THERMOBAT

A Ferrosilicon Latent Heat Thermophotovoltaic Battery

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Silicon and Boron Resource Mapping

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Abstract

The eutectic Fe-Si-B alloy is studied for thermal energy storage as a part of the THERMOBAT project. A key objective is to develop a new process for producing this alloy using raw or waste materials. The goal is to reduce the cost and environmental impact of the process. In this regard, geological surveys, mining companies, and industries involved in the project is collected to facilitate the mapping of iron, silicon, and boron resources.

Natural boron minerals can be discovered through geological surveys. Secondary or waste materials containing boron can be sourced from the boron mining industry, borosilicate glass production, and agriculture. Natural boron minerals have boron content higher than 55 wt. % after removing crystal waters. Boron mining waste has boron content ranging from 19-28% after the loss on ignition (LOI) removal. However, these materials also contain multiple oxides that needs removal. Borosilicate glass has lower boron levels, 10-20% depending on usage, and fewer impurities that also need removal. Agricultural minerals contain oxides similar to those in boron mining waste.

Europe offers multiple opportunities for sourcing different grades of silicon. Elkem, the largest silicon producer in Norway, plays a significant role in the industry. If radiclone dust and quartz residues can be used for the process, this will increase the efficiency of the silicon industry and reduce waste going to landfills. There are likely oxides that needs to be removed from these materials as well, that will not be removed through slag.

Ferroboron and ferrosilicon are especially interesting from the iron industry. Ferroboron provides both iron and boron, and potentially decreases the boron content necessary for the boron source. However, ferroboron's higher melting point is a challenge. Ferrosilicon, widely produced in Europe, provides both iron and silicon. Additionally, the ferrosilicon production process also creates siliceous dust. This material is currently a waste material, and if used in the process, could improve the efficiency of ferrosilicon production, and reduce landfill waste.

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1. Introduction

The demand for energy storage is increasing with the increasing demand for renewable energy sources. Especially variable energy sources need cost-effective energy storage. One solution for this would be thermal energy storage (TES). Although there is an efficiency penalty converting heat to energy, the low cost is an advantage. From the previous AMADEUS project, it was found that ferrosilicon alloys exhibit promising properties for latent-heat TES (LHTES). Consequently, the eutectic alloy Fe-Si-B has emerged as the primary focus of the THERMOBAT project, within which this study is taking part. The project will, among others, develop a new process for producing FeSiB alloys from raw or waste material. The foundation of this new process is Reaction 1 below, although other alternatives will be considered.

$$B_2O_3 + \frac{3}{2}Si = 2B + \frac{3}{2}SiO_2 \qquad 1$$

The goal of this new process is to minimize cost and mitigate environmental impact. In order to achieve this, a thorough material mapping is crucial. Boron is the greatest factor with regards to cost, this study predominantly focuses on mapping boron. Additionally, a brief overview of silicon and iron production in Norway is provided, and along with a brief introduction to thermal energy storage and phase change materials. Several experiments were conducted on borosilicate glass to determine its composition and test the characterization methods applied to this type of material.

2. Thermal energy storage

Thermal energy storage (TES) is based on the principle of using energy to cool, heat, melt, solidify or vaporize a material, and retrieve this energy again as heat when reversing the process. There are two main categories for TES: Sensible heat thermal energy storage (SHTES) and latent heat thermal energy storage (LHTES) [1].

2.1. Sensible heat thermal energy storage

SHTES is based on storing thermal energy through increasing the temperature of a solid or liquid, utilizing the materials change in heat capacity and temperature during charging and discharging. The amount of heat stored can be given as a function, equation 2, of the specific heat of the material, the temperature change and the mass of the material.

$$Q = \int_{T_i}^{T_f} mC_p dT = mC_{ap}\left(T_f - T_i\right) \qquad 2$$

where Q is the quantity of heat stored, T_i and T_f are the initial and final temperature respectively, m is the mass of the material, C_p is the specific heat, and C_{ap} is the average specific heat between T_i and T_f. Heat will be reduced through radiation, conduction, and convection by both the storage material and through the reduced temperature due to cloudy weather or cooler nights. An example of this kind of system is a space heating system using tanks of warm water as TES [1].

2.2. Latent heat thermal energy storage

LHTES is based on a material absorbing and releasing heat to undergo a phase change, typically a solid-liquid phase change. Solid-gas and liquid-gas changes are impractical due to the large volume change. Solid-solid and liquid-liquid changes have small volume change but have a smaller heat capacity than a solid-liquid change. The material used for this kind of energy storage is called a phase change material (PCM), and the storage capacity is given by Equation 3 below:

$$Q = \int_{T_i}^{T_m} mC_p dT + ma_m \Delta H_m + \int_{T_m}^{T_f} mC_p dT \qquad 3$$

where Q is the quantity of heat stored, T_i, T_m and T_f are the initial, melting, and final temperature respectively, m is the mass of the material, C_p is the heat capacity, a_m is the fraction melted, and ΔH_m is the heat of melting per unit mass. LHTES has higher storage density in a narrower temperature range due to the high heat capacity at the phase transition [1].

3. Phase change Materials

PCMs can store and release energy as both sensible and latent heat, where latent heat has the highest energy density. There are multiple criteria to the properties of the material to achieve the best PCM possible, which are as follows [1]:

Thermal properties:

- Melting temperature in operating range
- High phase transition latent heat per unit volume
- High heat capacity to provide extra storage through sensible heat
- High thermal conductivity of both phases

Physical properties:

- Small volume change under phase transition
- Low vapor pressure at operating temperature
- Favorable phase equilibrium
- Congruent melting of the PCM
- High density

Kinetic properties:

- No super-cooling
- High nucleation rate
- Adequate rate of crystallization

Chemical properties:

- Long term chemical stability
- A completely reversible cycle
- Compatibility with the construction materials
- No corrosion influence on the construction material
- Non-toxic, non-flammable and non-explosive for safety

Most materials are unable to meet all the criteria, but progress in design and characterization of new materials are opening for new possibilities [1]. Khare et al. [2] found that aluminum, magnesium, and silicon were useful for TES in the range 400-700 °C. Gilpin [3] tried to use pure silicon for ultra-high temperature energy storage. However, as silicon has a thermal expansion of 10%, breakage of the crucible is likely during solidification. Datas et al. [4] proposed a Si-B alloy. Homa et al. [5] found that this alloy had strong penetration in a graphite crucible. An Fe-Si-B alloy was suggested as a possible PCM material for the AMADEUS project due to its low volume change, high latent heat, thermal conductivity, moderate melting point, and low cost [6].

3.1. Fe-Si-B alloy

In a study byJiao et al. [6] the eutectic Fe-Si-B alloy was studied. This alloy was found to consist of 64 wt. % iron, 26 wt. % silicon, and 9 wt. % boron and has high latent heat at the theoretical melting temperature 1157 °C. The experiments were done in an isotropic graphite crucible. The isotropic structure and properties make it easy to machine, and the covalent bonds make the crucible electrically conductive. The crucible is able to withstand long term use at temperatures above 2000 °C and is chemically stable with some exceptions. The low thermal expansion and high thermal conductivity give a good shock resistance. The materials were tested using 1 to 4 thermal cycles of 1157 ± 20 °C and 1157 ± 100 °C.

The study found that the theoretical fusion enthalpy of eutectic Fe-Si-B was 1250 kWh/m^3, higher than most other PCM candidates. SiC and B_4C were found at the edge of the treated alloy in the crucible. The alloy penetrated the crucible, however these materials act as a shield against further penetration. The penetration is therefore negligible and there were no degradation effects on the container. A shrinkage was found in the alloy, causing porosity. However, the lack of expansion is positive for the use as a PCM [6].

4. Boron

When looking for Boron to recycle into Fe-Si-B alloy, there are multiple options. The ones studied in this report are borates, boron waste from mining, borosilicate glass, and boron in agriculture. Borates are compounds that contain boric acid and are found in minerals like borax, ulexite, and colemanite [7]. The boron waste from mining, on the other hand, has multiple impurities of varying levels. Thus, refining must be done if the impurities are not removed through the slag. Borosilicate glass is a type of glass with a composition that includes SiO_2 and B_2O_3 as its main components. In agriculture, boron often comes as a mineral or an acid [8], or it is mixed into fertilizer. As mineral from agriculture, it will be similar to the boron waste from mining.

4.1. Borates

Borate refers to any compound that contains boric oxide (B_2O_3). Borates are widely distributed in nature in low concentrations in soil and rock. It is primarily found as salts of sodium, calcium, and magnesium and has been found in over 150 minerals, with the most important being borax, ulexite, and colemanite [7]. Although borate minerals are found in many countries, production is limited. The United States and Turkey are the dominant producers, supplying around 90% of the world's borate supplies. Table 1 summarizes the common borate minerals in the world.

Table 1: Common Borate Minerals. [7]

Mineral	Empirical Formula	B_2O_3 Content (wt. %)
Sassolite	$B(OH)_3$ or $B_2O_3 \cdot 3H_2O$	56.4
Borax (Tincal)	$Na_2B_4O_7 \cdot 10H_2O$	36.5
Tincalconite	$Na_2B_4O_7 \cdot 5H_2O$	48.8
Kernite	$Na_2B_4O_7 \cdot 4H_2O$	51.0
Ulexite	$NaCaB_5O_9 \cdot 8H_2O$	43.0
Probertite	$NaCaB_5O_9 \cdot 5H_2O$	49.6
Priceite (Pandermite)	$Ca_4B_{10}O_{19} \cdot 7H_2O$	49.8
Inyoite	$Ca_2B_6O_{11} \cdot 13H_2O$	37.6
Meyerhofferite	$Ca_2B_6O_{11} \cdot 7H_2O$	46.7
Colemanite	$Ca_2B_6O_{11} \cdot 5H_2O$	50.8
Hydroboracite	$CaMgB_6O_{11} \cdot 6H_2O$	50.5
Inderborite	$CaMgB_6O_{11} \cdot 11H_2O$	41.5
Kurnakovite	$Mg_2B_6O_{11} \cdot 15H_2O$	37.3
Inderite	$Mg_2B_6O_{11} \cdot 15H_2O$	37.3
Szaibelyite (Ascharite)	$Mg_2B_2O_5 \cdot H_2O$	41.4
Suanite	$Mg_2B_2O_5$	46.3
Kotoite	$Mg_3B_2O_6$	36.5
Pinnoite	$MgB_2O_4 \cdot 3H_2O$	42.5
Boracite (Strassfurite)	$Mg_3B_7O_{13}Cl$	62.2
Datolite	$Ca_2B_2Si_2O_9 \cdot H_2O$	21.8
Cahnite	$Ca_2AsBO_6 \cdot 2H_2O$	11.7
Danburite	$CaB_2Si_2O_8$	28.3
Howlite	$Ca_4Si_2B_{10}O_{23} \cdot 5H_2O$	44.5
Vonsenite (Paigeite)	$(Fe,Mg)_2FeBO_5$	10.3
Ludwigite	$(Fe,Mg)_4Fe_2B_2O_7$	17.8
Tunellite	$SrB_6O_{10} \cdot 4H_2O$	52.9

Turkey has significant borate deposits, mainly in Bigadic, Kestelek, Sultancayiri, Emet, and Kirka, as seen in Figure 1. These deposits are created during volcanic activity. They are generally interbedded with conglomerate, sandstone, tuff, tuffite, claystone, marl, and limestone. They are usually enveloped by, or grade into, limestones or claystones [7].
Each deposit has its unique characteristics [7]:

1. Bigadic: the borates contain the world's largest colemanite and ulexite.
2. Sultancayiri: priceite is abundant, along with colemanite and howlite.
3. Kestelek: colemanite, ulexite, and probertite are the main minerals.
4. Emet: the borates mainly consist of colemanite with minor ulexite, hydroboracite, and meyerhofferite.
5. Kirka: the only deposit in Turkey contains sodium borates like borax, tincalconite, and kernite. Borax is the main mineral, with lesser amounts of colemanite and ulexite.

These deposits play an important role in Turkey's economy, with some being the largest of their kind globally.

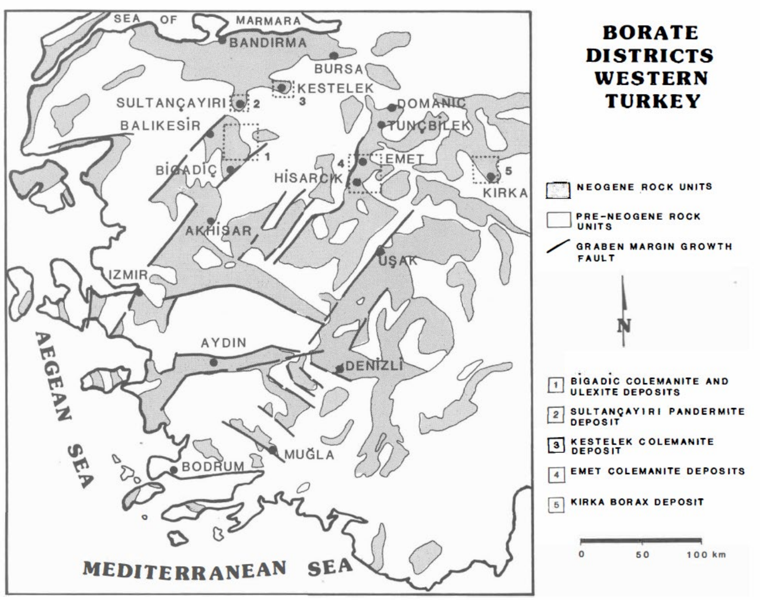

Figure 1: Borate districts of western Turkey. [7]

4.1.1. Colemanite

Colemanite ($Ca_2B_6O_{11}\cdot 5H_2O$) is the most commonly available boron mineral, contains 40±0.50% B_2O_3. This mineral dissolves gradually in water and quickly in acidic environments. The ore undergoes enrichment in a processing plant. Afterward, the concentrated product is passed through crushing and grinding processes respectively to obtain milled product. Finally, it is packaged and prepared for sale [9]. The chemical composition of commercial colemanite is shown in Table 2, while the content of heavy metals is presented in Table 3.

Table 2: Chemical content in the commercial colemanite. [9]

Component	Content (wt. %)	
	- 45 Micron	-75 Micron
B_2O_3	40.00 ± 0.50 %	40.00 ± 0.50 %
CaO	27.00 ± 1.00 %	27.00 ± 1.00 %
SiO_2	4.00 - 6.50 %	4.00 - 6.50 %
SO_4	0.60% max	0.60% max.
As	35 ppm max	35 ppm max.
Fe_2O_3	0.08% max	0.08% max.
Al_2O_3	0.40% max	0.40% max.
MgO	3.00% max	3.00% max.
SrO	1.50% max	1.50% max.
Na_2O	0.50% max	0.50% max.
Heat loss	25.00% max	25.00% max.
Humidity	1.00% max	1.00% max.
Bulk density	1.00 ton/m^3 max	1.00 ton/m^3 max.

Table 3: Heavy metal content. [9]

Component	Content (ppmw)
As	35 max.
Cd	<0.005
Pb	<0.010
Cr	<0.005
Hg	<0.010

Raw colemanite (unmilled) undergoes decrepitation at its decomposition temperature (~412 °C). Accordingly, the decrepitation breaks the colemanite particles into fine powders. So, unmilled colemanite minerals have to be calibrated at around 600 °C before using at high temperatures, aiming to remove the crystal water [10]. According to the thermal behavior of the raw materials with the DTA-TG analysis (Figure 2), colemanite loses approximately 20 wt.% of its crystal water through endothermic reactions at temperatures between 300 and 460°C. Dehydration occurs at 335 and 370°C in raw material samples. So, colemanite decomposed to B_2O_3 and CaO in their amorphous forms upon calcination of 3h at 600 °C. This property can be used to separate colemanite from impurities. Upon further heating above 670°C, raw material colemanite is hardened [11].

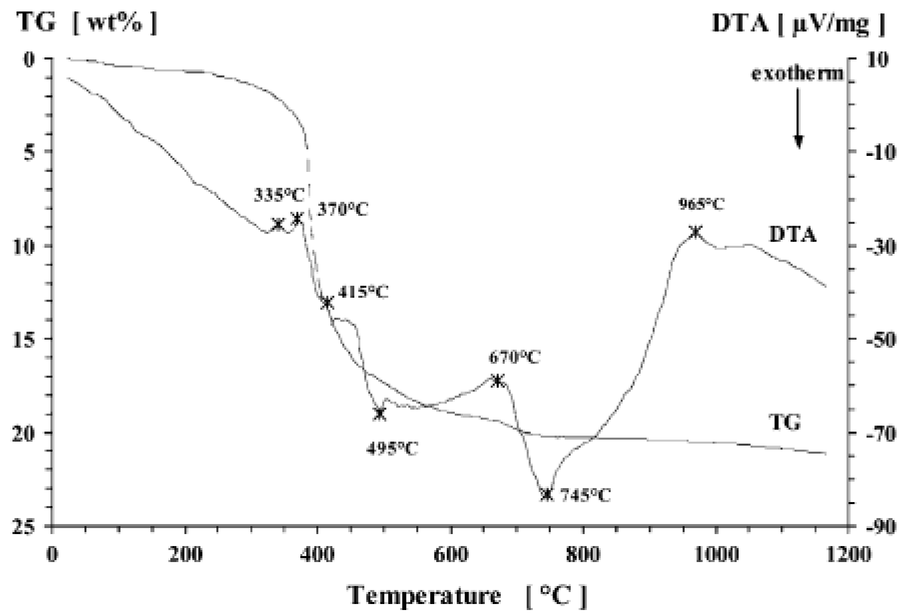

Figure 2: DTA-TG analysis of commercial colemanite. [11]

4.2. Boron mining wastes

An issue with the current boron production is the storage of boron wastes. These have been disposed in tailing dams, which has the potential of leaching and polluting groundwater and soil, potentially resulting in substantial environmental concerns [12,13]. This also results in an economical loss as 500 kg of dewatering sieve waste is created per ton of borax production [14,15]. According to Kavas [13], the Etibank Kirka borax plants in Turkey produces 120 000 tonnes of clay and fine wastes annually.

4.2.1. EtiMine

Turkey has the largest Boron reserve in the world, having 73% of the total world boron reserves according to Eti Maden. The most abundant boron minerals are Tincal ($Na_2B_4O_7 \cdot 4H_3O$), Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) and Ulexite ($NaCaB_5O_9 \cdot 5H_2O$). Etimine S.A. (subsidiary of Etimaden) had a total refined boron production of approximately 2.7 tons in 2017 [16].
Boron waste from Turkey has been in multiple studies for use in cement and brick. Studies with boron composition above 10% have been selected and the chemical compositions of the wastes are summarized in Table 4, where LOI represents Loss on ignition of a mineral.

Table 4: Chemical composition of boron waste from boron production in Turkey from multiple studies.

Study	B_2O_3	SiO_2	MgO	CaO	Na_2O	Al_2O_3	Fe_2O_3	K_2O	SrO	LOI

[15]	22.48	14.01	14.12	16.43	8.32	1.68	1.57	1.39	-	20.00
[12]	12.60	15.20	14.20	16.80	4.10	1.70	0.20	0.60	-	34.10
[13]	11.92	8.26	15.56	10.75	7.63	0.09	0.13	-	1.23	43.33
[13]	13.09	12.53	14.97	11.18	7.63	0.44	0.24	-	0.67	36.24
[17]	16.23	12.24	2.85	12.15	12.9	4.37	0.15	-	-	39.11
[18]	19.70	16.10	6.90	26.40	0.20	0.90	0.10	0.50	1.20	28.00

When heated, the LOI will evaporate, resulting in an increase of the compositions. These values are estimated and are summarized in Table 5 below. The B_2O_3 contents have increased from 11-23 % to 19-28 %.

Table 5: Estimated chemical composition of boron waste from boron production in Turkey after removal of LOI with the corresponding studies for original values.

Study	B_2O_3	SiO_2	MgO	CaO	Na_2O	Al_2O_3	Fe_2O_3	K_2O	SrO
[15]	28.10	17.51	17.65	20.54	10.40	2.10	1.96	1.74	0.00
[12]	19.27	23.24	21.71	25.69	6.27	2.60	0.31	0.92	0.00
[13]	21.45	14.86	28.00	19.34	13.73	0.16	0.23	0.00	2.21
[13]	21.55	20.63	24.64	18.40	12.56	0.72	0.40	0.00	1.10
[17]	26.65	20.10	4.68	19.95	21.19	7.18	0.25	0.00	0.00
[18]	27.36	22.36	9.58	36.67	0.28	1.25	0.14	0.69	1.67

4.2.2. Rio Tinto

Rio Tinto was founded in 1873 in Andalusia, Spain. They worked in multiple fields in 35 countries [19]. One of these was borate mining in Boron, California. This mine produced one million tonnes of refined borates annually, approximately 30% of the global demand. The mine is operated by their borax business, U.S. Borax [20] .

4.3. Borosilicate glass

Glass making can be traced back to 2600 BC in Mesopotamia, and it's a process that has been refined for thousands of years. Glass has many applications: windows, dinnerware, cookware, shower walls, mirrors, etc. Thus, there are also many types of glass. Some common classifications are fused quarts or fused silica glass which is highly resistant to weathering and is used in tube lights and furnaces. Soda-lime silica glass is used in windows. Sodium borosilicate glass is less prone to cracking and therefore used in lab equipment and kitchenware. Lead oxide glass has high reflective properties and is used in jewelry. Clear glass, which is clear and transparent, is used in panoramic windows. Lastly, there is tinted glass, which is made with a coating or film to bestow color and reduce light transmission [21].

There are multiple processes for making glass, depending on the material and product. One common method is making float glass using a float line. This process creates flat squares which can be used for example for windows. The float line process consists of the following steps [21,22]:

1. **Melting and refining:** The raw materials, comprising of silica sand, sodium oxide, calcium oxide and magnesium are mixed. Feldspar (Al_2O_3) is also added. The materials are then heated in a furnace at 1500 °C.
2. **Float bath:** The melt flows into a float bath, consisting of molten tin. The material is cooled down to around 650 °C and take a solid ribbon shape.
3. **Annealing:** Annealing is done to remove internal stress in the glass. The solid ribbon passes through a layer cooling the material giving the final shape. This makes it easier and more predictable when cutting the glass.
4. **Inspecting:** The glass is inspected using inspection technology throughout the manufacturing procedure. Air bubbles, stress or grains of sand are identified to check the quality.
5. **Cutting:** Finally, the glass is cut to squares using diamond steels.

To create borosilicate glass, B_2O_3 is added to the mix when melting. Additionally, some new techniques are used. This gives a densely cross-linked glass network. The glass is characterized by high chemical durability and thermal resistance [23]. The chemical composition of different studies on borosilicate glass waste can be seen in Table 6. From this we see that the B_2O_3 is around 10-20 wt. %.

Table 6: Chemical composition of borosilicate glass waste from multiple studies (wt. %).

Study	B_2O_3	SiO_2	MgO	CaO	Na_2O	Al_2O_3	Fe_2O_3	K_2O	PbO
[24]	15.00	77.00	-	-	4.50	2.00	-		1.50
[25]	16.70	58.20	1.30	10.30	11.00	2.20	-	0.22	-
[26]	13.00	81.00	-	-	4.00	2.00	-		-
[27]	16.63	74.25	-	2.09	3.83	1.65	0.16	0.93	-
[28]	12.30	79.80	-	-	4.80	2.30	-	0.80	-

4.3.1. Corning

Corning is a MultiTech company in USA with research centers in North America, Europe, and Asia. Corning serves in five markets: optical communications, mobile consumer electronics, display, automotive, and life sciences [29]. One of the products Corning makes is pharmaceutical glass. This is made of borosilicate glass, and can be in the shape of vials, glass packaging, and pharmaceutical tubing. The tubing is then converted into glass vials, cartridges, ampules, and syringes by the customer [30].

4.3.2. Schott

Schott is founded in Jena, Germany, in 1884. Otto Schott explores and develops a number of new glass types and becomes the founder of the Schott & Associates Glass Technology Laboratory, which later becomes Schott AG. In 2020, Schott announces they would become climate neutral by 2030 [31]. Today, Schott is one of the leading specialty glass companies in the world, with units in 34 countries [32].

4.3.3. Gerresheimer

Gerresheimer is a company based in Germany who does medicine packaging, drug delivery devices and solutions focused on pharma, health, well-being, and biotech. One material they use is borosilicate glass, which they receive as glass tubes from Schott and Corning. The borosilicate glass tubes are processed into ampules, vials, and cartridges at Gerresheimer. Table 7 and Table 8 show the chemical composition of borosilicate glasses in Gerresheimer.

Table 7: Chemical composition of 51A and 51D tubing supplied to Gerresheimer by Corning (wt. %).

Material	B_2O_3	SiO_2	CaO + MgO	Na_2O	Al_2O_3	Fe_2O_3	K_2O	BaO	TiO_2
51A [33]	10.5	70.2	1.0	5.8	5.8	1.0	1.3		3.0
51D [34]	11.2	73.0	1.0	6.8	6.8	<0.04	1.2	<0.04	<0.03

Table 8: Chemical composition of FIOLAX clear and amber tubing supplied to Gerresheimer by Schott (wt. %).

Material	B_2O_3	SiO_2	CaO	Na_2O	Al_2O_3	Fe_2O_3	K_2O	BaO	TiO_2
Clear [35]	10.5	75.0	1.5	7.0	5.0	-	-	-	-
Amber [36]	7.5	70.0	<1.0	6.5	6.0	1.0	1.0	2.0	5.0

4.4. Agriculture

Boron is an essential micro-nutrient for plant development, growth, crop yielding and seed development in agriculture. Boron is typically added in agriculture as a borate, generally divided into refined and minerals. Refined sodium borates can be applied directly to the soil or by spraying on plants. Boric acid is often added in clear liquid-based foliar fertilizer. Disodium octaborate tetrahydrate is a borate specially made for agriculture and has a higher solubility than minerals and the previously mentioned refined products. The minerals colemanite and ulexite are added to the soils and are slow releasing borate compounds. It has also been reported that these have been used in liquid applications [8].

5. Silicon

In this project, our goal is to create a method capable of manufacturing FeSiB alloys through the silicothermic reduction in a molten state. The primary chemical reaction involved is $3/2Si + B_2O_3 = 2B + 3/2SiO_2$. The process begins with a molten mixture of ferrosilicon alloy ($FeSi_x$) and B_2O_3 based materials, and the reaction generates a molten FeSiB alloy and SiO_2 combining with other oxides. Therefore, attention in this report will be paid on the sources of waste silicon materials.

The element silicon has atomic number 14 and belongs to group 6A in the periodic table. Silicon is estimated to make up 27.5 wt. % of the earth's crust and is the second most abundant element after oxygen [37]. Silicon has a melting point of 1414 °C and is one of the few materials which expand during solidification (~10%) [3,38]. It is usually found in nature as silicon oxides such as sand (silica), quartz, rock crystal, etc. Silica can be treated with carbon to create silicon by the following reaction.

$$SiO_2 + 2C = Si + 2CO \quad (4)$$

This silicon production does not result in pure silicon, but rather at least 96 % silicon with some tramp elements. Silicon is commonly used for alloying other metals, especially aluminum, feedstock for the silicone industry, semiconductors, and solar industry. More than 90 % of electronic components are silicon-based. Solar cell is also an important market in Norway [37].

SIBELCO (Belgium), Quarzwerke (Germany), Mikroman Maden, Kula mine (Turkey), along with ERIMSA, RAMSA, and Cuarzos Industriales (Spain) are the main suppliers of quartz and silica sand across Europe. These companies are pivotal in ensuring the availability of these essential raw materials in the production of silicon-based alloys.

A list of smelters with silicon products in European area can be found in Table 9 below. There are 3 companies with smelters for silicon materials in Norway: Elkem, Washington Mills, Wacker Chemie, and Ferroglobe. As seen, Elkem has multiple locations for different products and is Norway's largest silicon producer [37].

Table 9: List of producers of silicon materials in Norway and their products. [39]

Producer	Owner	Product
Elkem Bremanger	Elkem	Metallurgical silicon and microsilica
Elkem Thamshavn	Elkem	Metallurgical silicon
Washington Mills	Washington Mills	Silicon carbide
Holla Metal	Wacker Chemie	Metallurgical silicon
Elkem Rana	Elkem	Microsilica
Elkem Salten	Elkem	Pure silicon and microsilica
Ferroglobe	-	Silicon Metal and Silicon based alloys

5.1. Elkem

Elkem is the largest silicon producer of Norway, and their main products are silicon, ferrosilicon, carbon, energy, and microsilica. Elkem has 4 smelters in Norway producing silicon and ferrosilicon. These are Bremanger, Thamshavn, Rana, and Salten. Additionally, Elkem has production units in Iceland, Bracil, China, Canada, and South Africa [37,39].

5.2. Wacker Chemie

Wacker is a German multinational company. In 2010 they bought Fesil's plant Holla metall in Sør- Trøndelag. With four furnaces the plant has an annual silicon production of about 40, 000 tonnes [37]. The silicon is then transported to Germany where it is mainly used for silicone production, making the company less dependent on the global market for metallurgical-grade silicon [40].

5.3. Washington Mills

Washington Mills is an American company producing abrasive grains, powders, surface treatments, and specialty fused minerals. They are the only producer of brown fused alumina, white fused alumina, silicon carbide and boron carbide crude ore in north America [41]. They have one production plant in Orkanger, Norway, for silicon carbide production [42].

5.4. Ferroglobe

Ferroglobe, our partner in the Thermobat project, is a prominent player in the global market as the largest merchant producer of silicon metal in the Western world and a leading producer of silicon-based alloys globally. The production of silicon metal was 253, 991 tonnes in 2021 and was 209, 341 tonnes in 2022 [43].

5.5. Silicon waste and scrap materials for FeSiB production

5.5.1. Si Dross

Silicon dross (also called Si sculls), a waste byproduct, is generated during the manufacturing and refining processes of silicon. Approximately 5 to 7 tonnes of silicon dross or slag is produced for every 100 tonnes of silicon. This byproduct is composed of 20 to 50 wt. % entrained silicon, while the remaining constituents are primarily silica-rich slag, comprised of calcium, aluminum, and silicon oxides. Currently, silicon dross is commercialized based on the amount of contained silicon, with prices ranging from 20% to 50% of the cost of pure silicon. Table 10 shows a typical composition of silicon dross in the plant [44].

Table 10: Typical composition of Si Dross. [44]

Substance	Content/wt. %
Si metal	45
SiO_2 (amorphous)	21-36
CaO	7-14
SiC	10
Al_2O_3	2-10
Quartz (crystalline silica)	<1

5.5.2. Si Refining Slag & Sculls

During the oxidative refining process of silicon, liquid silicon is tapped from the furnace into a ladle, in which a mixture of air and oxygen is bubbled through the melt. Consequently, silicon oxide forms at the points where bubbles interact with the melt and on the upper surface of the melt. As refining continues, reactive impurities in the melt oxidize to form metal oxides, thereby transferring the impurities from the melt to the slag

phase. When the ladle is full, the refined metal is poured into molds, and the remaining dross/slag is removed before the next tapping can take place. In general, the empty ladle weight increases from one tap to the next, since some solidified material, or sculls, are deposited.
Scull formation is a challenge in the day-to-day silicon production, since excessive scull growth causes the ladle to get smaller while at the same time changing the ladle thermal balance. On the other hand, some scull formation may be favorable since the sculls protect the ladle walls from the liquid metal. [45]
According to Elkem, their furnaces produce slag and sculls in the range of 10-15 % of total production. Table 11 shows that the Si composition is 35-40 wt. % in the Si slag and sculls producing from Elkem's Norwegian plants.

Table 11: Elkem's Norwegian plants availability of Si Slag & Sculls. (Source: Elkem)

SisAl partner name	Plant data			Material name	Chemical composition					Sizing			New Volume	Legacy Volume		Handling procedure today
	Plant name	City	Country		%SiO_2	%CaO	%Al_2O_3	%Si (metallic)	%SiC	Min	d_{50}	d_{99}	mtpa	mt	Accessible (Yes/No)	(please describe)
Elkem ASA	Elkem Bjølvefossen	Ålvik	Norway	Si Slag/sculls	Mainly	Mainly	Mainly	35-40	1-10	0		500 mm	4.500			Sold uncrushed
Elkem ASA	Elkem Rana	Mo i Rana	Norway	Si Slag/sculls	Mainly	Mainly	Mainly	35-40	1-10	0		500 mm	10.000			Sold uncrushed
Elkem ASA	Elkem Salten	Straumen	Norway	Si Slag/sculls	Mainly	Mainly	Mainly	35-40	1-10	0		500 mm	10.000			Sold uncrushed
Elkem ASA	Elkem Thamshavn	Orkanger	Norway	Si Slag/sculls	Mainly	Mainly	Mainly	35-40	1-10	0		500 mm	5.500			Sold uncrushed

A metallurgical silicon (MG-Si) production site, like Wacker's Holla site, Kyrksæterøra, Norway is typically generating several thousand tonnes of sculls (in the form of lumps) per year. Having a capacity of more than 50.000 tonnes Si per year, we could assume that the sculls production should be about 5.000 – 7.500 tonnes per year. Table 12 shows the typical composition of Si sculls producing from Wacker.

Table 12: Wacker's sculls composition. (Source: Wacker)

Oxide	Typical/wt. %
MG-Si	10-40
SiO_2	20-60
Al_2O_3	10-30
CaO	10-30

Based on above drivers the total European (incl. Eastern Europe and Russia) production of slag and sculls is estimated to be about 121000 to 182000 tonnes per year.[1]

5.5.3. Recycled PV Panels

Most models in bibliography assume 30-year average panel lifetime with 99.99% probability of loss after 40 years. [46] Silicon is, by far, the most common semiconductor material used in solar cells, representing approximately 95% of the modules sold today, in the form of crystalline silicon (c-Si). [47]

[1] Total silicon production 1213000 tonnes and 10-15% yield

Figure 3 shows the materials used from different PV panels technologies as a percentage of total panel mass from 2014 to the estimated year of 2023. By weight, typical c-Si PV panels today contain about 76% glass (panel surface), 10% polymer (encapsulant and back sheet foil), 8% aluminum (mostly the frame), 5% silicon (solar cells), 1% copper (interconnectors) and less than 0.1% silver (contact lines) and other metals (mostly tin and lead). [48]
The end-of-life PV panels are increasing at a very high rate. Only in Germany in 2050 there will be more than 4.4 million tonnes of waste PV panels with an estimated disposal cost of 200€/tonnes. At global level the estimated cumulative PV panel waste will be 60 to 78 million tonnes.
If we assume that the PV Cell represents the 5% of the PV panel weight, then by 2050 220000 tonnes will have to be disposed, only in Germany. Table 13 shows the composition of the PV cell and the ribbon, so the total silicon can be recycled is about 205436 tonnes by 2050.

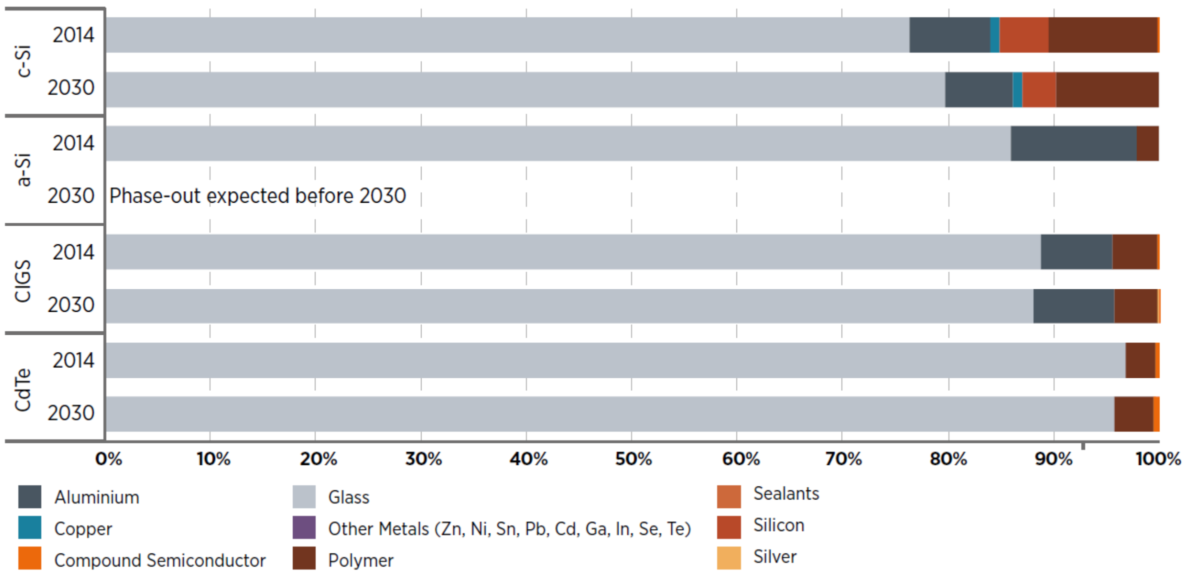

Figure 3: Evolution to 2030 of materials used from different PV panels technologies as a percentage of total panel mass. [46]

Table 13: The composition of the PV cell and the ribbon.

PV Cell	Element	Si	Al	Ag	Bi
	wt. %	93.38	5.25	0.91	0.011
PV Ribbon	Element	Cu	Pb	Sn	Ag
	wt. %	79.6	5	8.64	3.02

5.5.4. Wastes from the manufacturing of silicon semiconductor-based devices

A large amount of silicon debris particles is generated during the slicing of silicon ingots into thin wafers for the fabrication of integrated-circuit chips and solar cells [49]. In silicon wafer manufacturing for solar cells, a great amount of hazardous kerf loss silicon with tiny silicon particles is produced, resulting in serious environmental problems [50]. The kerf loss silicon is in the form of slurry that consists of pure fine particles of silicon, silica, abrasive silicon carbide (SiC) particles, metal impurities from cutting wire, polyethylene glycol solution, and additives for better particle suspension. This waste is about 90000 tonnes a year worldwide. Waste silicon slurry can be separated using physical, chemical methods or flotation [51,52]. Also decommissioning at the end of the life cycle of photovoltaic modules, which are expected to last around 30 years, is source of silicon waste. [53]

6. Iron

Steel is used by virtually everyone daily. Thus, steel has one of the greatest influences on resource consumption. The steel industry is among the highest energy-intensive industries in the world, but many work hard to be efficient and sustainable in the use of raw materials, energy, and other natural resources. One of the advantages with steel is the ability to be 100 % recycled without loss of properties. Steel has an estimated reuse of 90 % and one third of the world's steel production is based on recycling of scrap. However, due to the high demand for steel, new steel must also be produced using virgin iron ore [54].

In the manufacturing of FeSiB alloys, utilizing waste materials from the production of Ferroboron or Ferrosilicon is often preferred. This is due to these waste materials' inherent composition of iron, boron, and silicon - elements essential for the FeSiB alloy. Consequently, we've charted the sources of Ferroboron and Ferrosilicon to ensure an efficient, sustainable production process.

6.1. Ferroboron

Boron forms compounds with iron, called iron borides or ferroboron. These are thermodynamically strong chemical compounds, and dissolution of boron in liquid iron releases a large amount of heat. Properties of the different iron borides are given in Table 14.

Table 14: Properties of iron borides. [38]

Boride	B [wt. %]	T_m [°C]	ρ [g/cm^3]	ΔH^0_{298} [kJ/mol]
Fe_2B	8.79	1380	6.89	-54.47
FeB	16.17	1557	6.47	-71.23
FeB_2	27.83	2075	5.00	-

Ferroboron has traditionally been produced through an aluminothermic method according to Reaction 5.

$$\frac{1}{2}B_2O_3 + Al = B + \frac{1}{2}Al_2O_3 \qquad 5$$

The chemical compositions must satisfy the requirements given in Table 15. Ferroboron is typically melted in electric furnaces, and the bulk of the smelt grades FeB17 and FeB10. The metal receives is lined with magnesite brick and the furnace bath is mounted on a trolley and rolled under the electrodes. The melting consists of three main steps: melt formation, oxide reduction and processing of slag by precipitant. To reduce the consumption of refractories and the melting cycle, it is possible to use a tilting furnace with the release of alloy and slag [38]. However, most of the ferroboron produced today are produced in China and Russia.

Table 15: Chemical composition of different grades of ferroboron (wt. %). [38]

Grade	B, no less	Si	Al	C	S	P	Cu
FeB20	20	≤ 2	≤ 3	≤ 0.05	≤ 0.01	≤ 0/015	≤ 0.05
FeB17	17	≤ 3	≤ 5	≤ 0.20	≤ 0.02	≤ 0.03	≤ 0.10
FeB17A	17	≤ 4	≤ 0.5	4			
FeB10	10	7-15	8-12				
FeB10A	10	≤ 5	8-12				
FeB6	6	≤ 12	6-12				
FeB6A	6	≤ 5	6-12				

6.2. Ferrosilicon

Ferrosilicon is a large group of alloys from iron and silicon system, widely used in the production of castings from iron and steel. There are multiple silicides in the Fe-Si system: Fe_3Si, Fe_2Si, Fe_5Si_3, FeSi, and $FeSi_2$. Ferrosilicon is produced from pre-washed, crushed, and sorted quartzite with a particle size of 20-80 mm. The quartzite must contain no less than 97 % SiO_2 and no more than 1.5 % Al_2O_3.

During smelting of ferrosilicon, gases with high contents of fine siliceous dust are created. These contain 80-95 wt. % SiO_2, and account for the bulk loss of silicon. This amounts to 10-15 % when observing smelting grade FS75 (GOST1415-93). A use for this material is an urgent task of ferrosilicon production, as this would save material resources and increase the efficiency of solving the environmental protection problem. One such possibility is to use the dust as part of building cement. [38]

In Europe, the key producers are typically found in Norway, Iceland, Spain, and France.

Elkem and Finnfjord [39] are the main ferrosilicon producers in Norway. Finnfjord is located in Finnsnes, Nordland. It is one of the most energy-efficient and environmentally friendly producers of ferrosilicon and is working towards becoming the first ferrosilicon producer in the world with no CO_2-emissions. In total they have 3 furnaces with a capacity of 100 000 tonnes of ferrosilicon [55].

Elkem Iceland (a subsidiary of Elkem ASA) [56] is the ferrosilicon producer in Iceland. The production capacity of the factory’s metal melting furnaces is approximately 120, 000 tons.

Ferroglobe, one of the largest global producers of ferrosilicon, operates ferrosilicon plants in Spain, France, and Slovakia within Europe. According to statistics, the production of silicon-based alloys by Ferroglobe reached 242,767 tonnes in 2021, and 204, 076 tonnes in 2022 [43].

7. Conclusion

All the sources of boron will need an additional step for removal of oxides that cannot be removed through slag. When comparing compositions, borates are the best option than others. Boron mining waste is clearly better than borosilicate glasses, due to its high levels of B_2O_3. Boron minerals from agriculture would be similar to the boron mining waste.

Borates are considered promising materials in the production of FeSiB alloys. The primary borates include borax, ulexite, and colemanite, with the United States and Turkey supplying 90% of the world's borate resources. These primary borates contain more than 36.5 wt. % B_2O_3. By removing the crystal water through calcination, the B_2O_3 content can be further increased to over 55 wt. %.

The boron mining wastes have good levels of B_2O_3 content, 11-23 % with LOI and 19-28 % after LOI removal. It would be a possible use for the waste material that is currently going to tailing dams. This will increase material efficiency for the boron industry, as well as reducing the potential boron pollution.

The borosilicate glass contains lower lever of impurities. Some of these must also be removed through an extra process, depending on the levels and to which degree they affect the final product. The borosilicate glass with low levels of impurities will usually be recycled, thus the glass wastes are likely to be material with higher impurities. The B_2O_3 content is also lower, depending on the borosilicate glass. The glass mentioned from Schott and Corning contain approximately 10-11wt. % B_2O_3. When mixing with iron, this will decrease. Thus, achieving the necessary boron content will be harder without another source of boron.

Boron from agriculture often comes in the form of minerals and boric acid. The minerals will be similar to the boron mining waste with regards to which oxides can be found in the material, although composition will differ. Very little information was found with regards to waste of boron in agriculture. As the minerals can be used as is or the minerals and boric acid can be added to fertilizer as needed, there is likely little waste useful for this project. Further research must be done if this route is to be considered.

Europe boasts numerous silicon production facilities, with Elkem, Wacker, and Ferroglobe leading the charge. The project has an interest in the silicon waste produced from these facilities, irrespective of its grade, indicating the vast potential for sustainable practices across the entire European silicon industry.

Europe is also an important supplier in the production of ferrosilicon, including Elkem, Ferroglobe, and Finnfjord. These companies operate large-scale production facilities capable of manufacturing various grades of ferrosilicon.

Ferroboron material would be beneficial as a source of both iron and boron and can potentially give an increase such that a source with lower levels of boron can be used.

However, most of the ferroboron produced today are produced in China and Russia, leaving Europe without a native ferroboron industry.

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Appendix

Boron companies

Table 16: Companies found with boron containing products or handles boron containing products.

Company name	Type	Country
Boral	Glass	Germany
Glastechnik kirste	Glass	Germany
GVB GmbH - solutions in glass	Glass	Germany
Eti maden - General directorate	Boron production	Turkey
Eti maden operations bandirma	Boron production	Turkey
Eti made operations kirka	Boron production	Turkey
Eti maden operations emet	Boron production	Turkey
Eti maden operations bigadic	Boron production	Turkey
Mirit glas	Glass	Denmark
Qingdao migo glass	Glass	China
Qingdao Hongya Glass	Glass	China
Schott	Glass	Germany
Borosil	Glass	India
Duran Wheaton Kimble	Lab glass	Germany
Corning	Multitech, glass, ceramics	US
Supertek	Lab glass	India
Asahi glass co, LTD	Multitech	Japan
De dietrich process systems	Multitech	France
Gerresheimer AG	Multitech	Germany
Hilgenberg GMBH	Glass capillaries	Germany
Kavalier (and Simax)	Multitech	Czech Republic
Noble glass works PVT. LTD	Multitech	India
Yaohui group	Tableware, solar	China
HFU	Tableware	China
ERP Norge	Recycling	Norway
Sirkel	Recycling	Norway
Retura	Recycling	Norway
Norsk gjenvinning	Recycling	Norway
Børstad Transport AS	Transport waste/trash	Norway
Stena Recycling AS	Recycling	Norway/Sweden
Rio Tinto (Borax)	Borax mining	US