na₂O) material balance. It has to be mentioned that in our previous calculation amount of sodium oxide (Na₂O) was not sufficient for manufacturing desired glass, consequently, we will solve with problem with addition of ash. New Given block is presented in Figure 11.

Given

$$d(0,M) = \text{SiO}_2$$

SiO₂ material balance

$$d(1,M) = \text{Al}_2\text{O}_3$$

Al₂O₃ material balance

$$d(2,M) = \text{B}_2\text{O}_3$$

B₂O₃ material balance

$$d(3,M) = \text{CaO}$$

CaO material balance

$$d(4,M) = \text{Na}_2\text{O}$$

Na₂O material balance

Figure 11. Given block with ash

Results of Given-Find block will be preliminary, further examination is needed again to achieve correct outcome. Addition of ash will decrease content of other compounds of

batch due to similar chemical composition with desired glass and batch components. New preliminary results are shown in Figure 12.

$$M := \text{Find}(M)$$

$$M = \begin{pmatrix} 43.344 \\ 9.957 \\ 18.28 \\ 20.398 \\ 21.749 \end{pmatrix} \begin{matrix} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \\ \text{ash} \end{matrix}$$

Figure 12. Find block with ash, $\frac{\text{kilograms of component}}{100 \text{ kilograms of glass melts}}$

Processing of results will be similar to previous part, but obviously some values will be different. Analyse of results will be left for the final part, when real results will be calculated with all corrections. At least let's mention that amount of ash is comparable with quantities of other compounds, which means that chemically ash suits batch quite efficiently.

Next step will be calculation of rated specific LOI consumption. This value according to received results in Equation 7 is also decreased due to low LOI of ash. That fact could be defining as an advantage because less mass is lost during the manufacturing process. Rated specific LOI consumption

$$M_{loi} = d(6, M) = 12.443 [kg] \quad (7)$$

Real composition of glass will be calculated. Also, checking will be done to be sure, that sum of each compound is 100%. Example of calculations and checking are shown in the Figure 13.

$$\begin{aligned} \text{SiO2_real} &:= 100 \cdot \frac{\text{SiO2}}{M_sgm} = 53.808 & \text{CaO_real} &:= 100 \cdot \frac{\text{CaO}}{M_sgm} = 21.721 \\ \text{Al2O3_real} &:= 100 \cdot \frac{\text{Al2O3}}{M_sgm} = 14.316 & \text{Na2O_real} &:= 100 \cdot \frac{\text{Na2O}}{M_sgm} = 0.494 \\ \text{B2O3_real} &:= 100 \cdot \frac{\text{B2O3}}{M_sgm} = 8.392 & \text{Fe3O4_real} &:= 100 \cdot \frac{d(5, M)}{M_sgm} = 1.269 \end{aligned}$$

$$\text{SiO2_real} + \text{Al2O3_real} + \text{B2O3_real} + \text{CaO_real} + \text{Na2O_real} + \text{Fe3O4_real} = 100$$

Figure 13 – real composition of manufactured glass with ash and check, %

Now it is possible to put that data into the Table 8 and compare composition of glass with different batch's components. As it shown composition almost matches desired results and lack of Na_2O is not an issue anymore. How to treat Fe_3O_4 is mention in the further parts, but after removing of iron oxide in discoloration process other percentages of components will be even more closer to desired composition. Iron in most cases just adds unpleasant color to glass, so it is only a problem, when transparency of the manufacturing glass is important. Resulting table is shown in the Table 14.

Table 14 – Comparison of real, real with ash and desired glass composition, %

Compound	SiO_2	Al_2O_3	B_2O_3	CaO	Na_2O	Fe_3O_4
Desired	54,500	14,500	8,500	22,000	0,500	0,000
Calculated	54,593	14,525	8,515	22,038	0,081	0,249
Calculated + ash	53,808	14,316	8,392	21,721	0,494	1,269
Relative difference	1,269	1,268	1,27	1,268	1,2	-

To calculate specific consumption of each batch material, it is necessary to multiply each element of batch by LOI percentage. This will give lost amount of material during the incineration process.

$$\text{loi_sand} := M_0 \cdot 0.0010 = 0.043$$

$$\text{loi_clay} := M_1 \cdot 0.0030 = 0.03$$

$$\text{loi_lime} := M_2 \cdot 0.1200 = 2.194$$

$$\text{loi_dolomite} := M_3 \cdot 0.4669 = 9.524$$

$$\text{loi_ash} := M_4 \cdot 0.03 = 0.652$$

Figure 14. Loss on ignition for each element, [kg]

Thus, specific consumption of each element will be calculated by subtraction of LOI from preliminary amount of used elements for glass manufacturing process.

$$\begin{aligned}
 \text{sand_real} &:= M_0 - \text{loi_sand} = 43.301 \\
 \text{clay_real} &:= M_1 - \text{loi_clay} = 9.928 \\
 \text{lime_real} &:= M_2 - \text{loi_lime} = 16.086 \\
 \text{dolomite_real} &:= M_3 - \text{loi_dolomite} = 10.874 \\
 \text{ash_real} &:= M_4 - \text{loi_ash} = 21.097
 \end{aligned}$$

Figure 15. Specific consumption of batch components, [kg]

The main purpose of this calculation is to estimate the influence of ash on batch composition and evaluate how much resource could be saved by that method. For that specific consumption for batch's components has to be calculated. Calculations and results are shown in the Figure 16.

$$\begin{aligned}
 M_0 &:= 100 \cdot \frac{\text{sand_real}}{M_sgm} = 42.751 & M_2 &:= 100 \cdot \frac{\text{lime_real}}{M_sgm} = 15.882 \\
 M_1 &:= 100 \cdot \frac{\text{clay_real}}{M_sgm} = 9.802 & M_3 &:= 100 \cdot \frac{\text{dolomite_real}}{M_sgm} = 10.736 \\
 M_4 &:= 100 \cdot \frac{\text{ash_real}}{M_sgm} = 20.829
 \end{aligned}$$

$M = \begin{pmatrix} 42.751 \\ 9.802 \\ 15.882 \\ 10.736 \\ 20.829 \end{pmatrix}$	sand clay lime borate dolomite fly ash
---	--

Figure 16. Specific consumption of batch components mixed with ash $\frac{\text{kilograms of component}}{100 \text{ kilograms of glass melts}}$

Now it is possible to compare two kinds of batches, one with ash and one without. At the first glance it is right to mention that ash is approximately 19 % of batch after mixing. Thus, addition of ash affected other compounds except lime borate because it is the only source of boron oxide in our batch. Content of silica sand required for glass manufacturing process lowered by approximately 21 %. Amount of aluminium needed was reduced by 31,3 % and quantity of dolomite is dropped by 32.6 % as well. That means that batch with ash is more effective and LOI is lower compared to normal batch. In whole it is possible to reduce amount of natural resources by almost 21,6 %, which is meaningful if taking into account that glass produced in significant amount all over the

world. Complete calculation could be found in Appendix 2. Comparison is shown in the Table 15.

Table 15. Comparison of batch consumption with and without ash

Component	Sand	Aluminium	Lime borate	Dolomite	Ash	Total
Calculated	54,178	14,266	16,113	15,443	-	100
Calculated + ash	42,751	9,802	15,882	10,736	20,829	100
Relative difference	21,091	31,291	1,431	32,590	-	-

6 DATA ANALYSIS

After analysing previously presented information about importance of sand and glass production, their strong connection become clear. Current sand consumption is roughly 290 million tonnes and glass manufacturing is responsible for 42 %, consequently it is could be estimated that 121 million tones of sand are used in glass manufacturing. Moreover, there are 3 main category of glass products: containers, flat glass and glass fibre. Let's assume that glass fibre is accountable for one third of all glass products. That means that almost 40 million tonnes of sand are used in glass fibre production. Taking into account data from MathCAD calculation that mixing batch with ash could reduce sand demand in glass production by approximately 21 percent it could be found that up to 8.4 million tonnes of silica sand will be saved if that method will be implemented. And simultaneously problem of ash disposal will be solved as well.

As it was stated before in production of coal combustion products globally is approximately 780 million metric tonnes (Mt.) of ash. China represents 395 million metric tonnes (Mt.) of ash and 265 million metric tonnes (Mt.) are utilized in China already. To estimate the amount of ash, which could be utilized in glass manufacturing process let's assume based on previous calculation that proportion of sand in the process without compared to ash usage in glass manufacturing process is 9 to 3,5 accordingly. Consequently, it would be possible to utilize approximately 15,5 million tonnes of coal

combustion products. To make it clear that amount of utilized coal combustion products will cover all production of Australia and Canada, which produce together almost 20 million metric tons of coal combustion products annually. (Heidrich, Feuerborn and Weir, 2013). That means that amount of coal combustion products in the world is sufficient to cover the whole glass manufacturing process globally. Thus, it is possible to utilize roughly 2 % of total amount of coal combustion products annually.

For the economical calculation China will be chosen as a main silica sand consumer and the fly ash and the glass producer.

As it was mention before it is possible to save up to 8.4 million tonnes of silica sand annually which means that 840 million U.S. dollars annually will be economized as well.

Moreover, the fly ash is always highly available in China, for example, in China, where coal-fired plants located mostly in the eastern part of country due to high industry intensity of the region. Thus, majority of glass manufacturing factories are also placed in that industry region or close to that region, that means that transportation costs will be relevantly low. Map of coal-fired plants on China showed in the Figure 17.

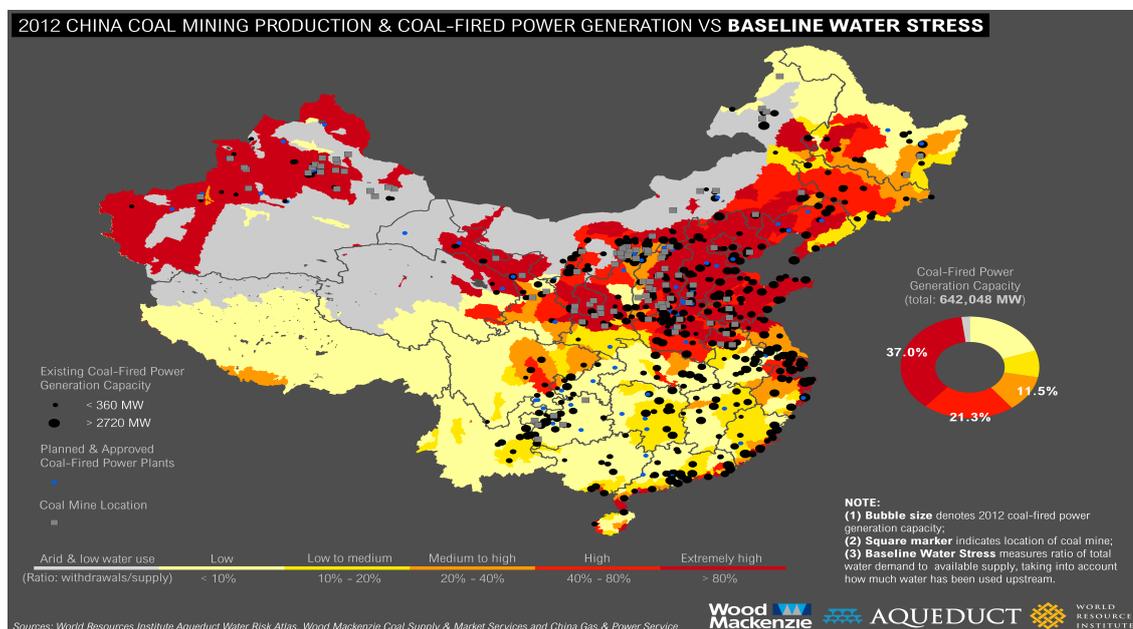


Figure 17. China coal mining production and coal-fired power generation

Source: World Resource Institute

It is quite difficult to estimate value of ash. As it was stated before storing of ash brings a lot of inconveniences and expenditures to the emitter of ash. Such as governmental

taxes, complex methods of storing and continuous contamination of nearest environment. Thus, utilization of ash is always a better option due to a negative price of ash since marginal cost of ash is zero, but external costs are significant and its very hard to define them correctly and real external costs could be even bigger. Consequently, it is economically beneficial to giveaway ash even for free because it will cause less problems to an ash emitter. The value of ash (or cost of ash disposal) is very much depending on the location of ash production. Somewhere it is of small value (e.g. for cement industry) but in many places it is almost zero value or there are some costs of the landfilling.

Moreover, during excavation process of sand some hazards occur. Sand itself is not toxic, but several activities involved in sand production required precautions.

Respiratory protection is obligatory to wear during a work with sand bags to avoid infiltration of sand dust into lungs, which may cause unpleasant consequences. (Silica sand MSDS.2011). Moreover, as it was stated before landscape and ground water suffer as well. Thus, lowering of sand usage will decrease those undesirable consequences.

Furthermore, the addition of the fly ash to the batch also decrease an amount of aluminium and dolomite required for the glass manufacturing process significantly.

Approximately 6 million ton of dolomite (600 – 1200 million dollars) and 3 million ton of alumina (1500 – 4650 million dollars) could be saved as well. Moreover, 0,2 million tons of lime borate (63 – 71 million dollars) could be saved. All together approximately 17.6 million tons of natural resources.

Now it is possible to summarize prices, economy and amount of saved natural resources into one Table 16.

Table 16. Total impact of ash addition to the batch

Mineral	Price, dollars per ton	Saved amount, million tons	Economy, million dollars
Sand	60 - 145	8.4	504 - 1218
Alumina	500 - 1550	3	1500 - 4650
Dolomite	100 - 200	6	600 - 1200
Lime borate	370 - 420	0,2	63 - 71
Total		17,60	2667 - 7139

7 CONCLUSION

Theoretically it is possible to use the fly ash in the glass manufacturing process. For problems with content of iron oxide in the ash commercial solutions are available. Background of previous ash utilization and glass manufacturing were studied and presented. Mathematical model of material balance of the glass manufacturing process was created and tested. MathCAD software was used as a main platform. Possible application of those model in different material balance calculations is possible. Results of those calculations were analysed. Potential amounts of saved natural resources are 8.4 million tons of sand, 6 million tons of dolomite, 3 million tons of clay and 0,2 million tons of lime borate. Moreover, 20 million tons of the fly ash could be utilized as well. Economical assumption was made based on China as a leader in the glass and the fly ash production and the silica sand consumption. Approximate economical benefit is 2667 - 7139 million U.S. dollars annually.

REFERENCES

- American Coal Ash Association (ACAA). 1996. Coal Combustion Byproducts Survey. Alexandria, Virginia: ACAA; 1997.
- Barnes, I. 2010. Ash Utilisation - impact of recent changes in power generation practices. In I. E. A. C. C. Centre (Ed.), Vol. Vol 1: pg. 51. London, England: International Energy Agency Clean Coal Centre.
- Barry E Scheetz and Russell Earle. 1998. Utilization of fly ash. Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA.
- Baylis, Robert, 2010, The Chinese boron market and the role of western suppliers: Industrial Minerals Congress, 20th, Miami, FL, March 21–24, Presentation, 31 p.
- Beiser, Vince. 2015. "The Deadly Global War for Sand". Wired (website). Retrieved 26 March 2015.
- Baylis, Robert, 2010, The Chinese boron market and the role of western suppliers: Industrial Minerals Congress, 20th, Miami, FL, March 21–24, Presentation, 31 p.
- Charles j. Kibert. 2002. Policy instruments for a sustainable built environment. Director and Professor, M.E. Rinker Sr. School of Building Construction, University of Florida, Gainesville, Florida.
- Cheng T.W., Chen Y.S. 2003. Characterisation of glass ceramics made from incinerator fly ash. Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC. Received 3 January 2003; received in revised form 25 April 2003; accepted 10 May 2003
- Chemical Composition - The Glass - Glasses Cebrace . 2015. Chemical Composition - The Glass - Glasses Cebrace . [ONLINE] Available at:
<http://www.cebrace.com.br/v2/us/glass/chemical-composition>.
- The Economist. 2009. "The hourglass effect". 8 October 2009. Retrieved 14 October 2009.
- Fanor Mondragon, Fabio Rincon, Ligia Sierra, Jaime Escobar, Jose Ramirez and John Fernandez. 1989. New perspectives for coal ash utilization: synthesis of zeolitic

materials. Department of Chemistry, University of Antioquia, A. A. 7226, Medellin, Colombia.

Feltz A. 1986. Amorphous and vitreous inorganic solids.

Freedonia. 2008. Slight Increase in Glass Container Demand.

Available at: <http://www.ceramicindustry.com/articles/89653-freedonia-projects-slight-increase-in-glass-container-demand-posted-12-10-08>.

Freedonia. 2013. World Aluminum.

Freedonia. 2014. World Industrial Silica Sand.

Freedonia. 2016. World Flat Glass Market. [ONLINE] Available at: <https://www.reportbuyer.com/product/1091125/world-flat-glass-market-freedonia.html>.

Garrett, D.E., 1998, Preface, *in* Borates—Handbook of deposits, processing, properties, and use: San Diego, CA, Academic Press, p. xi–xiv.

Gehring D. 1990. Fly ash used in environmental cleanup. *Southwest Contractor* :16-24.

Gehring D. 1988. Lime fly ash stabilization & in-place pulverization provide economical road reconstruction method. *In* California Builder Engineer :81-87.

Global Industry Analysts. 2010. Worldwide Consumption of Magnesium

Available at:

http://www.prweb.com/releases/magnesium_magnesite/dolomite/prweb770024.htm.

Halstead WJ. 1986. Use of Fly Ash in Concrete. National Highway Research Program Synthesis of Highway Practice #127. Washington, DC: Transportation Research Board;

Harris D. 2014. Fly Ash Utilization in China // Proceedings of the V Conference “Ashes from TPPs: removal, transport, processing, storage”, Moscow, April 24–25, 2014 — M.: MPEI Printing House, 2014. P. 133 – 136.

Hedrick, C., Ward, C. R., & Gurba, L. (Eds.). 2007. Coal Combustion Products Handbook (Ed 1. ed.). (Vol. Vol 1). Brisbane, Australia: Cooperative Research Centre for Coal in Sustainable Development.

Heidrich, C. 2005. Summary of Technical Options for Coal Combustion Products Utilisation in Australia Ed. 1 ed.: pgs 6. Wollongong: Ash Development Association of Australia.

Heidrich, C, Hans-Joachim Feuerborn, Anne Weir. 2013. Coal Combustion Products: a Global Perspective. World of Coal Ash (WOCA) Conference - April 22-25, 2013 in Lexington, KY

Industrial Minerals. 2008. Serving China's ceramics: Industrial Minerals, no. 488, May, p. 35.

Jushi Group. 2014. Glass fiber composites market

Kapsch Mike. 2016. Silica Sand Mining: Another Way to Play Cheap Natural Gas - Investment U. Available at: <http://www.investmentu.com/article/detail/29669/silica-sand-mining>.

Kentucky Ash Education Site. 2016. What happens to CCBs? Environmental Benefits of Utilization - Coal, Combustion, By-Products, Leaching, Greenhouse, Gas, Reduction, Sustainability - - UK CAER. Available at: <http://www.caer.uky.edu/kyasheducation/whathappens2.shtml>.

Kiselstein L. Y, Oaks N. V, Szpirglas, A. L. 1993. Components of ashes and slags from TPPs.

Kiselstein L. J. 2002. Ecogeochemistry of elements-impurities in coals. Shpirt, M. Y. 1986. Non-Waste technology. Waste disposal of mining and processing of solid combustible minerals.

Kimmel W. 1983. The impact of acid mine drainage on the stream ecosystem. In Pennsylvania Coal: Resources, Technology, and Utilization. Pennsylvania, PA: The Pennsylvania Academy of Science:429.

Lamb DW. 1973. Ash disposal in dams, mounds, structural fills, and retaining walls. In Proceedings of the Third International Ash Utilization Symposium: Pittsburgh, PA; 1973 March 13. Edited by Faber JH, Eckard WE, Spencer JD. Morgantown, WV, Morgantown Energy Research Center, ERDA, in Coal Ash Utilization, Fly Ash, Bottom Ash, and Slag. Edited by Torrey S, Park Ridge, NJ: Noyes Data Corporation; 1978:262-280.

Lin YK. 1971. Compressibility, strength, and frost susceptibility of compacted fly ash [PhD Thesis]. Michigan: University of Michigan.

Marc A. Angulo and Robert D. Crangle, Jr. 2010. U.S. GEOLOGICAL SURVEY MINERALS YEARBOOK.

Melnikov I. 2013. Artistic glass processing. Glass and its properties. Raw materials for glassmaking. Batch preparation

Meyers JJ, Pichumani R, Kapples BS. 1976. Fly ash - a highway construction material. Monroeville, PA: Prepared for the Federal Highway Administration by GAI Consultants.

Metal Bulletin, 2011, Spotlight—China may shut boron loophole on steel exports: Metal Bulletin, January 24. Available at: [http:// www.metalbulletin.com/](http://www.metalbulletin.com/)

Owens PL. 1976. The development of fly ash as a pozzolan for economic concrete. In Proceedings of the Fourth International Ash Utilization Symposium: 1976 March 24; St. Louis, MO. Compiled by Farber JH, Babcock AW, Spencer JD. ERDA Morgantown, WV: Morgantown Energy Research Center.

Panteleev V. G, Larina E. A, Melentiev V. A. 1985. The composition and properties of ash and slag of thermal power plants: a guidebook.

Reidelbach JA. 1970. An industrial evaluation of fly ash bricks. In The US Department of the Interior, Bureau of Mines, Information Circular Number 8488. Washington, DC: US Department of the Interior.

Riga. 1989. Inorganic glasses, coatings and materials.

Silica sand MSDS. Simplot. 2011.

Saint-Gobain Vetrotex. 2002. E, R and D glass properties. Deutschland GmbH.

Twin Cities Testing and Engineering Laboratory. 1970. Inc: 'Investigation of Fly Ash for Use as Compacted Fill, ': 1970 Oct; St. Paul MN. In Fly Ash A Highway Construction Material. SW Washington, DC: US Department of Transportation, Federal Highway Administration.

Virgilio Panapanaan. 2015. Lectures. Basic course on environmental management. LUT.

WCA. 2013, Vol. 2013: World Coal Association.

Weir, A. 2011. World Customs Organization's Harmonized System can put Coal Ash in a Class of its Own, *World of Coal Ash*: pgs 9. Denver, Colorado USA: WOCA.

World Coal Association. 2016. *Coal use & the environment* | *World Coal Association*. [ONLINE] Available at: <http://www.worldcoal.org/environmental-protection/coal-use-environment>.

Xu A. 1997. Fly ash in concrete. In *Waste Materials Used in Concrete Manufacturing*. Edited by Chandra S. Westwood, N J: Noyes Publications;142-183.

Yudovich Y. E, Katniss M. P. 2002. *The Inorganic matter of the coals*.

APPENDIX 1

Material Balance of glass manufacturing

1. Legend and basic data

1. 1. Legend

$C_{i,k}$ - mass content of k oxide within i component, $\frac{\text{kgOxide}}{\text{kgComponent}}$

M_i - specific consumption i component within batch, $\frac{\text{kgComponent}}{100\text{kg GlassMelts}}$

1. 2. Composition of glass, %

$\text{SiO}_2 := 54.5$ $\text{Al}_2\text{O}_3 := 14.5$ $\text{B}_2\text{O}_3 := 8.5$ $\text{CaO} := 22$ $\text{Na}_2\text{O} := 0.5$ $\text{Fe}_3\text{O}_4 := 0$
 $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} = 100$

1. 3. Composition of batch and fly ash, %

	Si	Al	B	Ca	Na	Fe	LOI									
$C :=$	0.9948	0.0014	0	0.0010	0.0015	0.0003	0.0010	$M :=$ <table style="display: inline-table; vertical-align: middle;"> <tr><td>0</td><td>sand</td></tr> <tr><td>0</td><td>clay</td></tr> <tr><td>0</td><td>lime borate</td></tr> <tr><td>0</td><td>dolomite</td></tr> </table>	0	sand	0	clay	0	lime borate	0	dolomite
0	sand															
0	clay															
0	lime borate															
0	dolomite															
	0.0030	0.9920	0	0.0010	0	0.0010	0.0030									
	0.0100	0.0060	0.4650	0.3950	0	0.0040	0.1200									
	0.0144	0.0050	0	0.5087	0	0.0050	0.4669									

*Si - SiO_2 , Al - Al_2O_3 , B - B_2O_3 , Ca - CaO , Na - Na_2O_2 , Fe - Fe_3O_4 , LOI - loss on ignition (CO_2)

1. 4. Density of CO_2 , $\frac{\text{kg}}{\text{m}^3}$

$\text{density}_{\text{CO}_2} := \frac{44}{22.4}$ $\text{density}_{\text{CO}_2} = 1.964$

2. Calculation of specific consumption of components

2. 1. Total specific consumption k oxide within batch, $\frac{\text{kgOxide}}{(100\text{kg GlassMelts})}$

$d(k, M) := \sum_{i=0}^3 (C_{i,k} \cdot M_i)$ - Auxiliary function

2. 2. Solve simultaneous equations

Given

$$\begin{aligned} d(0, M) &= \text{SiO}_2 && \text{SiO}_2 \text{ material balance} \\ d(1, M) &= \text{Al}_2\text{O}_3 && \text{Al}_2\text{O}_3 \text{ material balance} \\ d(2, M) &= \text{B}_2\text{O}_3 && \text{B}_2\text{O}_3 \text{ material balance} \\ d(3, M) &= \text{CaO} && \text{CaO material balance} \end{aligned}$$

$$M := \text{Find}(M)$$

$$M = \begin{pmatrix} 54.139 \\ 14.284 \\ 18.28 \\ 28.919 \end{pmatrix} \begin{array}{l} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \end{array}$$

3. Processing of results

3. 1. Preliminary result

3. 1. 1. Rated specific glass melts consumption, kg

$$M_{\text{sgm}} := \sum_{k=0}^5 d(k, M) = 99.829$$

3. 1. 1. Rated specific LOI consumption, kg

$$\text{loi_sand} := 54.139 \cdot 0.0010 = 0.054$$

$$\text{loi_clay} := 14.284 \cdot 0.0030 = 0.043$$

$$\text{loi_lime} := 18.28 \cdot 0.1200 = 2.194$$

$$\text{loi_dolomite} := 28.919 \cdot 0.4669 = 13.502$$

$$\text{loi_sand} + \text{loi_clay} + \text{loi_lime} + \text{loi_dolomite} = 15.793$$

$$M_{\text{loi}} := d(6, M) = 15.793$$

3. 2. Definitive result

3. 2. 1. Real composition of glass, %

$$\text{sand_real} := M_0 - \text{loi_sand} = 54.085$$

$$\text{clay_real} := M_1 - \text{loi_clay} = 14.241$$

$$\text{lime_real} := M_2 - \text{loi_lime} = 16.086$$

$$\text{dolomite_real} := M_3 - \text{loi_dolomite} = 15.417$$

$$\text{sand_real} + \text{clay_real} + \text{lime_real} + \text{dolomite_real} = 99.829$$

$$\text{SiO2_real} := 100 \cdot \frac{\text{SiO2}}{\text{M_sgm}} = 54.593$$

$$\text{CaO_real} := 100 \cdot \frac{\text{CaO}}{\text{M_sgm}} = 22.038$$

$$\text{Al2O3_real} := 100 \cdot \frac{\text{Al2O3}}{\text{M_sgm}} = 14.525$$

$$\text{Na2O_real} := 100 \cdot \frac{\text{d}(4, \text{M})}{\text{M_sgm}} = 0.081$$

$$\text{B2O3_real} := 100 \cdot \frac{\text{B2O3}}{\text{M_sgm}} = 8.515$$

$$\text{Fe3O4_real} := 100 \cdot \frac{\text{d}(5, \text{M})}{\text{M_sgm}} = 0.249$$

$$\text{SiO2_real} + \text{Al2O3_real} + \text{B2O3_real} + \text{CaO_real} + \text{Na2O_real} + \text{Fe3O4_real} = 100$$

3. 2. 2. Specific consumption of batch's components, $\frac{\text{kgComponent}}{100\text{kg GlassMelts}}$

$$M_0 := 100 \cdot \frac{\text{sand_real}}{\text{M_sgm}} = 54.178$$

$$M_2 := 100 \cdot \frac{\text{lime_real}}{\text{M_sgm}} = 16.113$$

$$M_1 := 100 \cdot \frac{\text{clay_real}}{\text{M_sgm}} = 14.266$$

$$M_3 := 100 \cdot \frac{\text{dolomite_real}}{\text{M_sgm}} = 15.443$$

$$M = \begin{pmatrix} 54.178 \\ 14.266 \\ 16.113 \\ 15.443 \end{pmatrix} \begin{array}{l} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \end{array}$$

3. 2. 3. Specific consumption of batch, $\frac{\text{kgBatch}}{100\text{kg GlassMelts}}$

$$M_{\text{sum}} := M_0 + M_1 + M_2 + M_3 = 100$$

3. 2. 4. Specific consumption of LOI,

$$\text{- mass, } \frac{\text{kg}}{100\text{kg GlassMelts}}$$

$$M_{\text{loi}} := 100 \cdot \frac{M_{\text{loi}}}{M_{\text{sgm}}} = 15.82$$

$$\text{- volume, } \frac{\text{m}^3}{100\text{kg GlassMelts}}$$

$$V_{\text{-loi}} := \frac{M_{\text{-loi}}}{\text{density}_{\text{CO}_2}} = 8.054$$

APPENDIX 2

Material Balance of glass manufacturing using fly ash

1. Legend and basic data

1. 1. Legend

C_{i,k} - mass content of k oxide within i component, $\frac{\text{kgOxide}}{\text{kgComponent}}$

M_i - specific consumption i component within batch, $\frac{\text{kgComponent}}{100\text{kg GlassMelts}}$

1. 2. Composition of glass, %

SiO₂ := 54.5 Al₂O₃ := 14.5 CaO := 22 B₂O₃ := 8.5 Na₂O := 0.5

SiO₂ + Na₂O + CaO + Al₂O₃ + B₂O₃ = 100

1. 3. Composition of batch and fly ash, %

	Si	Al	B	Ca	Na	Fe	LOI		
C :=	0.9948	0.0014	0	0.0010	0.0015	0.0003	0.0010)	
	0.0030	0.9920	0	0.0010	0	0.0010	0.0030)	sand
	0.0100	0.0060	0.4650	0.3950	0	0.0040	0.1200)	clay
	0.0144	0.0050	0	0.5087	0	0.0050	0.4669)	lime borate
	0.5	0.2	0	0.2	0.02	0.05	0.03)	dolomite
)	fly ash [2], [3]
								M :=	
)	

*Si - SiO₂, Al - Al₂O₃, B - B₂O₃, Ca - CaO, Na - Na₂O₂, Fe - Fe₃O₄, LOI - loss on ignition (CO₂)

1. 4. Density of CO₂, $\frac{\text{kg}}{\text{m}^3}$

$$\text{density}_{\text{CO}_2} := \frac{44}{22.4} \quad \text{density}_{\text{CO}_2} = 1.964$$

2. Calculation of specific consumption of components

2. 1. Total specific consumption k oxide within batch, $\frac{\text{kgOxide}}{(100\text{kg GlassMelts})}$

$$d(k, M) := \sum_{i=0}^4 (C_{i,k} \cdot M_i) \quad \text{- Auxiliary function}$$

2. 2. Solve simultaneous equations

Given

$$d(0, M) = \text{SiO}_2 \quad \text{SiO}_2 \text{ material balance}$$

$$d(1, M) = \text{Al}_2\text{O}_3 \quad \text{Al}_2\text{O}_3 \text{ material balance}$$

$$d(2, M) = \text{B}_2\text{O}_3$$

$$d(3, M) = \text{CaO} \quad \text{CaO material balance}$$

$$d(4, M) = \text{Na}_2\text{O} \quad \text{Na}_2\text{O}_3 \text{ material balance}$$

$$M := \text{Find}(M)$$

$$M = \begin{pmatrix} 43.344 \\ 9.957 \\ 18.28 \\ 20.398 \\ 21.749 \end{pmatrix} \begin{array}{l} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \\ \text{fly ash} \end{array}$$

3. Processing of results

3. 1. Preliminary result

3. 1. 1. Rated specific glass melts consumption, kg

$$\text{loi_sand} := M_0 \cdot 0.0010 = 0.043$$

$$\text{loi_clay} := M_1 \cdot 0.0030 = 0.03$$

$$\text{loi_lime} := M_2 \cdot 0.1200 = 2.194$$

$$\text{loi_dolomite} := M_3 \cdot 0.4669 = 9.524$$

$$\text{loi_ash} := M_4 \cdot 0.03 = 0.652$$

$$\text{loi_sand} + \text{loi_clay} + \text{loi_lime} + \text{loi_dolomite} + \text{loi_ash} = 12.443$$

$$M_{\text{sgm}} := \sum_{k=0}^5 d(k, M) = 101.286$$

3. 1. 1. Rated specific LOI consumption, kg

$$M_{\text{loi}} := d(6, M) = 12.443$$

3. 2. Definitive result

3. 2. 1. Real composition of glass, %

$$\text{sand_real} := M_0 - \text{loi_sand} = 43.301$$

$$\text{clay_real} := M_1 - \text{loi_clay} = 9.928$$

$$\text{lime_real} := M_2 - \text{loi_lime} = 16.086$$

$$\text{dolomite_real} := M_3 - \text{loi_dolomite} = 10.874$$

$$\text{ash_real} := M_4 - \text{loi_ash} = 21.097$$

$$\text{SiO2_real} := 100 \cdot \frac{\text{SiO2}}{M_{\text{sgm}}} = 53.808$$

$$\text{CaO_real} := 100 \cdot \frac{\text{CaO}}{M_{\text{sgm}}} = 21.721$$

$$\text{Al2O3_real} := 100 \cdot \frac{\text{Al2O3}}{M_{\text{sgm}}} = 14.316$$

$$\text{Na2O_real} := 100 \cdot \frac{d(4, M)}{M_{\text{sgm}}} = 0.494$$

$$\text{B2O3_real} := 100 \cdot \frac{\text{B2O3}}{M_{\text{sgm}}} = 8.392$$

$$\text{Fe3O4_real} := 100 \cdot \frac{d(5, M)}{M_{\text{sgm}}} = 1.269$$

$$\text{SiO2_real} + \text{Al2O3_real} + \text{B2O3_real} + \text{CaO_real} + \text{Na2O_real} + \text{Fe3O4_real} = 100$$

3. 2. 2. Specific consumption of batch's components, $\frac{\text{kgComponent}}{100\text{kg GlassMelts}}$

$$M_0 := 100 \cdot \frac{\text{sand_real}}{M_{\text{sgm}}} = 42.751$$

$$M_2 := 100 \cdot \frac{\text{lime_real}}{M_{\text{sgm}}} = 15.882$$

$$M_1 := 100 \cdot \frac{\text{clay_real}}{M_{\text{sgm}}} = 9.802$$

$$M_3 := 100 \cdot \frac{\text{dolomite_real}}{M_{\text{sgm}}} = 10.736$$

$$M_4 := 100 \cdot \frac{\text{ash_real}}{M_{\text{sgm}}} = 20.829$$

$$M = \begin{pmatrix} 42.751 \\ 9.802 \\ 15.882 \\ 10.736 \\ 20.829 \end{pmatrix} \begin{array}{l} \text{sand} \\ \text{clay} \\ \text{lime borate} \\ \text{dolomite} \\ \text{fly ash} \end{array}$$

3. 2. 3. Specific consumption of batch, $\frac{\text{kgBatch}}{100\text{kg GlassMelts}}$

$$M_{\text{sum}} := M_0 + M_1 + M_2 + M_3 + M_4 = 100$$

3. 2. 4. Specific consumption of LOI,

- mass, $\frac{\text{kg}}{100\text{kg GlassMelts}}$ $M_{\text{loi}} := 100 \cdot \frac{M_{\text{loi}}}{M_{\text{sgm}}} = 12.285$

- volume, $\frac{\text{m}^3}{100\text{kg GlassMelts}}$ $V_{\text{loi}} := \frac{M_{\text{loi}}}{\text{density}_{\text{CO}_2}} = 6.254$