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Leaching of Glass Waste

Structure and Humidity Cell Tests

Elin Sandgren

ABSTRACT

Leaching of Glass Waste – Structure and Humidity Cell Tests

Elin Sandgren

Glass production has historically occurred at around 50 glassworks in Sweden, in a region known as the Kingdom of Crystals (Glasriket). Today, most of these sites are no longer active and left behind is glass waste of different forms (both as fragments of finished glass as well as unrefined glass melts). Consequently, increased concentrations of different metals, especially arsenic, lead and cadmium, have been found around the sites, both in soil as well as in ground and surface water. Between 2016 and 2019, the Geological Survey of Sweden (SGU) assigned Golder Associates AB (Golder) to evaluate the environmental risks at three different glassworks: Flerohopp, Åryd and Alsterbro. The results, based on humidity cell tests (HCT) conducted on glass samples from each site, showed that glass itself leached to a surprisingly high extent. Based on this, the aim of this master thesis has been to explain trends in glass leaching by a thorough literature review and through the analysis of HCT data of glass samples. Additionally, the speciation of different metals in the leachate was investigated based on geochemical modelling using PHREEQC.

Results from the literature review show that one of the possible mechanisms for the leaching of glass in contact with water is ion exchange, which occurs at the surface of the glass, namely between glass components and H^+ ions in water. Additionally, the literature also argues that glass with higher silica content form a more resilient structure, in contrast to glass which contains a large amount of modifiers, such as Na and Ca. Researchers speculate that adding such modifiers to the glass mass opens up the structure, making it more vulnerable upon contact with water. Looking at the total concentration of elements from the three glassworks, the results show a variation in silica content in relation to other elements. In line with this hypothesis, the sample from Åryd, which contained a higher proportion of modifiers, showed a high leaching rate of both Na and Si.

Furthermore, the result shows that the leaching of Na and As follows the same pattern over the HCT period for all glassworks. This is, to some extent, also the case for Pb although the correlation is not as significant. This could be explained by the result from geochemical modelling, showing that As tends to dissolve into the leachate while Pb is more prone to forming secondary minerals. Hence explaining their differences in leaching behavior. The result from this study showed no clear correlation between Ca and either As or Pb which could potentially be explained by the formation of precipitates. However, another approach to describe the difference in the behavior between Na and Ca is based on the glass structure itself as well as the hypothesis that Na^+ participate in ion exchange to a larger extent than Ca^{2+} . Consequently, the leaching of Na^+ makes the surface structure more vulnerable, thereby promoting the leaching of other components such as As and Pb.

Keywords: Glass structure, glass leaching, glass modifiers, humidity cell test, saturation index, arsenic, lead.

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REFERAT

Lakning av glasavfall – Struktur och fuktkammarförsök

Elin Sandgren

Produktion av glas har historiskt skett på cirka 50 glasbruk i Sverige i ett område som kallas Glasriket. I dag är produktionen vid majoriteten av dessa glasbruk avvecklad och kvar på platserna finns glasavfall i olika former, både som skärvor av färdigt glas och som ej färdigställd glasmassa. Som en konsekvens av detta har förhöjda halter av olika metaller, särskilt arsenik, bly och kadmium, påträffats i jorden såväl som i grund- och ytvattnet kring glasbruken. Mellan åren 2016 och 2019 gav Sveriges geologiska undersökning (SGU) i uppdrag till Golder Associates AB (Golder) att uträtta huvudstudier och bedömma risker vid tre olika glasbruk, Flerohopp, Åryd och Alsterbro. Resultaten, baserade på fuktkammarförsök på glassavfall, påvisade att glas lakade till en överraskande hög utsträckning. Detta resultat lade grunden till detta examensarbete med frågeställningar i syfte att förklara lakning av glas baserat på en genomgående litteraturstudie samt analys av resultat från fuktkammarförsöken. Vidare har även geokemisk modellering med programmet PHREEQC gjorts för att identifiera olika specifieringar av metaller som kan förväntas påträffas i lakvätskan.

Resultat från litteraturstudien visar att en möjlig process som kan förklara lakning av glas vid kontakt med vatten är jonbyte mellan glasets beståndsdelar och H^+ -jonerna i vattnet. Tidigare studier påvisar att ett högre kiselinnehåll i glaset skapar en mer motståndskraftig struktur än glas som innehåller en förhållandevis hög andel modifierare, såsom Na och Ca. Forskare spekulerar kring huruvida tillsatsen av modifierare till glasmassan bidrar till att öppna upp glasstrukturen och som en konsekvens av detta göra strukturen mer sårbar. Vid analys av prover tagna vid de tre olika glasbruken påvisade resultaten ett varierat kiselinnehåll i förhållande till övriga ämnen. I linje med denna hypotes påvisade provet från Åryd den högsta andelen modifierare och samtidigt även den högsta lakningen av Na såväl som Si.

Vidare påvisar resultatet att lakningen av Na och As följer samma mönster över hela fuktkammarförsöket. Detta kan delvis ses för Pb men korrelationen är inte lika signifikant som för As. En förklaring till detta baseras på resultat från geokemisk modellering, där As tenderar att gå i lösning medan Pb kan förväntas forma sekundära mineral vilket därmed kan antas kontrollera lakningen. Resultatet från denna studie visade ingen korrelation mellan varken Ca och As eller Ca och Pb vilket också skulle kunna förklaras av utfällningar i form av Ca-mineral i lakvätskan. En annan utgångspunkt för att beskriva den skillnad som kan ses mellan Na och Ca baseras på själva glasstrukturen och hur Na^+ deltar i jonbyte till en högre grad än vad Ca^{2+} gör. Som en konsekvens av detta bidrar lakningen av Na^+ till att ytan på glaset blir mer sårbar och på så sätt gör att ämnen som As och Pb blir mer lättåtkomliga. Detta resulterar i en större möjlighet för dessa att delta i reaktioner på ytan och därmed laka ut från strukturen.

Nyckelord: Glasstruktur, lakning av glas, glasmodifierare, fuktkammarförsök, mättnadsindex, arsenik, bly.

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PREFACE

This master thesis work covers 30 credits and has been conducted over a period of 20 weeks from January to June 2019. This is the final part needed for my degree in the Master Programme in Environmental and Water Engineering an education I started in 2013 at Uppsala University, Sweden. The work has been conducted at Golder Associates AB (Golder), Stockholm, supervised by Henning Holmström and Henrik Svanberg with data owned by the Geological Survey of Sweden (SGU). My subject reviewer has been Dan Berggren-Kleja at the Swedish University of Agricultural Sciences and my examiner has been Björn Claremar at the Department of Earth Sciences at Uppsala University.

To start with, I want to thank Henning Holmström at Golder, that gave me the opportunity to do my work at Golder's office in Stockholm and - Henrik Svanberg for his knowledge and how he has answered my questions with patience and great interest throughout the whole semester. In addition, SGU also deserves my gratitude for letting me use their data to make the analyses performed in this master thesis possible. A lot of gratitude goes out to my subject reviewer Dan Berggren-Kleja, for his responsiveness and good input during the project. I also want to show appreciation to my fellow students, which I have struggled and laughed beside during this long education. Without them it would have been even harder. Lastly, I want to thank Erik Svensson Grape for always standing by my side, for always making me believe in myself and making me want to strive to always get better. For participating in discussions and giving me input throughout all my years as a student, on sunny days as well as rainy.

The content in this report is my interpretation of information and data which I hope can be of help regarding the knowledge about the reasons for why such a persistent material as glass leaches when exposed to different environmental conditions.

Elin Sandgren

Uppsala, May 2019

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Leaching of Glass Waste – Structure and Humidity Cell Tests

Elin Sandgren

Glas är en produkt som har använts av människan i århundranden. Förenklat kan materialet beskrivas som en stelad smälta av olika ämnen som har kylts ned så hastigt att den kemiska strukturen helt saknar ett tydligt mönster. Det mest tillverkade glaset i världen som används till bland annat dricksglas och glödlampor består framförallt av kiseldioxid, natrium och kalcium. Den dominerande komponenten är kiseldioxid som fungerar som stommen i glasstrukturen medan natrium tillsätts för att förenkla tillverkningsprocessen då detta gör att smältpunkten sänks. Kalciumet tillsätts för att ge särskilda egenskaper till glaset såsom lyster och glans. Även andra ämnen tillsätts för att till exempel undvika att bubblor uppstår i glaset samt att ge glaset en viss specifik färg. Exempel på sådana tillsatser är arsenik och bly.

I Sverige har glas historiskt sett producerats framförallt i landets södra del där de fyra småländska kommunerna Nybro, Emmaboda, Lessebo och Uppvidinge tillsammans utgör det område som i vardagligt tal kallas för Glasriket. Här har storskalig glasproduktion skett i ett femtiotal glasbruk under de senaste seklen men i dag är majoriteten av dessa nedlagda. Under produktionsåren har både ingredienser till glaset såväl som ofärdig glasmassa och defekt färdigt glas hamnat i naturen och finns i dag kvar i områdena både under och ovan jord. Tidigare trodde man att glas var ett mycket tåligt material som inte skulle påverkas alls av väder och vind och på så sätt inte vara farligt att deponera utan försiktighetsåtgärder. Under de senaste decennierna har det dock visat sig att detta inte är fallet då det förekommer höga halter av många metaller kring de nedlagda glasbruken, bland annat bly och arsenik som båda är giftiga och skadliga för människors och djurs hälsa.

Miljökonsultföretaget Golder har på uppdrag av Sveriges geologiska undersökning (SGU) bedömt risker med avseende på förorening av bland annat arsenik och bly vid tre nedlagda glasbruk i Sverige vid namn Flerohopp, Åryd och Alsterbro. Från vardera glasbruk har prover från de glasavfall som hittats på dessa områden tagits och skickats på analys till ett laboratorium vid namn ALS. De har i sin tur gjort analyser på vilka ämnen proverna innehåller, i vilken andel, samt gjort försök att påvisa vad som kan hända med proverna om de utsätts för naturliga förhållanden i fält (såsom nederbörd) genom ett test som kallas fuktkammarförsök. Detta försök innebär att proverna utsätts för tre dagar torr luft följt av tre dagar fuktig luft för att därefter sköljas med avjoniserat vatten för att se vilka koncentrationer av ämnen såsom kisel, natrium, kalcium, arsenik och bly som kan påvisas. Dessa cykler har upprepats 21 gånger och resultaten visade att glaset gav i från sig höga koncentrationer av metallerna. Resultatet var överraskande och motsvarade inte vad Golder förväntade sig och viljan att förklara varför det såg ut som det gör lade därför grunden till detta arbete.

Huvudsakligen har detta arbete syftat till att ta reda på teorin bakom varför inte glaset är så stabilt som en kan tro. Tidigare forskning på området visar att vissa tillsatser till glasmassan försämrar glasets hållbarhet och gör det mer känsligt. Tillsatser såsom

natrium och kalcium kan leda till att glaset får en mer öppen struktur som är mer sårbar än ett glas som enbart består av smält kiseldioxid. Den mer öppna strukturen kan innebära att vattenmolekyler kan komma åt glaset lättare och därmed kan reaktioner ske som gör att glaskomponenter löses upp (vittrar) och kan transporteras (lakas) bort om rinnande vatten är närvarande.

Genom att jämföra innehållen i glasprov från de olika glasbruken så har glas med mer tillsatser visat en trend att vara mer sårbart. Åryd, som hade störst andel tillsatser var också det prov där de högsta koncentrationerna uppmättes av olika glaskomponenter efter fukt-kammarsförsökets 21 veckor. Resultatet från studien har också visat att natrium och arsenik transporteras ut ur glaset med samma mönster, något som kan ses i prover från samtliga glasbruk. En förklaring till detta skulle kunna vara att natrium och arsenik är del av samma mineral som löses upp från glaset eller att de båda kan ses som relativt lösliga. En annan skulle kunna vara hur och var arseniken återfinns i glaset i förhållande till natriumet. Detta skulle kunna studeras närmare genom att kolla på strukturen i elektronmikroskopi för att på så vis kunna se var i glaset som respektive metall sitter.

Studien har dock en del osäkerheter som måste tas i åtanke vid bedömning av resultaten. Framförallt är det proverna i sig som jämförts mellan de olika glasbruken som gör att inga definitiva slutsatser kan dras. Glasavfallet som studerats från de olika glasbruken är representerade av en mix i både färg och storlek samt färdigt glas och stelnade glassmältor. Proverna har också legat i olika miljöer under olika lång tid vilket även gör det svårt att bedömma hur mycket som redan hänt med glasets struktur i fält i förhållande till hur det såg ut från början. En utveckling av studien vore att kolla på opåverkat glas av samma typ för att göra en mer rättvis och noggrann utvärdering gällande hur glasets komposition påverkar dess frigörelse av metaller.

ABBREVIATIONS AND GLOSSARY

Alkali metal ions	Group in the periodic table represented by for instance Li, Na and K. Often found as cations with a charge of +1
Alkaline earth metal ions	Group in the periodic table represented by for instance Be, Ca and Mg. Often found as cations with charge of +2
BO	Bridging Oxygen
BSG	Boro-Silicate Glass
HCT	Humidity cell test, a kinetic laboratory test to determine leaching of materials
LG	Lead Glass
Lime	Calcium (Ca) containing minerals
NBO	Non-Bridging Oxygen
Oxide glass	Made up by oxide components, most common one is SLSG. Often used for containers.
SLSG	Soda-Lime-Silicate Glass
Soda	Compounds containing sodium (Na) such as sodium carbonate, sodium hydroxide or sodium oxide

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1. INTRODUCTION

1.1. BACKGROUND

Glass is produced by melting minerals, mainly silicate, and adding different metals to the melt to receive different glass properties (Nationalencyklopedin [NE], 2019). Alkali metal ions are often used to decrease the melting temperature of the final melt and alkaline earth metals are added to increase glass stability and give properties such as luster and gloss. Metals are also added in the process to give glass a variation of colors and to prevent bubbles in the melted glass (Shelby 2005). Depending on the chemical composition, glass is divided into different categories with different properties and resistance (NE, 2019) represented by for example light bulbs, laboratory glass and crystal glass (Ashby 2013)

Sveriges geologiska undersökning [SGU] (2019) describes how four counties in southern Sweden makes up the region known as the Kingdom of Crystals (Glasriket). Historically, glass has been produced at around 50 glassworks in this region, but at the majority of them, glass manufacturing is no longer conducted. Despite the glassworks not being in use any longer the soil, as well as ground and surface water at those areas have shown increased concentrations of metals, especially arsenic, lead and cadmium. Overall, glass waste has been found at all sites concerned, in soil as well as in surface landfills (SGU, 2019).

During 2016–2019 SGU assigned Golder Associates AB (Golder) to evaluate the environmental risks at three different glassworks in Flerohopp, Åryd and Alsterbro. When evaluating the leaching of glass samples from the three sites through humidity cell testing, all three showed signs of metal leaching, yet with varying rates between the glassworks. This result was somewhat surprising since glass in general is known as a durable material and used for purposes such as drinking vessels and food storage containers. The combination of the unexpectedly large amounts of leaching and the former view of a stable glass structure was the reason why Golder wanted to further investigate the properties of glass and try to find an explanation as to what might have happened with the analyzed samples. This is what laid the foundation to this master thesis work.

1.2. AIM AND PROBLEM STATEMENT

Following problem statements has laid a foundation for the work made in this master thesis:

- How does the glass waste behave from a chemical perspective?
- What processes occur during the humidity cell tests that have been conducted on samples from the three different sites?
- Can leaching of As and Pb be related to leaching of other, more dominant, glass components?
- What species distribution of As and Pb can be expected and what precipitates may be present by taking results from humidity cell test into account?

1.3. PROJECT SCOPE AND LIMITATIONS

The limitations of this master thesis are based on results and knowledge found during the literature review for this project, resulting in a focus in the leaching behavior of primarily Si, Na and Ca from glass. The idea is that certain elements can be seen as to represent different components which are added in the glass production process: the major network former (Si), the major modifier oxides (Na) and property modifiers (Ca). Furthermore, the apparent leaching behavior of As and Pb has also been investigated based on their different properties and toxicity in relation to other glass components. Additionally, these elements were also chosen since they have been found in increased levels in the area around the glassworks.

Considering the literature review in this report, it is centered around oxide glass and the primary focus is on soda-lime-silicate glass since this is the composition that represents the majority of the glass produced in the world (Ashby 2013) and also the glass type that best represents the main production at the three glasswork compared in this report. Therefore, this glass type is the focus when describing the chemical composition as well as the reactions which might occur upon contact with water.

For the geochemical modelling done in this study only five separate weeks, chosen to represent the full HCT period, have been chosen. The modelling has also only considered an oxidative environment, rather than a reducing due to the properties of HCT. The reason for these limitations is that modelling over the whole HCT period while also adding another condition (oxidative vs. reducing conditions) would have enlarged this study significantly and due to time limitations, this was considered unfeasible.

2. THEORY

2.1. GLASS CHARACTERISTICS

2.1.1. General glass definition and common glass types

A glass can, in its simplest form, be defined as either a supercooled liquid or a solid (Zachariassen 1932). The structure is obtained by cooling down a melt of different components to a final temperature at which the atoms move so slow that they are unable to create a crystalline structure (Le Bourhis 2014). There is no significant periodicity in the structure of glass (Zachariassen 1932) which stands in contrast to the long-range order found in crystalline materials (Le Bourhis 2014). The order in glass is instead only short-ranged (Le Bourhis 2014) and the atomic structure is defined, on an atomic level, by a three-dimensional network with neither periodicity or symmetry, which is what separates it from a crystalline structure (Zachariassen 1932).

In general, glass is produced by melting minerals together with alkali metal ions (Nationalencyklopedin [NE], 2019). Depending on the manufacturing process and chemical composition, glass is classified into different categories and for oxide glasses some of the main ones is known as soda-lime-silica glass (SLSG), borosilicate glass (BSG), and lead glass (LG) (NE, 2019). Ashby (2013) is further describing different types of glass and their compositions with SLSG as the most common glass type in bottles, lightbulbs, as well as windows. The general composition of this type of glass is in the

range of 70–75% SiO₂, 13–17% Na₂O, 5–10% CaO, 4% MgO and 1% Al₂O₃, see Figure 1. BSG, that has a higher resistance against expansion and thermal shock than SLSG, is often used when producing glassware, ovenware and glass used in laboratories. The chemical composition for BSG is approximately 74% SiO₂, 15% B₂O₃, 6% PbO, 4% Na₂O and 1% Al₂O₃, see Figure 1 (Ashby 2013). LG is defined as a glass which contains at least 24% PbO which gives the glass a high light-transmission capacity and is thereby used for the manufacturing of tableware and art glass (NE, n.d). According to the Swedish Consumer Agency, glass containing more or equal to a composition of 24% PbO is defined as full lead crystal glass while crystal glass with lower PbO content is defined as just crystal glass as long as the total concentration of the oxides ZnO, BaO, K₂O and PbO or BaO, PbO, K₂O in combination stands for at least 10% of the chemical composition of the glass (Edling & Norstedt 1998).

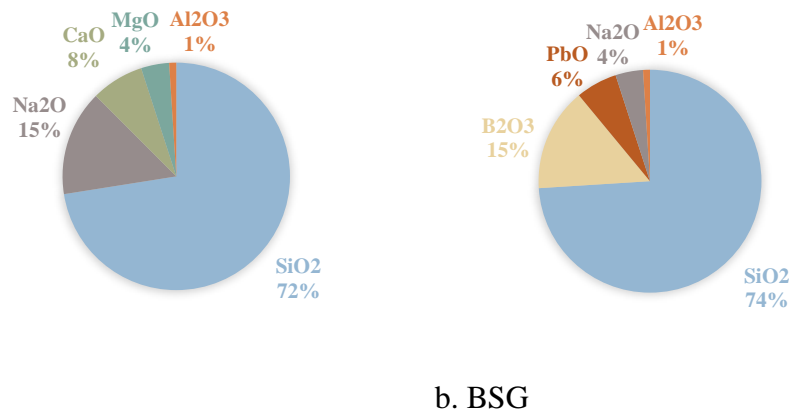


Figure 1 Showing approximate chemical distribution in SLSG (a) and BSG (b) (Ashby, 2013).

2.1.2. Network formation of oxide glass

Le Bourhis (2014) describes how Dietzel categorized oxides according to their ability to form a glass network, dividing them into three categories: *network formers*, *intermediates*, and *modifiers*, see Table 1. Dietzel did this by defining the intensity (A) at which the cation tends to form a network, depending on the valance (Z) and the radius of the cation (r_c) and oxygen (r_o), see equation 1 (Dietzel, 1941,1942,1943,1981,1983 in (Le Bourhis 2014)). This is further described by Stanworth (1950) in Shelby (2005) stating that the *network formers* are defined by cations which bond to the oxygen predominately by covalent bonds, rather than ionic bonds, and thus creates a strong and persistent glass. The category of *intermediates* is represented by cations that cannot create a glass network by themselves but can participate in the network formation. The last group of *modifiers* is cations that have a very low electronegativity towards oxygen and hence forms bond of a more ionic character and, as the name suggest, these cations modify the glass network rather than creating one (Stanworth 1950; Shelby 2005).

$$A = \frac{Z}{(r_c + r_o)^2} \quad (1)$$

Table 1 Categorization of cations based on their Dietzel field intensity (Data retrieved from Dietzel 1941,1942,1943,1981,1983 in (Le Bourhis 2014))

Cation	Z	rc [Å]	ro [Å]	A	Category
Si	4	0,40	1,4	1,23	<i>Network Formers</i>
B	3	0,25	1,4	1,10	
Ge	4	0,53	1,4	1,07	
Ti	4	0,74	1,4	0,87	<i>Intermediates</i>
Al	3	0,53	1,4	0,80	
Zr	4	0,86	1,4	0,78	
Be	2	0,41	1,4	0,61	
Mg	2	0,86	1,4	0,39	
Zn	2	0,88	1,4	0,38	
Ca	2	1,14	1,4	0,31	
Pb	2	1,33	1,4	0,27	
Li	1	0,90	1,4	0,19	
Na	1	1,16	1,4	0,15	
K	1	1,52	1,4	0,11	

2.1.3. Different glass components and their role in glass making

Glass components can be divided into five different characteristics: *network formers* (glass formers), *modifier oxides* (flux), *property modifiers*, *colorants*, and *fining agents* further presented in Table A1. Additionally, depending on the purpose, the same compound can be classified into different categories (Shelby 2005). Common network formers are usually represented by the oxides: silicone dioxide (SiO₂) and boron trioxide (B₂O₃) (usually as borax or boric acid) (NE, 2019). Shelby (2005) states that even though there are several oxides that can create or participate in forming a glass network, SiO₂ is the dominant oxide used. Yet, using exclusively SiO₂ as network former is inefficient due to its high melting temperature of > 2000 °C. To decrease the melting temperature of the glass mass, *modifier oxides* (flux) are added. Most commonly used are alkali oxides such as Na₂O (soda), K₂O and Li₂O but also PbO is used. Adding alkali oxides as flux components leads to a more effective glass production but does also lead to a degradation of many of initial properties of the glass. To counter the degradation of properties, such as durability, *property modifiers* are added to the glass mass (Shelby 2005) which also gives the glass properties such as refractive index, gloss and luster (NE, 2019). This category is often dominated by alkaline earth ions (Shelby 2005), in shape of the minerals feldspar (KAlSi₃O₈-NaAlSi₃O₈-CaAl₂Si₂O₈), calcium carbonate (CaCO₃), dolomite (CaMg(CO₃)₂), and barium carbonate (BaCO₃), yet zinc oxide (ZnO) and lead oxide (PbO) are also used (NE, 2019).

The group of *colorants* are added in small quantities and only for the purpose of controlling the color of the final glass (Shelby 2005). To get different colors, a large diversity of components are added depending on which tone that is desired for example cerium oxide (CeO₃), iron oxide (FeO), cadmium sulfide (CdS), cobalt oxide (CoO), copper(di)oxide (Cu₍₂₎O), chromium oxide (Cr₂O₃), manganese oxide (Mn₂O₃), nickel

oxide (NiO), sulfur (S), titanium oxide (TiO₂) and uranium oxide (U₂O₃) (Falk *et al.* 2011). Arsenic oxide (As₂O₃) and antimony oxide (Sb₂O₃) are also added as colorants in some cases (Hujova & Vernerová 2017).

Final agents are added in very low quantities (usually <1 wt%) to prevent bubbles to form in the final melt (Shelby 2005). Hujova & Vernerová, (2017) states that the two most commonly used fining agents for glass production is arsenic or antimony oxide (As₂O₃, Sb₂O₃) which are hard to substitute when producing glass at very high melting temperatures, or when making glass of high quality. A glass with relatively high concentrations of alkali and alkaline earth oxides helps stabilize the less volatile higher oxidation states of both As and Sb (Hujova & Vernerová 2017). Other final agents used to prevent bubbles are potassium nitrate (KNO₃), sodium nitrate (NaNO₃), sodium chloride (NaCl) and fluorides, such as CaF₂, NaF, NaAlF₆ and different sulfates (Shelby, 2005).

2.1.4. The structure of glass

Le Bourhis (2014) describes how the glass structure is based on one Si-atom that connects to four different O-atoms with covalent bonds, in 3D-view the O-atoms is forming a tetrahedron around the Si-atoms located in the center, see Figure 2. According to Zachariasen (1932) the network of Si-O-Si chains formed is non-periodic and made up from randomized chains with no long-range order, making it impossible to predict the atomic structure arrangement in the glass (Zachariasen 1932 in (Le Bourhis 2014)). The differences between the periodic crystalline SiO₂ and the aperiodic amorphous form is presented in Figure 3a and Figure 3b.

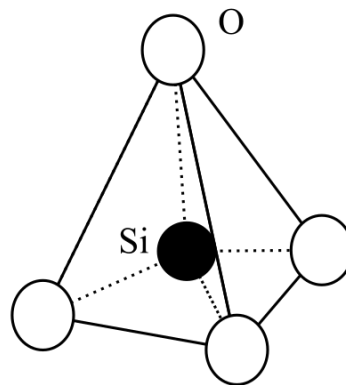


Figure 2 Showing the tetrahedral structure of the SiO₂ molecule with the silica atom located in the center surrounded by four oxygen atoms.

Le Bourhis also describes what occurs when modifiers are added to the glass. When alkali or alkaline earth oxides are added to the structure, this forms so called non-bridging oxygen (NBO) which lead to structural changes, hence the name modifiers, see Figure 3c. The addition of modifiers to the glass melt is done to disrupt the network and lower the viscosity as well as the melting temperature. Yet, the introduction of NBOs reduces the strength of the glass network. Alkali metal ions, such as Na⁺ or K⁺, are mobile and may cause an increase in electrical conductivity as well as ion migration. On the other hand, alkaline earth metal ions, such as Ca²⁺ and Mg²⁺ are less mobile and adding these to the glass structure can inhibit diffusion of alkali metal ions and may thereby also

improve the glass durability. Further on, adding alkaline earth cations such as Ca^{2+} leads to less viscosity change compared to adding only Na^+ , since Ca^{2+} connects to two NBOs in comparison with Na^+ that just links to one. Thus, depending on the modifier cation's Dietzel field intensity, the interaction with the NBOs varies. For cations with high intensity the interaction can be assumed to be more intensified than for a cation with low intensity (Le Bourhis 2014). Some evidence shows that the alkali metal ions are clustered together in the glass network or that they at least are paired together at the same NBO. This makes for speculations regarding the possibility of channel formation in the network caused by the clustering and potential leaching of alkali metal ions (Shelby 2005).

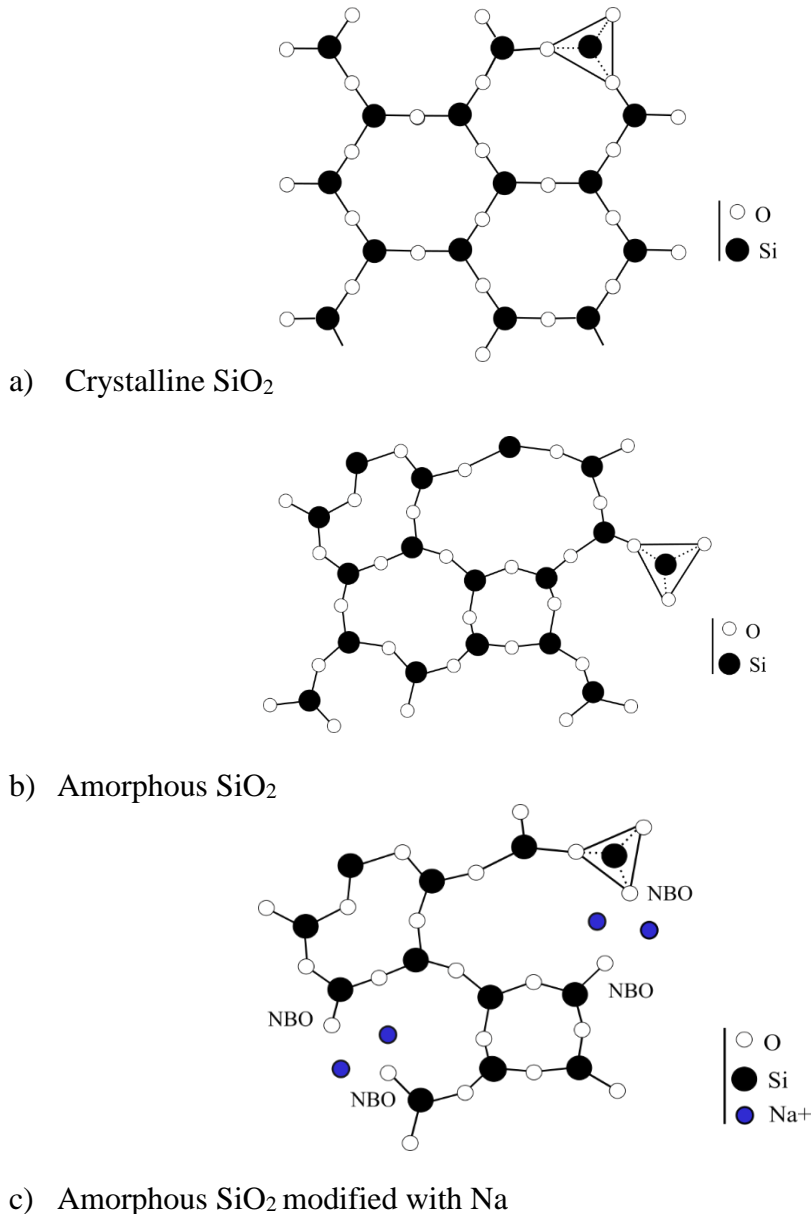


Figure 3 Showing the different structures of SiO_2 : a) crystalline SiO_2 , b) amorphous SiO_2 , c) amorphous SiO_2 modified with Na^+

2.2. GLASS IN CONTACT WITH WATER

2.2.1. Chemical durability and corrosion of glass

The bulk structure of glass depends on the concentration of modifiers and network formers and this is also what decides the durability of the glass. It is the surface of the glass that can interact with the atmosphere and which, through chemical and physical interactions, may change the properties of the whole glass structure (Le Bourhis 2014). Structural changes first occur at the surface of the glass, which then penetrate further into the material, especially when in contact with water (Davis & Tomozawa 1995).

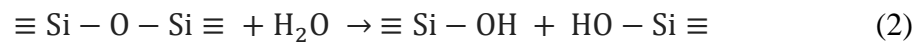
Bunker (1994) describes that three different reactions can occur when glass is in contact with water:

1. Hydration (water molecules penetrates the glass)
2. Hydrolysis (water reacts with metal-oxygen bonds and forms hydroxyl groups)
3. Ion-exchange (modifying cations in the network are replaced)

Bunker further states that all three reactions that causes the glass structure to disintegrate is strongly connected. The hydrolysis opens the structure that enhance the penetration of both water molecules as well as H_3O^+ . In addition, the ion exchange also extends the free space in the glass network which simplifies the transport of water into the structure (Bunker 1994).

2.2.2. Hydration and Hydrolysis

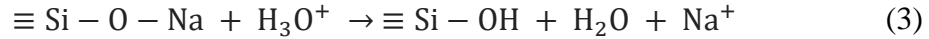
Bunker (1994) defines the two ways at which the water molecules can enter a glass network as either via hydration or hydrolysis. Hydration occurs when the water molecule, as an intact shape, diffuse into the structure through free spaces in the network structure. The rate of hydration depends on the free space in the network where larger space results in a faster diffusion rate (Bunker 1994). Hydrolysis of silica-glass happens when in contact with water as the water molecules reacts with the Si-O-Si bonds as in reaction 2 which depolymerizes the network. This leads to a decrease of the glass durability by changing the surface viscosity and increasing the chance that the glass will crack (Le Bourhis 2014).



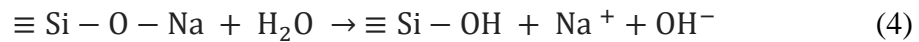
According to Bunker (1994) the hydrolysis is a non-reversible reaction, resulting in presence of both molecular water and hydroxyl groups in the glass network. Glass containing NBOs opens up the network and hence hydrolysis of the network occurs at a faster rate in comparison to a non-modified SiO_2 network which only contains bridging oxygens (BOs) (Bunker 1994).

2.2.3. Ion-exchange

The third reaction at which reaction of glass may occur is when the structure contains alkali or other mobile ions that endure ion-exchange with H_3O^+ ions when in contact with water (Shelby 2005), causing the alkali metal ions to leach to the water solution as a consequence of the reaction 3 (Le Bourhis 2014).



Further on, reaction 4 can also occur (Bunker 1994):



These reactions incorporate water into the surface structure, creating a silica gel surface which usually is about $0.1 \mu\text{m}$ thick, see Figure 4 (Le Bourhis 2014). This ion-exchange can furthermore result in reaction products which accumulate at the surface and which can enhance dissolution of the material, Figure 4 (Shelby 2005). The rate at which the ion-exchange occurs depends on the glass structure and the chemical composition of the surrounding solution (Bunker 1994).

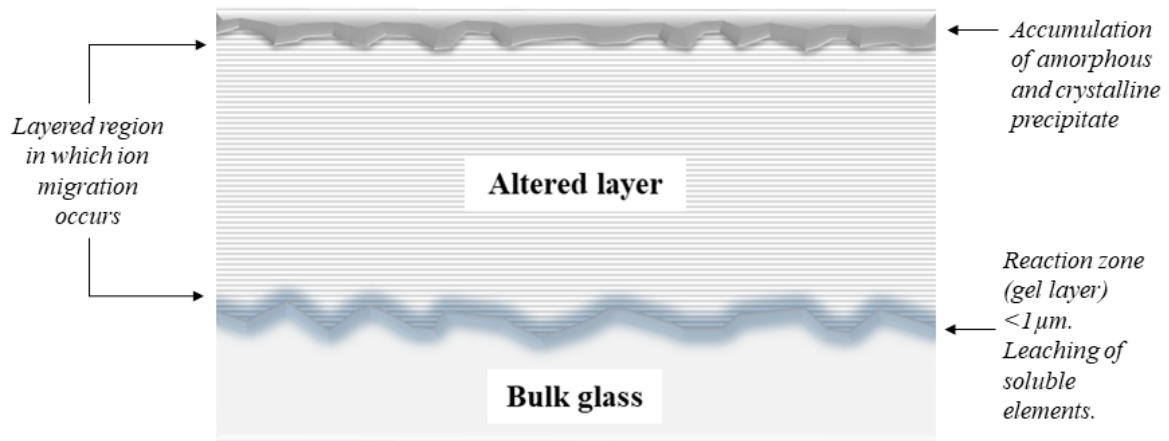
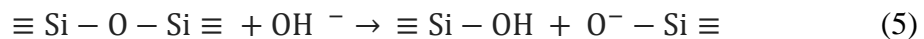


Figure 4 A description of what is happening at the glass surface, top down shows the precipitate that might accumulate, the altered layer where ion migrates and the reaction zone (marked in blue) followed by the bulk glass. The picture is modified based on ideas from a picture presented in Mendel (1984).

When modifying alkali metal ions (for example Na^+ and K^+) diffuses toward the glass surface this increases the pH in the contacting solution (Le Bourhis 2014). A higher pH in the surrounding solution, increases the solubility of silica (see more under section 2.2.9) and therefore enhance dissolution of the glass (Shelby 2005). If the pH increases to 9, and above, reaction 5 may occur



which is more detrimental to the glass network than ion exchange since this causes a depolymerization of the structure (Le Bourhis 2014). Shelby (2005) states that if the glass does not contain alkali or alkaline earth metal ions this pH increase will not happen and instead the solution may become saturated with silica at higher pH and the dissolution rate will decrease or even cease completely. However, the pH in the solution depends on the volume of solution to sample area ratio meaning that even small concentrations of ions can result in a significant increase of the pH (Shelby 2005).

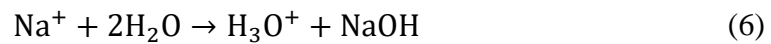
2.2.4. Weathering of glass

Weathering includes the interaction between the glass and temperature, light, ambient air, acidifying gases, airborne particles and relative humidity (RH). Several of these parameters can together form a critical environment for the glass structure (De Bardi *et al.* 2015). The interaction between glass and water vapor is usually defined as weathering while chemical durability and corrosion often is referring to the interaction with liquids (Shelby 2005).

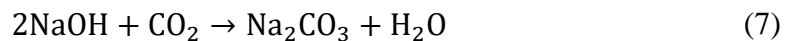
The weathering process of glass can be described by the following steps: First, air moisture, rain or some other source of water creates a thin water film. Second, acidifying gases from the atmosphere decrease the pH in the water film if absorbed to it. Last, the network modifying atoms such as Na⁺, K⁺, Ca²⁺ and Mg²⁺ participate in ion-exchange with H⁺ from the water, resulting in a leaching of these metals (Melcher *et al.* 2010). This results in a gel layer (same as presented under section 2.2.3 in Figure 4), also referred to as the leached layer (Melcher & Schreiner 2004) or the hydrated layer (Melcher *et al.* 2010).

2.2.5. Difference between weathering and leaching of glass

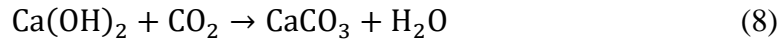
Initially, the weathering of glass is somewhat similar to the leaching of glass. Ion exchange also occurs during weathering, although the water availability differs from leaching since only the water in the air is available and this is absorbed at the glass surface as a thin layer (De Bardi *et al.* 2015). During weathering conditions, there is no liquid available to transport the weathered elements which causes the diffused ions to remain at the glass surface where further reactions can occur with the surrounding atmosphere as described in the formula 6 below (Shelby 2005).



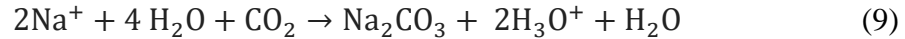
These formed hydroxides can then react with carbon dioxide in the atmosphere to form carbonates, as in the formula 7:



or through formula 8:



While surrounded with acidifying gases (SO_2 and CO_2 for example) this thin layer of water around the glass surface might gain a decrease in pH which results in an increase in the ion exchanging process (De Bardi *et al.* 2015). The full reaction is then following the formula 9:



2.2.6. Water availability and glass weathering

De Bardi *et al.* (2015) distinguish two different scenarios depending on if the water at the surface is exchangeable or not. First is the scenario of not being able to replace the water at the glass surface, in this case the pH will slowly increase since the H^+ ions are consumed during the leaching process (reaction 3). This pH increase results in alkaline corrosion conditions resulting in a dissolution of the network. The second and more serious situation occurs when the glass is exposed to alternately dry and wet conditions. These cycling variations can form and dissolve corrosion products on the surface of the glass which can change the appearance of the glass product (De Bardi *et al.* 2015). When the humidity decreases this will make the leached layer dewatered and the volume of this layer will shrink. This volume change in the leached surface layer causes stress on the bulk glass that has an unchanged volume which can cause the leached layer to peel of the bulk, leaving craters in the remaining glass (Shelby 2005).

The damages done by the weathering reactions can occur after only hours to year of exposure to water depending highly on the composition of the glass, the surface structure and the environment in which the glass is located (Walters & Adams 1975). A surface treatment of the glass would help avoiding the problem of leaching since weathering is something that occurs at the surface of the glass structure. For example, a reduction in the number of alkali metal ions at the surface will result in less ion exchange and thus make the glass more resistant to weathering (Shelby 2005).

2.2.7. Parameters impacting corrosion rate

Mendel (1984) presents the parameters impacting the corrosion rate of glass stating that the composition of the glass, the environment of the aqueous medium, temperature and time is of high importance when considering the corrosion of the glass surface. Taking the glass composition into consideration it highly depends on the alkali/silica-content. A glass with high alkali content shows a rapid alkali leaching as well as network dissolution and furthermore the effects of leachate product accumulation is high. The opposite occurs for glass with low alkali content when in contact with water (Mendel 1984). Le Bourhis (2014) claims that what is causing the processes to occur is the introduction to NBOs in glasses containing alkali metal ions that creates an opening in the structure. The relative concentration of BOs and NBOs is therefore of high importance when considering the properties of glass. The type of metal present as modifier to the network is therefore of

great importance since alkali metal ions and alkaline earth metal ions generates different number of NBOs (Le Bourhis 2014). Zachariasen (1932) presents the size of the ion as another property that varies and hence impact the ability for the metal to migrate in the network. He states that smaller cations are more mobile than larger and thus the migration of Na^+ will occur at a higher rate than the migration of K^+ . Zachariasen (1935) also adds that what also might impact the ability for ions to migrate in the network is the surrounding temperature which results in an increase of migration as the temperature rises.

Mendel (1984) further states that two parameters to take into extra consideration are the two glass components Si and Al which are two elements which solubility highly depends on pH. For a situation where these elements are saturated, they do not fall out into the aqueous medium, instead they stay at the glass surface and in some cases forms a stable layer that might serve as a protective barrier to the remaining bulk glass. In contrast, if the concentration of these elements is low in the aqueous phase, they will leach out in almost the same rate as the alkali metal ions which may result in high impact on the glass structure and result in a very fragile bulk structure. Thus, the type of water that the glass surface is exposed to has to be considered while studying the water/glass-interaction. In groundwater, saturation of silica will occur faster in comparison with deionized water which contains no silica and hence saturation will occur much slower (Mendel 1984). Le Bourhis (2014) also defines oxides that may act as barrier to the glass network and hence limits the corrosion as Al_2O_3 , B_2O_3 , TiO_2 and ZrO_2 . This list of oxides is also supported by studies made by Smets et al. (1984) showing that for glass in which the Na-ion is bonded to the oxides AlO_4^- and BO_4^- , the leaching tends to decrease. They explained this as due to a significantly slower ion exchange reaction when the alkali ions is bonded to these oxides in comparison to when bonding to silicate (Smets *et al.* 1984).

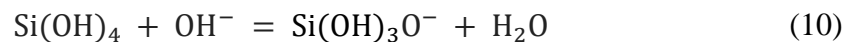
According to Mendel (1984) the total exposure time between glass and the aqueous medium surrounding it is important since this parameter decides the transformation of the glass surface and hence the reaching of steady-state with the contacting solution. For long contact periods it is considered that the material loss will reach a constant rate. This also control changes in other parameters such as pH increase due to alkali leaching and approach towards saturation for parameters such as Si and Al. To illustrate this further, Mendel (1984) explains two extreme cases. The first is a scenario at which the volume to water ratio is high (high dilution) or the water exchange occurs at a high level (rapid flowing water). Considering this case, the accumulation of components from the leaching process will be small in comparison and will therefore not impact the interaction. The pH of the solution will not change, the contact with glass does not impact in this case. Compounds such as Si and Al that is solubility-limiting will not change significantly in the leachate water and will thus not impact the leaching rate. The other extreme case considering water in contact with a glass surface that Mendel is presenting is when a large glass surface is in contact with an aqueous medium (large dissolution) for a longer time (slow flowing water). In this case the interaction between the water and the glass will be strong. The pH will change depending on the leaching of alkali and alkaline earth ions further on the saturation of Si and Al will be determining the levels in the aqueous phase (Mendel 1984).

2.2.8. A previous study to evaluate the differences in composition variation for SLSG

In a study by Carmona *et al.* (2005), different glasses of the type $R_2O-CaO-SiO_2$ (where R is represented by either Na^+ or K^+) were exposed to different accelerating weathering tests with a variation in temperature and relative humidity (RH). The result from their study showed that a glass with characteristics similar to a standard SLSG-structure was significantly affected while exposed to changes in RH and temperature. For all glass tested, result showed that an ion exchange occurred starting with the H^+ from the atmospheric water exchanging with the alkali metal ions K^+ and Na^+ . The SLSG that contained more Na^+ in comparison with the other three test glasses, where the dominated alkali was K^+ , seemed to be most affected by this ion exchange. This could further be explained by the overall higher alkali content (16 mol %) in the SLSG in comparison to the other glass tested, containing K_2O (representing 7, 11 and 15 mol % alkali). According to their study it also seems as the content of CaO affects the resistance in the glass structure, the higher the CaO concentration the more resistant the glass structure tend to be. This is explained by the stabilizing property that CaO has on the glass network. Furthermore, according to results from their study, it seems as the resistance of the glass can be described using the R_2O/CaO ratio where the resistance of the glass decreases as the ratio increases (Carmona *et al.* 2005).

2.2.9. Solubility of amorphous silica

Amorphous silica tends to show a higher solubility in water in comparison to crystalline silica (for example quartz). Result from their study show that when in contact with an aqueous solution, at a temperature of 25 °C, the solubility of amorphous silica occurs as an equilibrium between the solid phase and a monomeric form, mostly dominant is $Si(OH)_4$ that goes into solution. In the research conducted, results present that if pH increases above 8 another component that might be present in the solution is $Si(OH)_3O^-$. Thus, the increasing solubility of silica depends on formula 10 (Alexander *et al.* 1954).



2.3. HUMIDITY CELL TEST (HCT)

2.3.1. Introduction to HCT

To characterize a material's ability to release solutes and acidity to the environment, different laboratory tests can be used. To determine the release rates over time, laboratory dissolution tests are usually conducted and one is the so called Humidity Cell Test (HCT) (Barnes *et al.* 2015). The method is based on a weekly cycle of an alternating exposure of dry and humid air to a sample. This is done for three days per treatment and on the seventh day water is added to the sample and the leachate is analyzed (Torstensson, 2002). This kinetic test is recommended to use for predicting primary reaction rates as a result of weathering during aerobic conditions (Price, 2009) and is preferably used on materials that can be assumed to have a slow reaction rate and where the release rate increases after a long term of weathering (Barnes *et al.* 2015). The results gathered from these tests can

be used to predict future geochemical conditions, such as pH, by taking the acid generation and acid neutralization into consideration (Price, 2009).

2.3.2. The ASTM D5744 standard

One of the most commonly used HCTs is based on the ASTM D5744 standard (Lapakko 2003). Following the ASTM D5744-96 method the initial step is to do a pre-analysis of the sample, to acquire information about the particle size, mineralogy and chemistry. Following this protocol, 1 kg of the sample is then crushed into fractions of $\leq 0.6\text{mm}$ and placed in a short column and exposed to three-day cycles of dry and humid air alternately at a rate of 1–10 l/min, see Figure 5. First, the sample is exposed to a three-day cycle of dry air with a relative humidity (RH) at $<10\%$ followed by a three-day exposure of humid air with a RH around 95%. At this step the ASTM D5744-96 standard recommends that the temperature of the humidifier is set at around 30 °C to enhance the weathering rate. On the seventh day deionized water is added to the cell either by “drip-tickle” or “flood”, the first referring to letting the water drain freely through the cell whereas the second is based on a closed system where the water remains in contact with the material for around 1 hour after adding it to the cell. The water added should correspond to a volume of 500–1000 ml stating in the protocol that a volume of 1000ml is recommended to enable rinsing of all the dissolved products. In contrast, a low liquid ratio can cause inefficiency due to the incomplete rinsing or precipitation of secondary minerals inside the cell. The ASTM D5744-96 standard requires a test duration of minimum 20 weeks (20 leaching cycles) stating that some samples can require between 60–120 weeks to reach a stable leaching rate (Lapakko 2003). Prior to analysis, the leachate is filtered to gain only the dissolved concentrations (Price 2009).

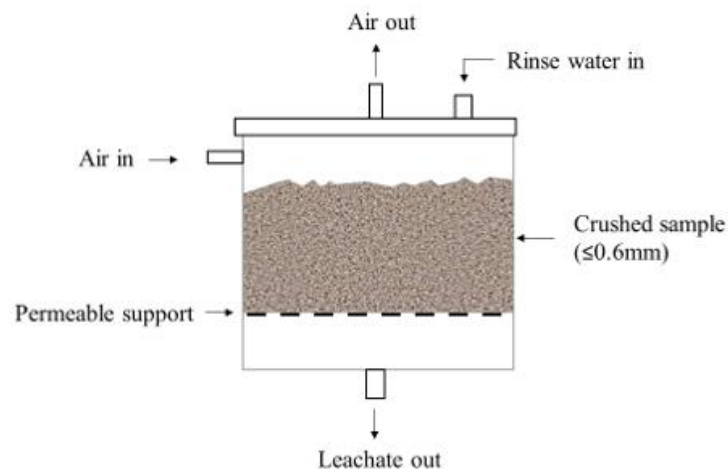


Figure 5 Flow chart describing the HCT process for tailings (The picture is modified based on ideas from MEND, 2009 presented in ALS Global, 2015)

2.3.3. Parameters that impacts the HCT result

The outcome of the HCT depends on many parameters. One that is of major concern while conducting the HCT is the temperature. It is important that the temperature is held constant throughout the whole test and that it corresponds to a relevant temperature that can occur in a landfill (Torstensson, 2002). Another parameter that highly affects the outcome of the HCT is the particle size of the material. This is especially important considering elements such as FeS, CaCO₃ and MgCO₃. For example, CaCO₃ and MgCO₃ minerals are efficient acid neutralizers and their dissolution rates depends on the surface area available. Consequentially, as the particle size of these minerals decrease, the acid neutralization increases (Lapakko 2003). Although, Meast & Nordström (2017) states that the surface area of minerals is hard to estimate since this can change due to temperature, chemical weathering and mass of added material. All these parameters cause an increase in surface area over time. Other factors that can affect the outcome of the result such as test length, the preparation of the sample, storage time before the tests starts, geochemical reaction, humidity and liquid to solid ratio (L/S), to mention a few (Maest & Nordstrom 2017).

Price (2009) defines one advantage with the HCT as the simplicity to reproduce the test, if it is done according to standards, which enables comparison with results from other HCTs. Another advantage with this type of test is that the weekly addition of water to the sample enables measurement of the primary reaction rates. Although, it must be considered that the flushing of water only removes weathering products that are water soluble (Price 2009). Lapakko (2003) summarizes some disadvantages with the ASTM D5744 method where one major drawback is the duration of the test. Although it can take years until reaching stable levels of leachate the test requires a duration time of minimum 20 weeks. Another disadvantage that is mentioned is that the method does not specify the temperature for the reaction environment, only an approximation of around 30 °C presented in the standard. Another dilemma with this method is the maintaining of constant air flow through the cell throughout the duration of the test. All these factors result in difficulties to maintain a controlled reaction and consistency which is one of the main intentions with the test (Lapakko 2003).

2.4. METALS IN SOIL AND WATER

According to Berggren Kleja *et al.* (2006) metals in water is represented by different groups, either they *bind to particles* such as clay minerals, organic material or iron hydroxides or they appear as *dissolved ions* (free ions, hydrated cations or anions, or as organic/inorganic complexes). When considering soil and groundwater, the majority of the metal is dissolved while in lakes, the most dominant form of metal is found bind to particles (Berggren Kleja *et al.* 2006).

Berggren Kleja *et al.* (2006) further describes that in soil, the most important mechanisms are *adsorption* and *precipitation* and the ability for the metal to participate in either of

these processes depends on the property of each metal. Eventually, the reverse processes can appear meaning that adsorbed metals may desorb and precipitated metals dissolves into the soil water. A consequence of this is that an increase in the metal concentration in the soil water can occur even a long time after the source is removed (Berggren Kleja *et al.* 2006). The redox potential is of great importance when considering the different species that may represent the metal in soil. Elements that are depending on the redox conditions and hence are called redox-sensitive are for example Fe, Cr, Cu, Co, Mn, Sb and As (Borch *et al.* 2010).

2.4.1. Precipitation of metals in soil water

According to McLean & Bledsoe (1992) one of the reactions that inhibits the movement of metals and hence hold down the release to ground water is precipitation. Precipitation of metals form a new three-dimensional solid product which occurs when the concentration of the metal is high enough in the solution. This form of solidification is of high importance when considering a contaminated area where the concentration of some metals, that naturally occurs in low concentrations, are high. Furthermore, the precipitation of metals depends on environmental parameters such as pH and concentration (activity) of the metal. A $\text{pH} > 7$ is assumed to maintain the largest retention of cations while a $\text{pH} < 7$ represents the greatest retention of anions. Considering Pb, the solubility decreases as pH increases meaning that Pb becomes more immobile at higher pH (McLean & Bledsoe 1992).

2.4.2. Adsorption of metals in soil

The other reaction, stated by McLean & Bledsoe (1992), that immobilize the metals in soil is adsorption. In comparison with precipitation, this process does not form any new three-dimensional solid phases, instead it attracts to surfaces of present soil particles (McLean & Bledsoe 1992). Metals can be absorbed to different particles in soil such as humus, clays, Fe-Mn and Al-hydrous oxides and some salts such as CaCO_3 . Humus has a negative charged surface which attracts cations to bind to this surface by *columbic forces* caused by electric differences. The metals that absorbs to the humus surfaces by this type of interaction are mostly represented by alkali and alkaline earth metal ions (Young 2013). In addition, this same electrostatically attractions occur between cations and clay minerals in the soil (Berggren Kleja *et al.* 2006). Adsorption can occur either as outer sphere complex or inner sphere complexes. The latter creates a stronger bond since the metal ions binds to a functional group in soil, either with covalent or ionic bond, without a water molecule present in between adsorbing surface and the metal which is the case for an outer sphere complex (Roberts *et al.* 2005). McLean & Bledsoe (1992) states that adsorption is the most important parameter when considering immobilization of metals while looking at natural conditions (compared with precipitation for contaminated soils). Although the authors further explains how the concentration of the metal is of highly importance where at low concentration all metals may be bound to surfaces while an increase in the concentration results in saturation at the charged surfaces (McLean & Bledsoe 1992). In addition to the metal concentration and the surfaces available,

parameters such as redox conditions, pH and the presence organic matter all affect the tendency for metals to absorb and hence decide the rate of immobilization.

2.4.3. Arsenic in soil

Considering anions in soil, arsenic as As(III) (arsenite) or as As(V) (arsenate) is of major concern considering contamination risks (McLean & Bledsoe 1992). The toxicity of these two oxide states of arsenic are both considered as the most toxic ones found in the environment although, As(III) is both more soluble and toxic (Newton *et al.* 2006). Even though most of the absorption surfaces in the soil are negatively charged, some particles may create a positive surface charge during low pH, which might immobilize the anions. Furthermore, considering immobilizations due to precipitation of arsenic, iron is the most important sink but precipitates with calcium and alumina can also occur (McLean & Bledsoe 1992). Except pH, another parameter that strongly effects how arsenic may appear in the environment is the redox potential. For situations represented by high redox As(V) is the dominant species while at reduced conditions As(III) is most abundant (Berggren Kleja *et al.* 2006).

2.4.4. Lead in soil

Dissolved Pb (Pb^{2+}) in water is frequently absorbed by a number of negatively charged surfaces in soil and hence the mobility of this element is strongly reduced (McLean & Bledsoe 1992). When the environmental conditions in the soil is oxidative with high pH and additionally the concentration of Pb is high, this may cause Pb to precipitate as either $PbCO_3$ (Cerrusite) and $Pb_5(PO_4)_3Cl$ (Pyromorphite) (Berggren Kleja *et al.* 2006).

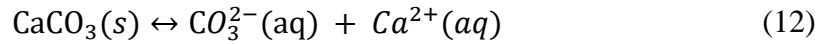
2.5. GEOCHEMICAL MODELLING

Elert *et al.* (2006) describe how chemical modeling can help in predicting the composition of different compounds from leaching data. For example, if data on total concentration and pH-values during leaching is available, they can be used to calculate the *saturation index (SI)* in the system determined (Elert *et al.*, 2006).

According to Langmuir (1997), SI is defined as equation 11 below where IAP stands for the ion activity product while K_{SP} is the solubility product that determines how much of the mineral that may dissolve into the water depending on the ion activity during certain conditions. Both parameters are mineral specific and defined at the same pressure and temperature. If the water is saturated the system is at equilibrium were $IAP = K_{SP}$ and hence $SI = 0$. If instead the water is supersaturated SI will be presenting values > 0 and during these conditions the mineral can be expected to precipitate into the solution. On the opposite, if the mineral is represented by a SI value < 0 , the condition is undersaturated and the mineral is expected to dissolve to the solution (Langmuir 1997).

$$SI = \log_{10}\left(\frac{IAP}{K_{sp}}\right) \quad (11)$$

Considering the theory behind the SI value, the CaCO_3 reaction (see reaction 12) will strive from left to right when $SI < 0$ and from right to left when $SI > 0$.



3. METHOD

3.1. SITE DESCRIPTION

In the southern part of Sweden around 50 closed-down glassworks is located in a region called Kingdom of Crystals (Glasriket). As a result of the glass production conducted at these sites, the soil in the area is polluted and glass waste that has been deposited and is now found in soil as well as in landfills. Studies conducted by the County Administrative Boards and the Glasswork Association between 2006 and 2007 showed that the contamination of metals in the area were high, especially considering arsenic, lead and cadmium (SGU, 2019).

Between 2016 and 2019, at the request of SGU, Golder has been conducting studies regarding contamination risk around the three glassworks Flerohopp, Åryd and Alsterbro (Figure 6). At each site, glass in different sizes and color has been sampled randomly at different locations, creating a composite sample to send for analysis (Golder, 2018). Figure 7 shows a selection of different glass waste taken at different locations at each glasswork. Figure 7a shows glass samples from Flerohopp that were sorted out from excavated soil in the area, Figure 7b depicts a landfill of mostly finished glass from Alsterbro while Figure 7c illustrates a glass mold of unfinished glass from Åryd. In Figure 7d, sorted glass samples from Alsterbro is presented. The focus of production at each sites is presented in Table 2.

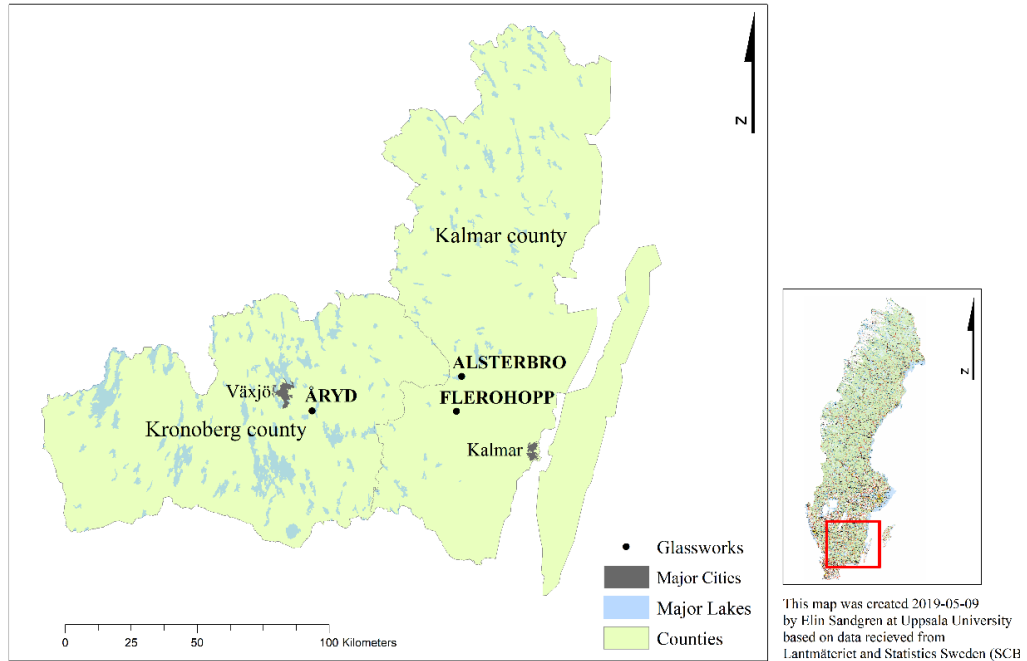


Figure 6 Map showing the location of the three glassworks analyzed in this study. Map data was received from Lantmäteriet© and Statistics Sweden (SCB), 2019-05-09.



a. Flerohopp 2016-11-22



b. Alsterbro 2017-08-25



c. Åryd 2017-12-05



d) Alsterbro 2018-06-12

Figure 7(a-d) Shows different type of glass waste, taken at different locations representing different environments, at each glasswork. All pictures are owned by Golder Associates AB and the date taken is presented underneath each picture.

3.1.1. Flerohopp

Flerohopp is a village with around 200 inhabitants located in Nybro municipality in Kalmar county (SGU, 2017). Between the period 1892 and 1960 glass production was conducted at Flerohopp glasswork, producing different glass such as light bulbs, lighting glass, thermo glass and crystal glass (SGU, n.d.). Prior to the glass production, iron was produced at the site during 1725 to 1879 as well as other productions such as a starch factory, frame saw and a bobbin factory (SGU, n.d.).

During the active years of glass production, glass waste from the production as well as construction waste has been disposed to landfills in the eastern part of the site in a gradient towards the Ljungby river. From a study conducted by SGU in 2006 results shows that the levels of metals such as arsenic, cadmium and lead are high in the area and especially close to the landfill (SGU, n.d.). Further investigations done by Golder shows that other pollutants, such as antimony, barium and boron, has been showing high levels in the area as well (Golder, 2018).

3.1.2. Åryd

The former glasswork in Åryd is located in a village around 15 km south east of the city Växjö and close to lake Årydsjön. Here, glass was produced between 1912 and 1921 with focus on producing glassware, vases and glass used in thermo flasks. Today, most of the buildings where the glass production previously occurred is now demolished, on the site there is just two buildings remaining that historically were used as melting ovens (SGU, 2017).

3.1.3. Alsterbro

In Alsterbro, the glasswork was established in 1871 and production was conducted until 1969. From the beginning, the main production at this location was bottle glass but due to an ownership change in 1880 the production shifted focus towards household glassware. Further on, in the 20th century pressed glass was also produced at the site. As the business became less beneficial the production focus again shifted around the 1960s when starting to produce glass in many strong colors (Jansson 2018) .

Table 2 Showing the major focus of production at the different glasswork studied

Glass work	Main production
Flerohopp	<i>Light bulbs</i> <i>Lighting glass</i> <i>Thermo glass</i> <i>Crystal glass</i>
Åryd	<i>Glassware</i> <i>Vases</i> <i>Thermo glass</i>
Alsterbro	<i>Bottle glass</i> <i>Glassware</i>

3.2. COLLECTING DATA

Material for this thesis work is owned by SGU that has assigned Golder to analyze and write reports covering the environmental conditions at the three shut-down glasswork Flerohopp, Åryd and Alsterbro. The field samples taken by Golder was sent to ALS Scandinavia AB for analysis and the results were then sent back to Golder. For this thesis work data from HCT and total concentrations, representing samples from the three glassworks, has been used.

3.2.1. Humidity Cell Test

Glass waste from the different glasswork were sampled by Golder for the purpose of conducting HCT which was done at ALS in Vancouver, Canada, according to the ASTM-5744 standard (ALS 2019). The specifics for these analysis is defined below (Golder, 2018):

- Sample crushed into fraction size of 6mm.
- 21 weeks duration time (0-20 weeks).
- 500 mL added volume water every seventh day.
- Leachate filtrated through a 0.45 µm filter prior to analysis.
- Analysis conducted in room temperature.
- The method “flood” was used for rinsing water.

To analyze the concentration of dissolved metal in the solution, ICP-MS was done for each leachate (ALS 2019). ICP-MS stands for Inductively Coupled Plasma Mass Spectrometry and is a method for determining element concentrations. The process combines a high temperature source (ICP) which transform the element to ions which is thereafter separated and detected by the mass spectrometer (MS) and results in order to detect complex matrices as well as low detection limits (Wolf & U.S Geological Survey (USGS) 2005). In addition, according to lab protocols from ALS from the three glassworks, the leachate was analyzed with electrodes in respect to pH and conductivity. The protocols also state that alkalinity was analyzed by potentiometric titration and furthermore inorganic components, such as F and Cl, was analyzed with ion chromatography and/or UV detection.

A selection of the results with the highest relevance for this thesis work is presented in Table B1(a-c). A simplification that has been made in this master thesis is that for result showing a concentration below the detection limit, the leachate concentration has been set to zero.

3.2.2. Total concentration analysis

To determine the initial total concentration of different elements in the glass waste from the different sites, samples were sent to ALS Scandinavia for analysis. Following their analyze package MG-1, total concentration of As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn in the samples were determined by drying the sample to 50°C after which the sample is leached in 7M HNO₃ or H₂O₂ (ALS, 2019). For the other substances, the samples were melted in a lithium metaborate and then dissolved in HNO₃ (ALS, 2019). The dried and the melted samples were then analyzed with ICP-MS (Golder Associates AB 2018) .The

result from this analysis, conducted by ALS, for all three glasswork is presented in Table B2.

3.3. CALCULATING PPM LEACHED METAL IN RELATION TO THE TOTAL CONCENTRATION

For the full set of HCT (0–20 weeks) the volume water added ($V_{in(i)}$) to the cell and the water released ($V_{out(i)}$) from the cell after leaching was collected for each of the glassworks, see Table B3.

For each week (i) of HCT for the glassworks, the leachate concentration ($C_{leachate(i)}$) [mg/l] of Na, Ca, Si, As and Pb was collected (see Table B1) and thereafter adjusted to weight metal ($m_{metal(i)}$) leached for each week by following equation 13:

$$m_{metal(i)} = V_{out(i)} * C_{leachate(i)} \quad (13)$$

By following equation 14 the total weight metal ($m_{metal(tot)}$) released after the HCT had been conducted was received by summarizing the result from week 0 through 20:

$$m_{metal(tot)} = \left(\sum_0^{20} m_{metal(i)} \right) * 10^{-6} \quad (14)$$

Since the total concentrations of these samples is presented as oxides from the ALS analysis, Table B2, the weight was converted in relation to the molar mass of the oxides ($M_{metaloxide}$) in relation to the metal itself (M_{metal}). This was done by following equation 15 and with the molar mass presented in Table B4.

$$m_{metaloxide} = m_{total} * \frac{M_{metaloxide}}{M_{metal}} \quad (15)$$

3.4. DATA EVALUATION

To enable comparison regarding how the leaching pattern for a specific parameter varies over time for the three glassworks, Si, Na, Ca, As, Pb and pH have been plotted in Excel over the whole HCT-period. Since the level of concentration varied widely between the glassworks, the values representing concentrations were converted to logarithmic to facilitate comparison in leaching pattern.

In this study, data analysis regarding comparison in leaching pattern between different parameters over time for each glasswork individually has been done. To get an idea whether the leaching of Na (alkali ion) or Ca (alkaline earth ion) from the glass network can relate to the weathering of the Si-matrix, leachate concentration of Si has been plotted

together with Na and Ca for each glasswork. The leaching of Si has also been plotted with pH over the HCT-period to investigate if the dissolving of Si can be related to pH variation. Lastly, leachate concentration of Na and Ca has been plotted against leachate concentration of As and Pb respectively for all glasswork for the whole period of HCT. This has been made to investigate whether the leaching pattern of some of the toxic parameters As and Pb can be expected to show the same leaching pattern as one of the major glass components. All data used for this analysis in Excel is found in Table B1.

3.5. GEOCHEMICAL MODELLING

3.5.1. PHREEQC Modelling

For this project, PHREEQC Version 3 was used and received from USGS (U.S Geological Survey [USGS] 2017) with the included database Minteq V4. The used input solutions were based on HCT data and have been representing an oxidative environment since the conditions during HCT can be considered aerobic. For each glasswork weeks 0, 5, 10, 15 and 20 have been analyzed to get an idea of what happens in the samples over time considering species distribution and saturation. The data used for modelling in PHREEQC for the three glassworks is presented in

Table C2, representing concentration of metals, alkalinity and pH. For all runs, the temperature has been set to 25°C.

3.5.2. PHREEQC result selection

The modelling result of interest for this study is the species distribution of Si in the solution and furthermore also the tendency of precipitation of minerals containing Si and Al since this might inhibit dissolving of the glass structure (Mendel 1984). For species distribution of Si focus has been at the two compounds $\text{Si}(\text{OH})_3\text{O}^-$ and $\text{Si}(\text{OH})_4$ since these two gives an idea of the silica solubility (Alexander *et al.* 1954) and these will further be presented as percentage of total concentration of Si in the leachate for the week of focus. In addition, the species distribution of As and Pb has been analyzed. For As, the most commonly found oxidation state has been identified and considering the distribution of Pb, the four most abundant species for each week have been identified and presented as percentage of total concentration in the solution. Considering the tendency of precipitation of minerals containing Si, Al, As or Pb only minerals with $-2 \leq \text{SI} \leq 2$ are presented. This selection was made since only minerals with a SI close to zero can be considered as a determinant factor when looking at the reaction mechanism.

4. RESULTS

4.1. TOTAL CONCENTRATION

Below, Figure 8 shows the distribution of different elements for the three glassworks based on results from the total concentration analysis. Figure 8a shows the distribution for Flerohopp showing that the most dominant component is SiO₂ (around 80%) followed by Na₂O (11%) and CaO (5%) and the rest of the components are represented by K₂, Al₂O₃, MgO and others. Figure 8b shows the distribution of elements for Åryd glasswork, with the most dominant component represented by SiO₂ (around 70%) followed by CaO (13%) and Na₂O (9%) and also K₂, Al₂O₃, MgO and others. The distribution for Alsterbro glasswork is presented in Figure 8c showing a somewhat different result than the previous two with a SiO₂ concentration of about 56%, a PbO concentration at 4% and arsenic representing 1% of the total concentration in this sample. Apart from the variations for these specific elements, Alsterbro also stands out by having a high percentage of elements defined as “others”, in comparison to the other two glassworks.

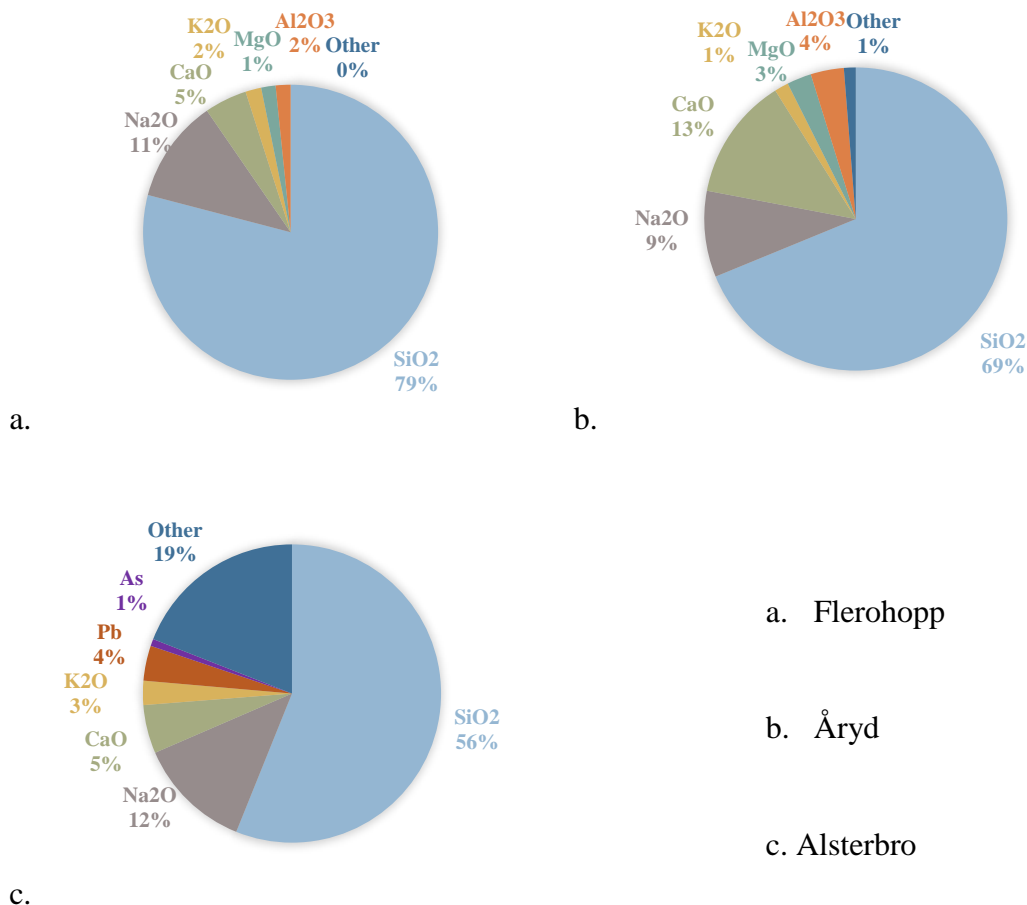
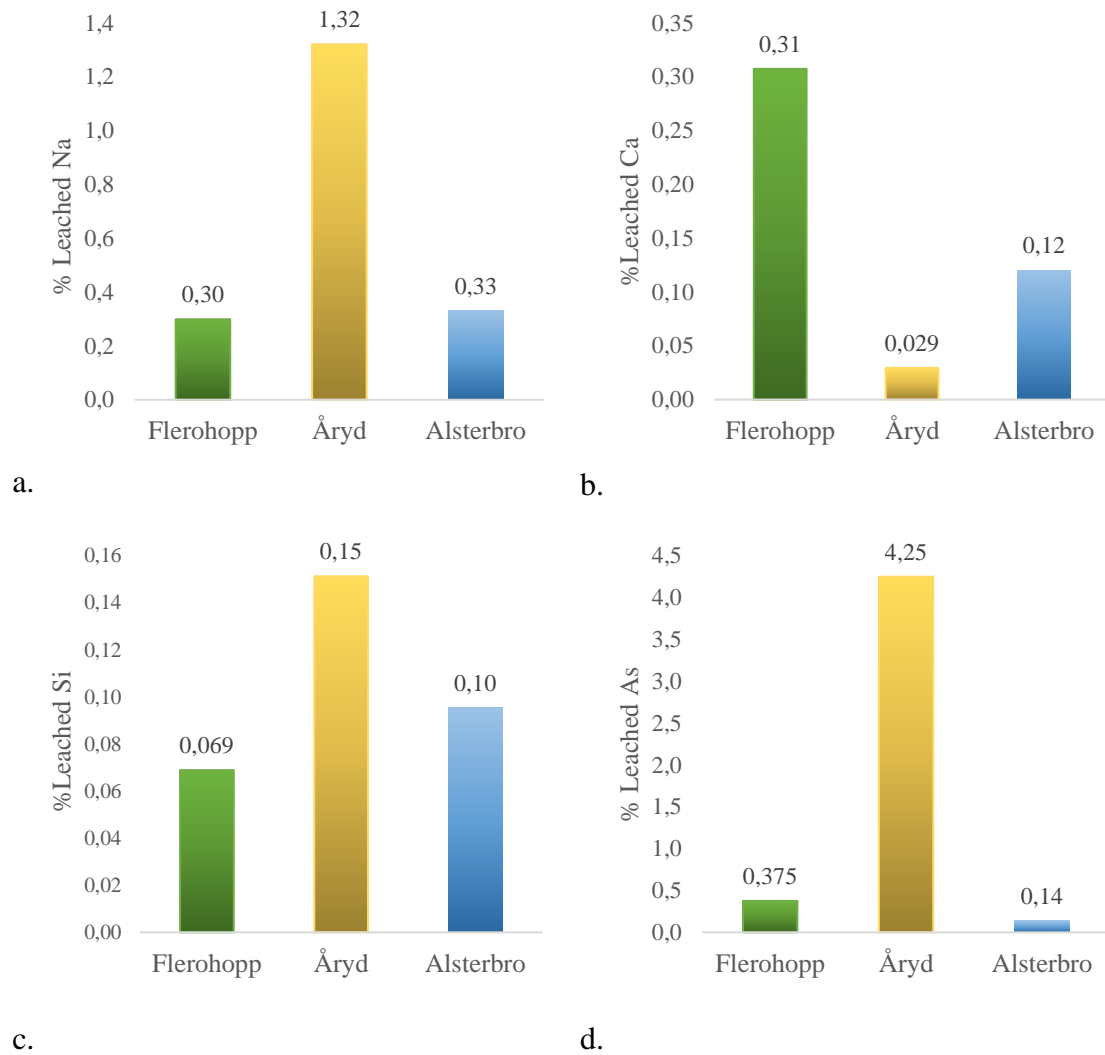
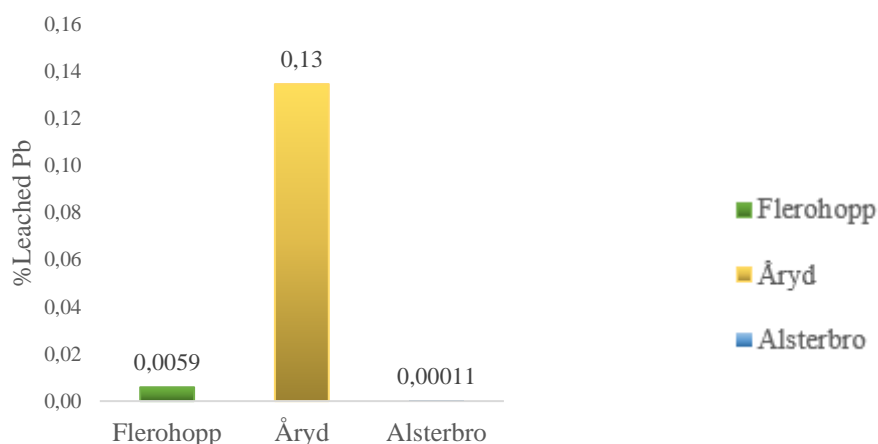


Figure 8 The percentage (by weight) of the six most abundant elements or compounds are shown for each glasswork, with other less abundant elements and compounds being labeled as “others”

4.2. CALCULATING CONCENTRATION LEACHED METAL IN RELATION TO TOTAL CONCENTRATION

Figure 9(a-e) shows the relative amounts of Na, Ca, Si, As and Pb which was leached during the full period of the HCT, calculated from the obtained total concentration (presented in 4.1). As seen in Figure 9, Åryd is the sample for which the highest proportion of leaching occurs in all cases except in the case of Ca (Figure 9b) where instead the sample from Flerohopp is the one which leach the most in relation to its initial concentration.





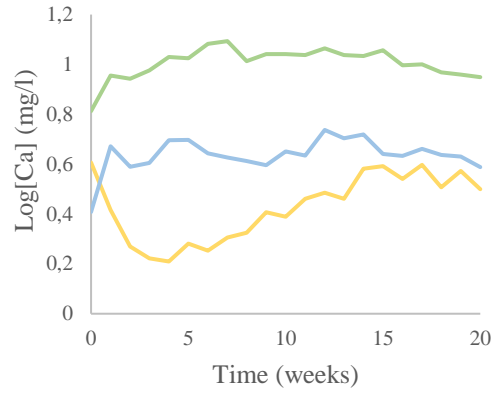
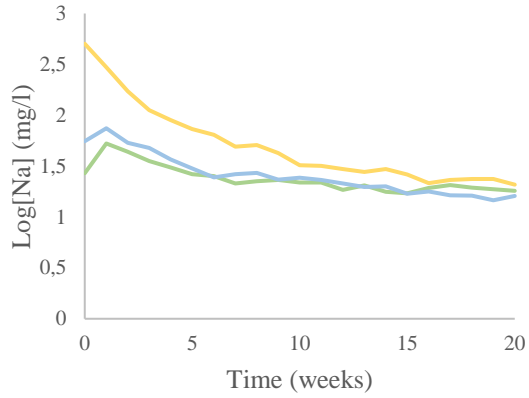
e.

Figure 9(a-e) Relative amounts leached during the HCT with respect to the total concentration presented in 4.1.

4.3. ANALYSING HCT DATA

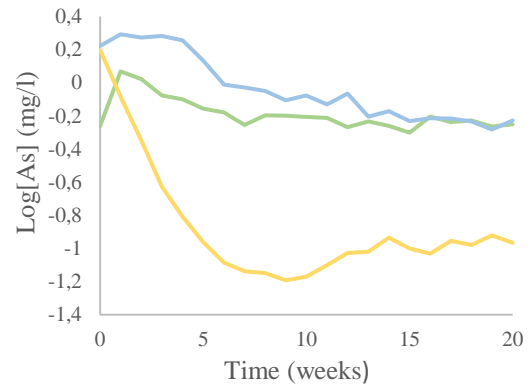
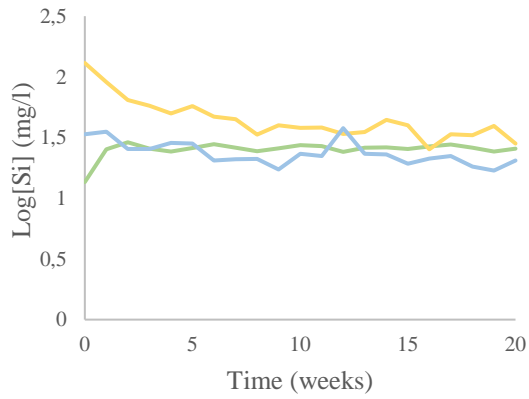
4.3.1. Different glass components against time

Figure 10(a-e) shows the logarithmic concentrations of Na, Ca, Si, As and Pb in the leachate for the complete set of the HCT weeks for the three glassworks. Considering the leachate concentration of Na (Figure 10a), a similar leaching pattern is shown in the later part of the HCT period for all three glassworks and there are also some similar trends between the leaching of Si between the glassworks (Figure 10c). Looking at the variation of Ca (Figure 10b), Flerohopp and Alsterbro seems to follow the same pattern although the concentration in the leachate from Alsterbro is lower than for Flerohopp, but no similarity is seen for Åryd. The same goes for the concentration of As (Figure 10d) in the leachate were Flerohopp and Alsterbro has the same leaching pattern while the Åryd sample stands out. Although, looking at Pb (8e) the leaching between Flerohopp and Åryd is more similar whereas the Alsterbro sample differs from the rest. Figure 10f shows the pH variation (non-logarithmic) over time were all glassworks has their maximum pH initially (Åryd has the highest at slightly above 10) whereafter a significant drop occurs followed by a fluctuation around 8.5-9 for the rest of the HCT.



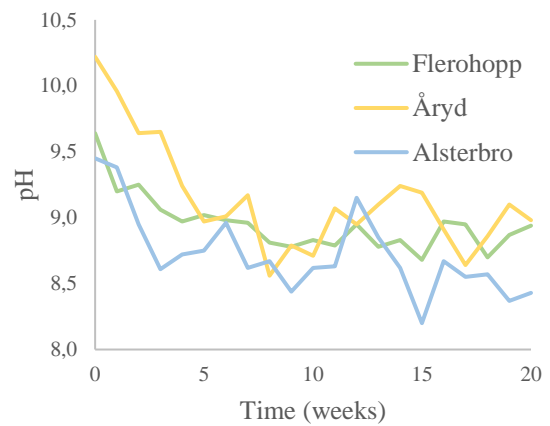
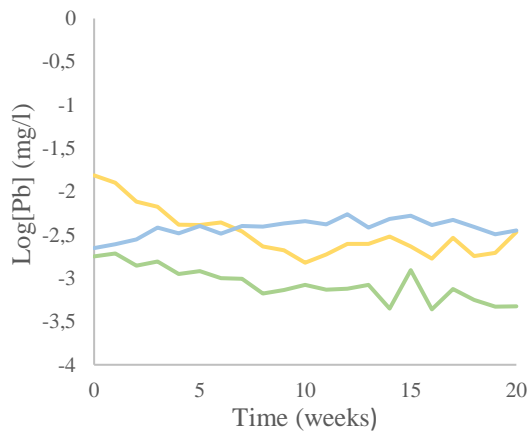
a.

b.



c.

d.



e.

f.

Figure 10(a-f) Comparison of leaching concentration as $\log[C]$ for Na (10a), Ca (10b), Si (10c), As (10d) and Pb (10e) between the three glassworks over the whole HCT period. Figure 10f shows a comparison of how pH varies over time for the three glassworks.

4.3.2. PH variation in the leachate against leaching of Si

Figure 11 shows the Si concentration and pH variation over the 21 weeks of the HCT. While comparing the parameters from the Flerohopp sample, no similar pattern can be distinguished, the Si concentration is rather constant while the pH shows a decreasing and fluctuate behavior throughout the HCT. Åryd and Alsterbro on the other hand shows similar trends in variation while considering these substances. When pH drops, the concentration of Si in the leachate also drops and the same goes for the extreme values, especially significant while looking at week 12 in Alsterbro were both the pH and the Si concentration increases drastically in comparison to previous weeks.

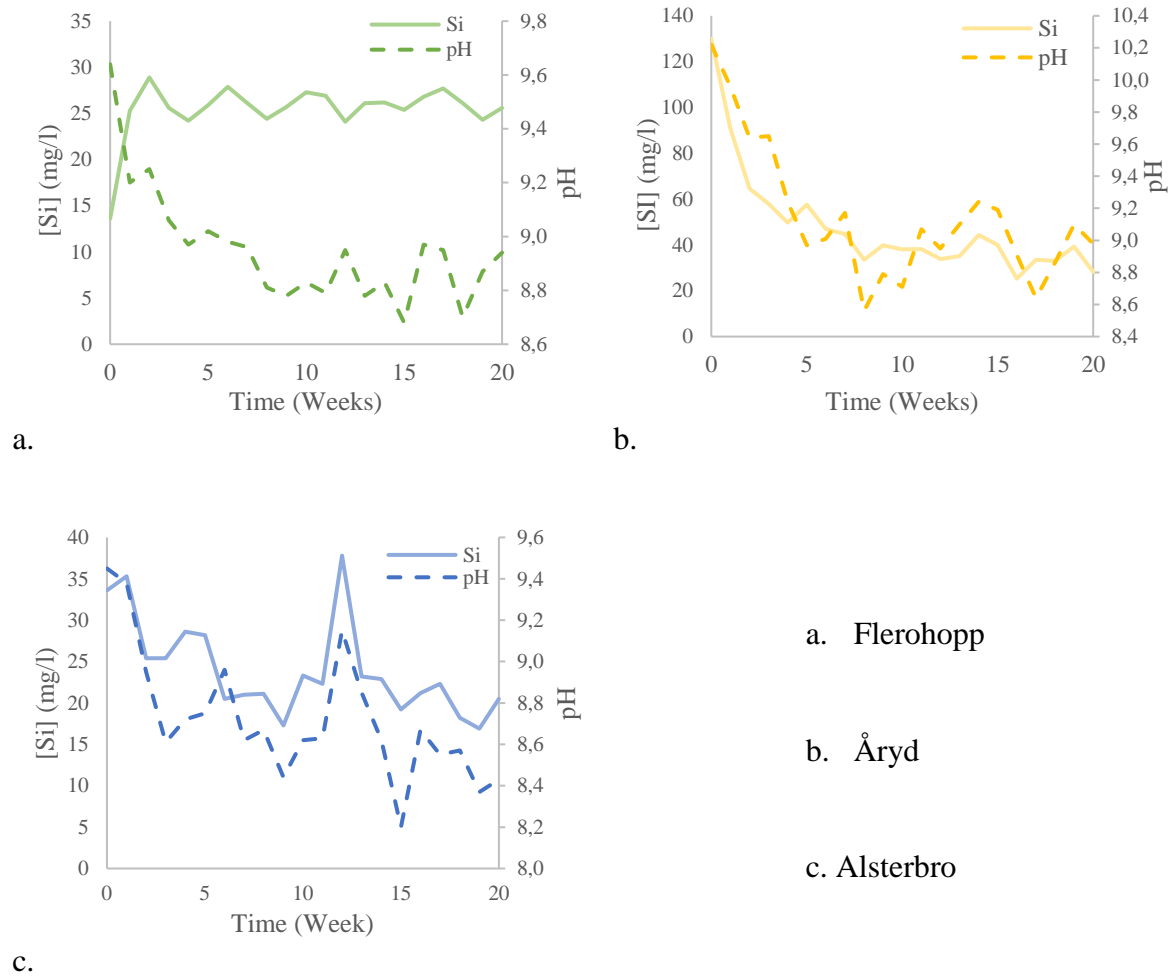
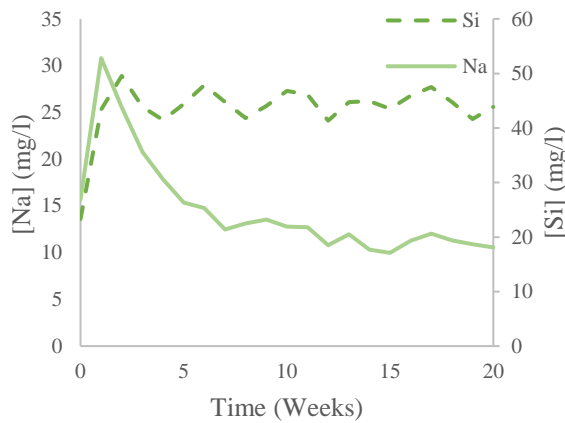


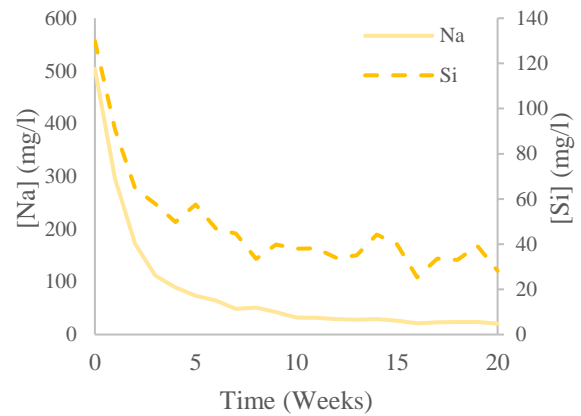
Figure 11(a-c) Concentration of Si (left y-axis) and the pH variation (right y-axis) based on result from the 21 weeks of HCT conducted on glass samples.

4.3.3. Leaching of Si against leaching of Na

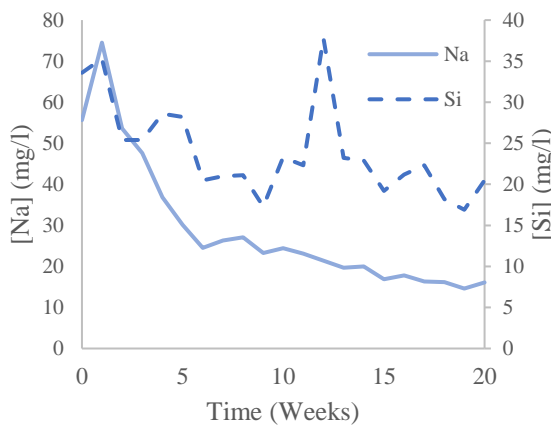
Figure 12(a-c) shows the leaching concentration of Na and Si over the whole period of the HCT. The results in the plots shows that the initial leaching pattern of Na and Si are somewhat similar for both substances. Later in the HCT, the sample from Flerohopp shows a similar leaching behavior were the concentration of Na and Si both remains somewhat constant throughout the rest of the HCT. This can to some extent also be seen for Åryd although the concentration of Na shows a somewhat flat curve while looking at Si there are more fluctuation. The leaching behavior between Na and Si for Alsterbro is not following the same pattern for the major part of the HCT.



a.



b.



c.

a. Flerohopp

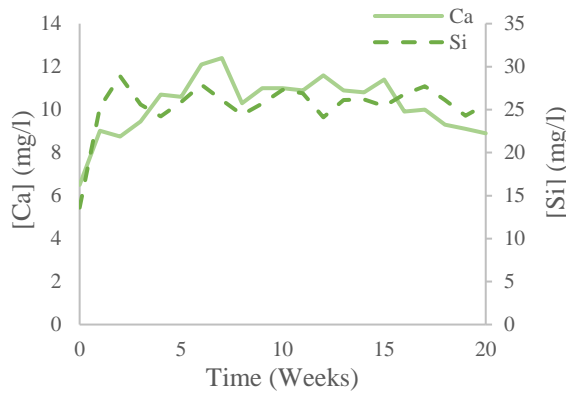
b. Åryd

c. Alsterbro

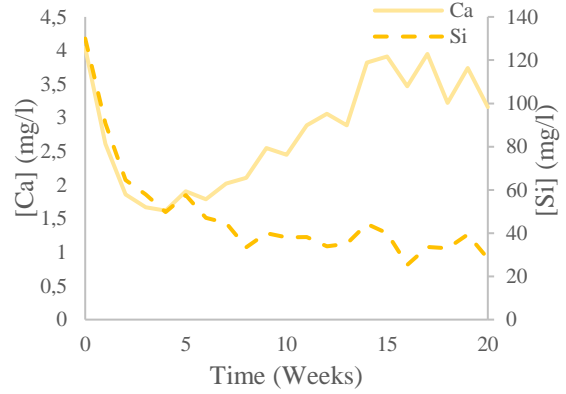
Figure 12(a-c) Plots showing the leachate concentration of Na (left y-axis) and of Si (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.3.4. Leaching of Si against leaching of Ca

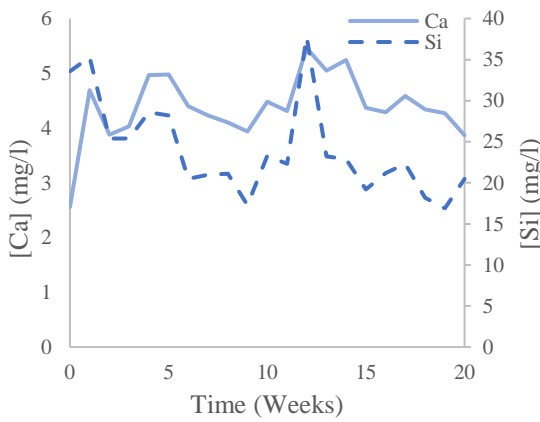
Figure 13(a-c) below shows the leachate concentration of Ca and Si over the 21 weeks of the HCT. For Flerohopp, the leaching pattern for Ca and Si is noticeably similar over the period whereas when looking at the sample from Åryd, a decreasing behavior is comparable for the first five weeks of the HCT whereafter the concentration of Ca increases while the value for Si decreases. Considering the plot representing Alsterbro, a trend can be seen especially considering the extreme pattern where the peaks seems to occur at the same week of the HCT.



a.



b.



c.

a. Flerohopp

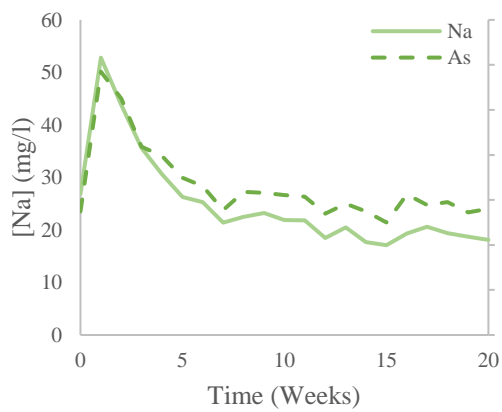
b. Åryd

c. Alsterbro

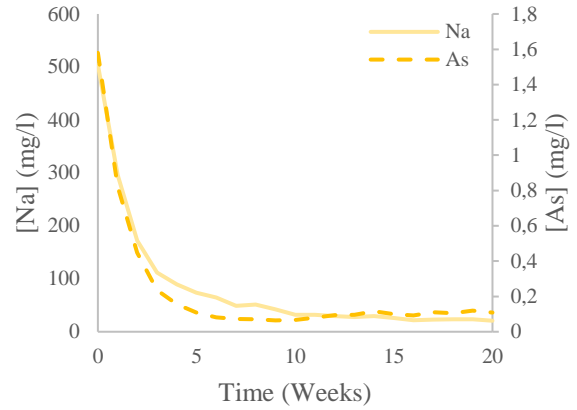
Figure 13(a-c) Plots showing the leachate concentration of Ca (left y-axis) and Si (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.3.5. Leaching of Na against leaching of As

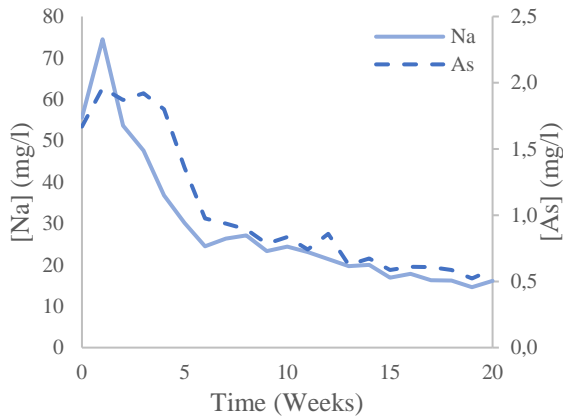
Figure 14(a-c) shows the variation of leachate concentration for Na and As during the whole period of HCT. For all three glassworks, the pattern for the two elements is strikingly similar. The exception is the first weeks for Alsterbro glasswork were Na peaks in concentration over a shorter period than As.



a.



b.



c.

a. Flerohopp

b. Åryd

c. Alsterbro

Figure 14(a-c) Shows the leachate concentration of Na (left y-axis) and As (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.3.6. Leaching of Na against leaching of Pb

The results in Figure 15(a-c) shows the correlation between leachate concentration of Na and leachate concentration of Pb. For Flerohopp and Åryd glasswork, the leaching pattern is somewhat similar over the weeks of the HCT with deviation considering the rapid peak of Pb concentration occurring for the Flerohopp sample during week 15 of the HCT. For the sample from Alsterbro, no similarities in the leaching pattern can be seen.

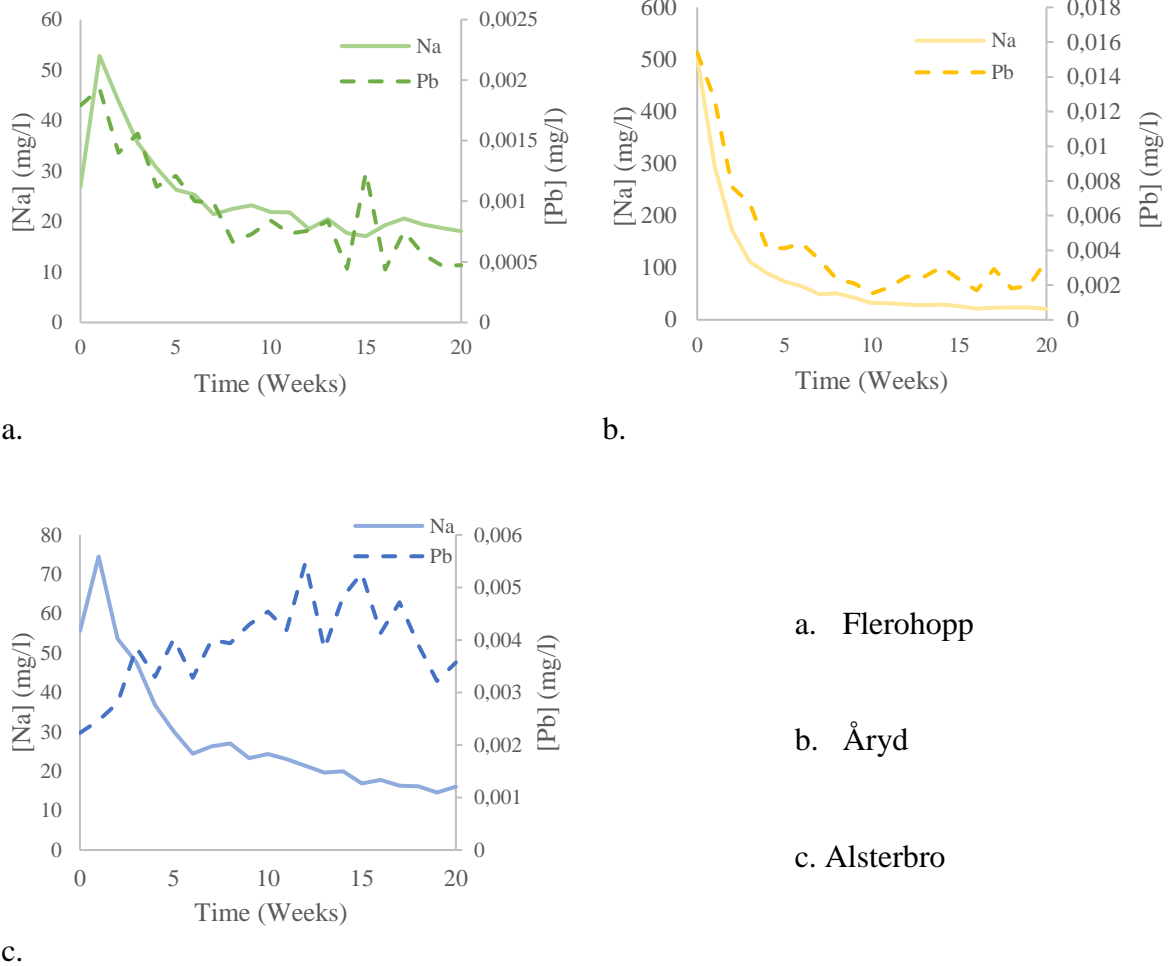
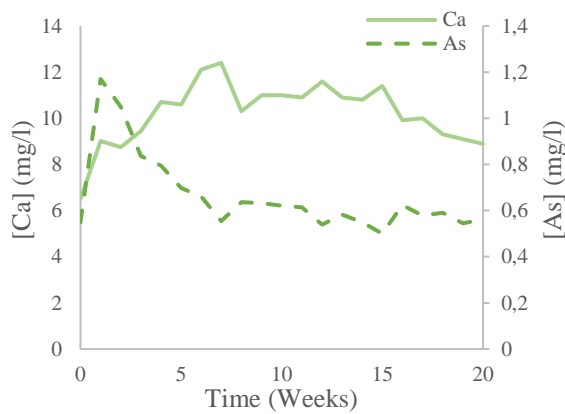


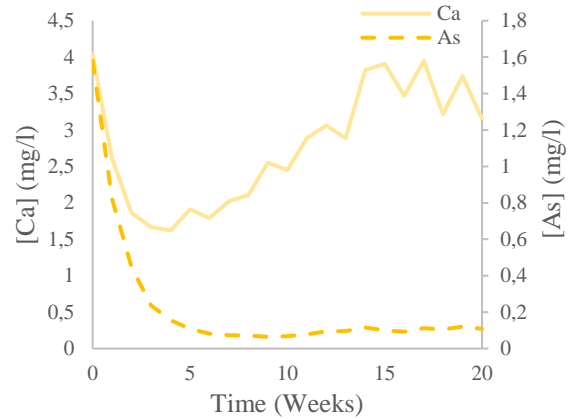
Figure 15(a-c) Shows the leachate concentration of Na (left y-axis) and the leachate concentration of Pb (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.3.7. Leaching of Ca against leaching of As

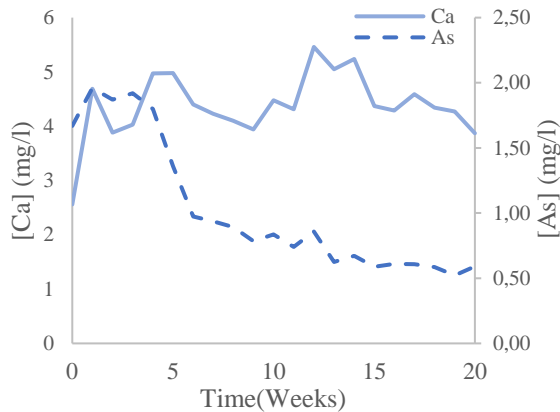
Figure 16(a-c) shows the leachate concentration of As and the leachate concentration of Ca for the complete set of HCT weeks for all three glassworks. As the result shows, no similarity in the leaching behavior is visible for either glasswork except for the initial weeks. The concentration of Ca seems to increase later in the HCT while the concentration of As decreases as the test continues.



a.



b.



c.

a. Flerohopp

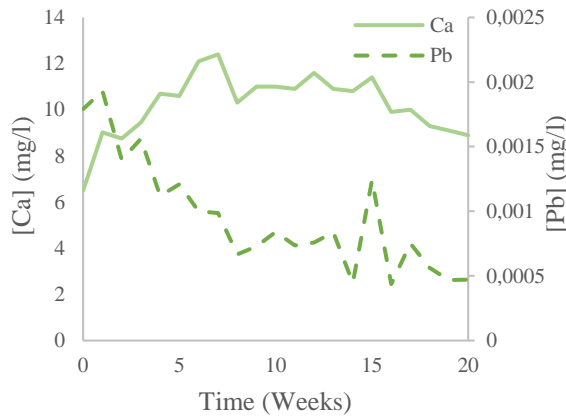
b. Åryd

c. Alsterbro

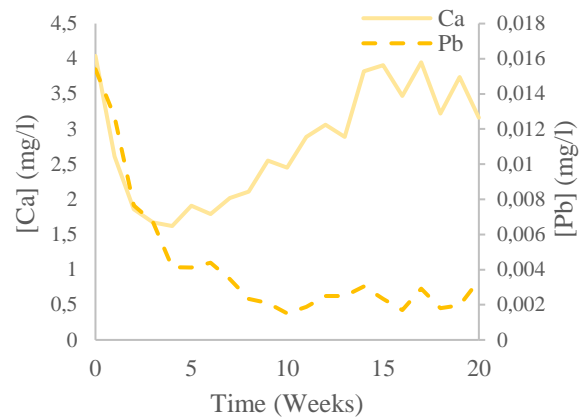
Figure 16(a-c) Shows the leachate concentration of Ca (left y-axis) against the leachate concentration of As (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.3.8. Leaching of Ca against leaching of Pb

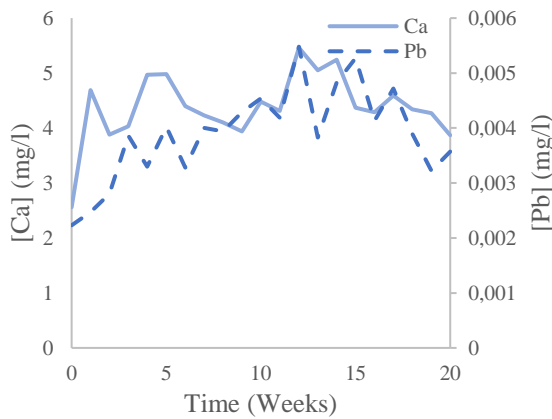
Figure17(a-c) shows the leachate concentration of Ca and the leachate concentration of Pb for the complete set of HCT weeks for all three glassworks. Considering the result from Flerohopp and Åryd, no similarity in the leaching behavior between the two components can be distinguished. The contrary is seen while looking at the Alsterbro data where the leachate concentration between Ca and Pb shows similar leaching pattern over the whole test period.



a.



b.



c.

a. Flerohopp

b. Åryd

c. Alsterbro

Figure17(a-c) Shows the leachate concentration of Ca (left y-axis) and leachate concentration of Pb (right y-axis), based on result from the 21 weeks of HCT conducted on glass samples.

4.4. GEOCHEMICAL MODELLING

4.4.1. pH variation against leaching of Si

Figure 18(a-c) below shows how the distribution of Si varies over the selected weeks of HCT based on modelling in PHREEQC. For all three glassworks, the result indicates that the highest representation of $\text{Si}(\text{OH})_3\text{O}^-$ occurs at the initial weeks of HCT which also represents weeks with maximum pH for the test periods. In general, the result shows that as the HCT period continues, the proportion of $\text{Si}(\text{OH})_3\text{O}^-$ in the solution becomes lower.

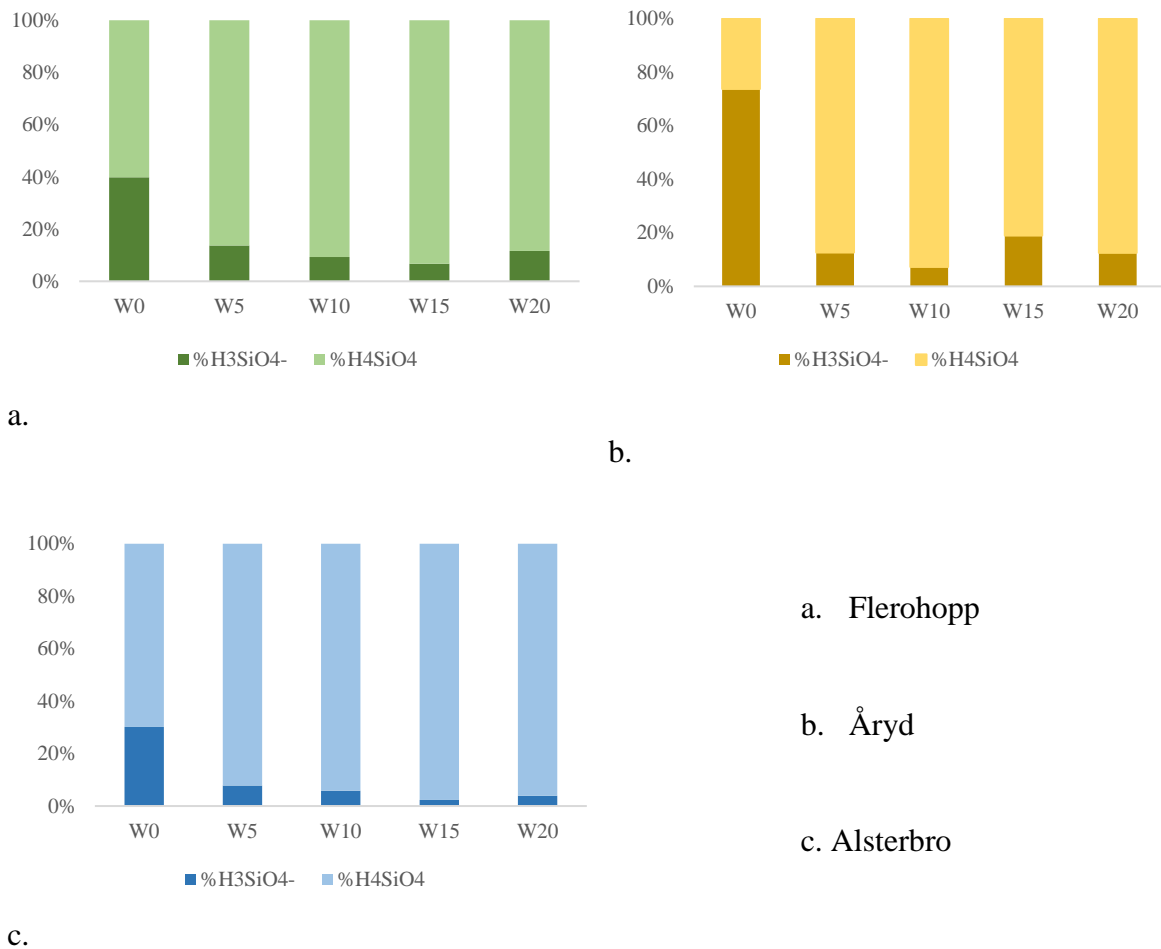
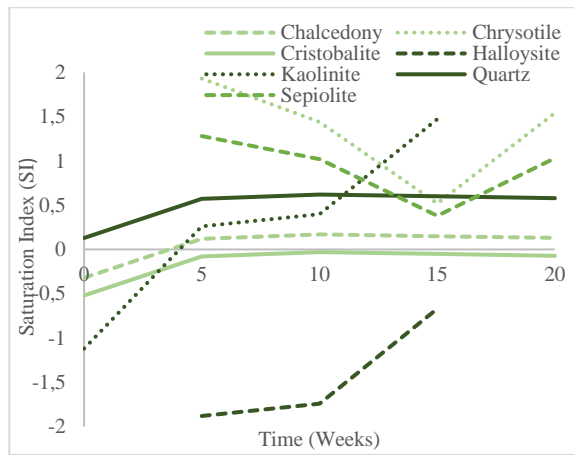


Figure 18(a-c) Presenting the distribution of silica as a result of the geochemical modelling conducted for the selected weeks of the HCT.

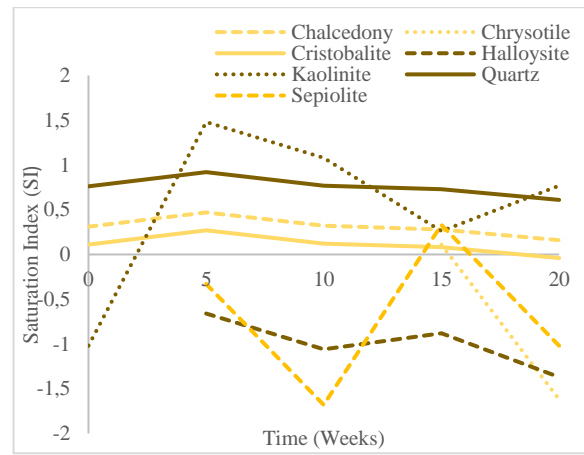
4.4.2. Saturation of Si and Al

Figure 19(a-c) and Figure 20(a-c) presents the mineral containing either Si or Al that shows a $-2 \leq SI \leq 2$ based on results from modelling with PHREEQC, for Flerohopp, Åryd and Alsterbro respectively. The chemical name, reaction and solubility product, as described in PHREEQS's database Minteq4, is presented in Table C1.

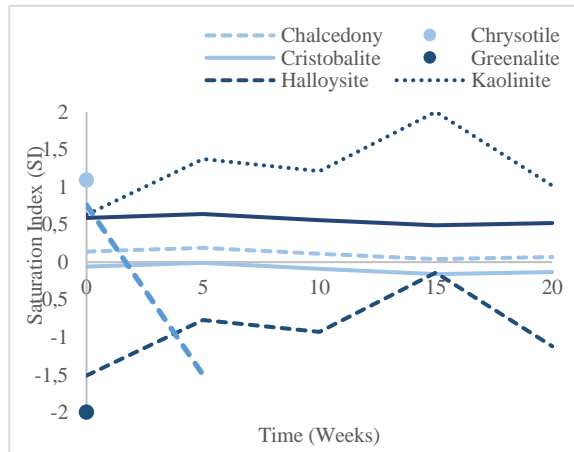
Considering Si containing minerals (Figure 19), a SI close to zero can be seen for cristobalite, chalcedony and quartz throughout the whole period and hence these minerals can be expected to control the solubility of Si in the leachate solution. Initially it seems like some precipitates of SI may occur as chrysotile, sepiotile and kaolinite. However, the SI of these components seems to decrease in later weeks of the HCT.



a.



b.



c.

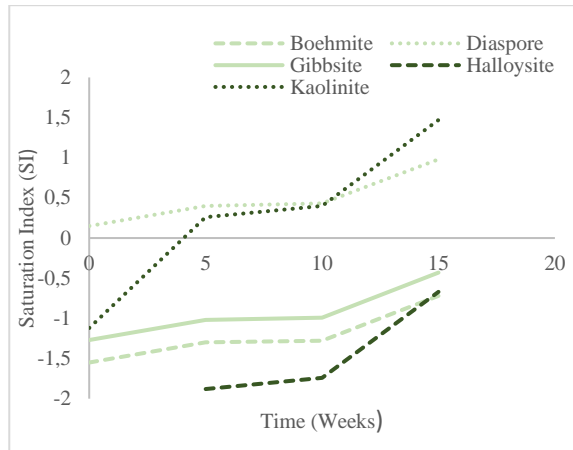
a. Flerohopp

b. Åryd

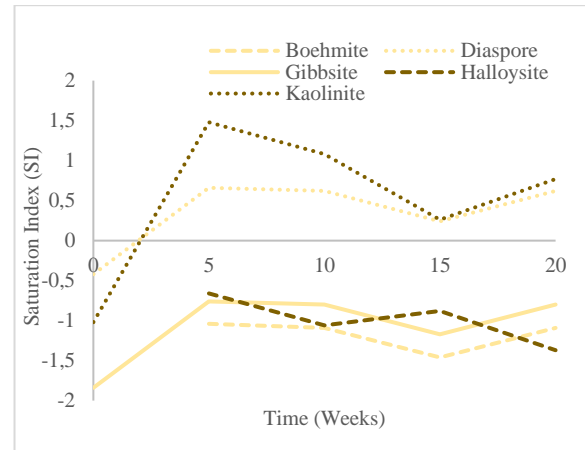
c. Alsterbro

Figure 19(a-c) Minerals containing Si that, from geochemical modelling with PHREEQC, showed values of $-2 \leq SI \leq 2$.

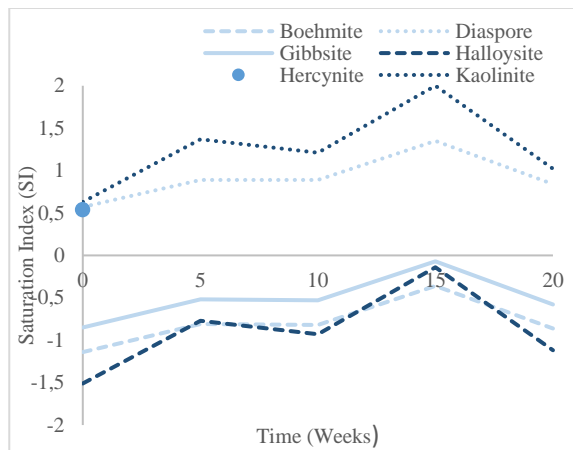
Regarding saturation of Al, (Figure 20), possible candidates that might control solubility in the leachate are diaspore and kaolinite with a value of SI around 1–2 for at least one of the minerals during one occasion. In general, all minerals, as presented in Figure 20, shows a SI-value close to zero (ranging from -2 to around +1,5) which indicates that all of these may control the equilibrium of Al between glass and the contacting solution.



a.



b.



c.

Figure 20(a-c) Minerals containing Al that, from geochemical modelling with PHREEQC, showed values representing $-2 \leq SI \leq 2$.

a. Flerohopp

b. Åryd

c. Alsterbro

4.4.3. Species distribution of As

In Table C3 the distribution of oxidation state for arsenic, based on the result from the geochemical modelling done with PHREEQC, is presented. As the result shows, the most dominant oxidation state of arsenic for the complete set of weeks for all glassworks is represented as As(V).

4.4.4. Species distribution of Pb

Figure 21(a-c) below shows the distribution of the four most abundant species of lead in the leachate as a result from geochemical modelling with PHREEQC. The result presented in the picture shows that, for all glassworks, the most abundant species of lead is found as PbCO_3 for most of the selected weeks. Although, during the initial weeks of the HCT, lead is also expected to be encountered as $\text{Pb}(\text{CO}_3)_2^{-2}$ in the leachate with the Åryd sample significantly standing out with the majority of lead found as $\text{Pb}(\text{CO}_3)_2^{-2}$ during the initial week of HCT. The result also shows that the concentration of $\text{Pb}(\text{OH})_2$ does not show any correlation between the glassworks. When looking at Flerohopp and Alsterbro the amount of $\text{Pb}(\text{OH})_2$ seems to decrease as the HCT goes on while for Åryd the concentration is higher in the later part. Another thing that can be seen is that the amount of PbOH^+ is expected to increase as the HCT continues for all three glassworks. Note should be taken that Alsterbro is the only sample in which Pb^{2+} and PbHCO_3^+ is representing the four most abundant species of lead.

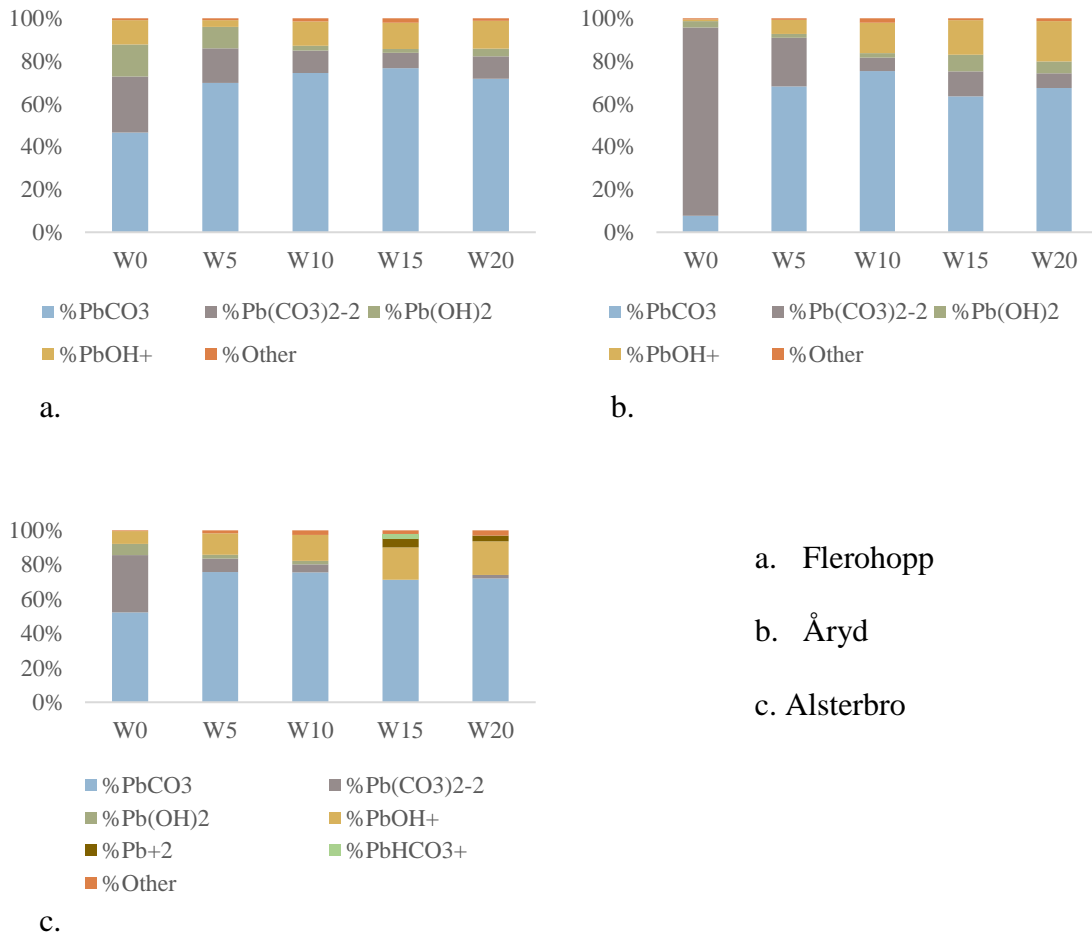
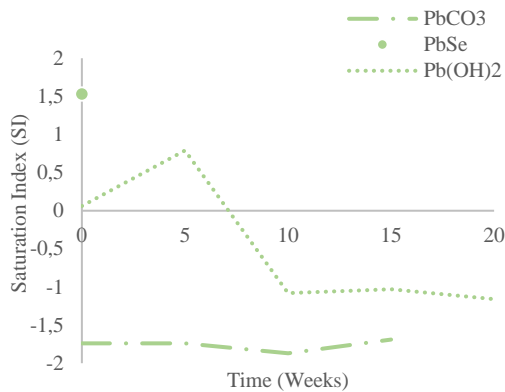


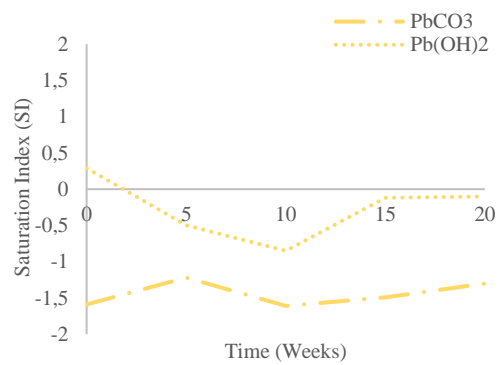
Figure 21(a-c) The four most dominant species of lead, as a percentage of total concentration in the leachate, as a result of geochemical modelling in PHREEQC for selected weeks of HCT.

4.4.5. Saturation of As and Pb in the leachate solution

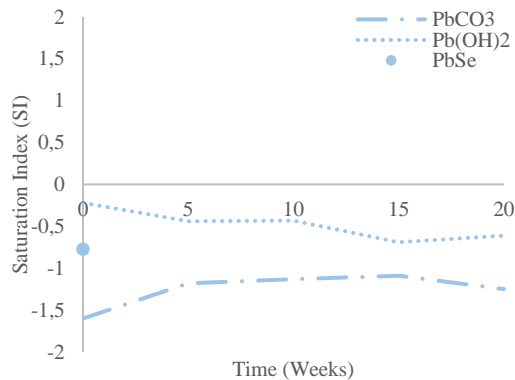
Figure 22(a-c) shows the mineral compounds containing Pb which, from geochemical modelling with PHREEQC, showed a SI in the interval $-2/+2$ and hence is close to equilibrium in the solution. For the samples from all three glassworks, it seems likely that $\text{Pb}(\text{OH})_2$ controls the solubility of Pb, with values fluctuating slightly above and below zero. In contrast, PbCO_3 shows SI values that are slightly below zero indicating that this mineral is unsaturated in the solution and does not control the solubility. During the first week, PbSe is represented in both Flerohopp and the Alsterbro sample but is not represented within the interval for the rest of the period. For As, no mineral represented by a SI value in this interval was found.



a.



b.



c.

a. Flerohopp

b. Åryd

c. Alsterbro

Figure 22(a-c) Minerals containing Pb with values representing $-2 \leq \text{SI} \leq 2$ based on result from geochemical modelling with PHREEQC for the selected weeks of HCT.

5. DISCUSSION

5.1. GLASS LEACHING BASED ON HCT RESULT

5.1.1. Total concentration

When comparing the results from total concentration of samples from the three glassworks in Figure 8(a-c) with the chemical distribution of common glass types presented in section 2.1.1 in Figure 1, the result shows a chemical composition somewhat similar to the SLSG composition. The main component for all three glassworks is Si with the highest ratio in the Flerohopp sample (79%) followed by Åryd (69%) and lastly Alsterbro (56%). Although, the result representing samples from Alsterbro is not comparable since many components is undefined and hence presented as “Other” in the diagram. In this case, something has apparently gone wrong during the analysis done at ALS which makes it hard to determine the definite concentrations for this sample, in turn making it hard to compare to the others.

Something that all three glassworks have in common is that all samples contains oxides of the alkali ions Na and K and the alkaline earth ion Ca. This indicates that modifiers were added to the glass network and consequently NBOs were introduced. Looking at the result in Figure 8(a-c), Åryd has a higher percentage of additional components other than network builders (Si in this case) in comparison to Flerohopp. This implies that the leaching of glass from Åryd might occur to a larger extent than of glass from Flerohopp since glass from Åryd may contain more NBOs and hence also a more open structure than Flerohopp. This hypothesis is further strengthened when looking at the result in Figure 9 where the total amount leached components such as Si, Na, As and Pb over the complete HCT (21 weeks) is higher for Åryd in comparison with the other samples. The possibility of a higher number of NBOs in the Åryd sample might indeed affect the glass network, making it more accessible for water interaction during the weeks with humid air in the HCT-process. This might explain why these components leach at a larger extent for Åryd than it does for the other two glassworks.

While looking at Ca on the other hand, this element shows the lowest total leaching in the sample from Åryd in comparison with the result from Flerohopp and Alsterbro. This result is somewhat surprising since the corresponding result of Na and Si shows that a high number of elements seems to leach from this sample. Looking at the result in Figure 10, the Ca concentration for Åryd is higher at first whereas the concentration drops and later increases again. One explanation for this might be that the glass structure is randomized and at first, the new surface available (which is able to participate in reactions since the samples are crushed prior to analysis) enables leaching of Ca from the surface which in that case explains the initial high concentration of Ca in the leachate. Following this hypothesis, the later drop can be described by the fact that Ca^{2+} ions are less mobile and therefore more unlikely to participate in surface reactions in comparison to Na ions. Although, as the HCT proceeds, the glass network is assumed to be even more dissolved and hence enables leaching of Ca^{2+} ions. While the leachate concentration of Ca for Åryd seems to increase later in the process, it seems to level off in the case of Flerohopp and Alsterbro. Looking at the leaching for Na and Si in Figure 10(a-b), the values for each element seems to reach somewhat similar values towards the later part of the HCT. This is probably caused by the leaching from previous weeks which eventually results in a

stagnation of the leaching in the later period, when all the easily accessed or mobile components have already leached out from the glass structure.

Due to the limitations of this study, it is hard to say for certain what has happened with the glass samples since all have, prior to the analysis in lab, been exposed to different environmental conditions for different time periods. The amount of leaching prior to the HCT for one sample can be very different from another and hence affect the result significantly. In addition, crushing of the sample will result in an increase in the number of available surfaces for reactions to occur at, which will consequently result in an overall higher vulnerability of the glass in comparison to the mixture of fraction sizes that is found on site. The uncertainties are further discussed in part 5.3.

5.1.2. pH variation and solubility of Si

As presented in section 4.3.2 a higher pH tends to result in a higher concentration of silica in the leachate. This is especially significant for Åryd when looking at pH values above 8 which corresponds well to the literature saying that the solubility of the silica matrix increases at higher pH (Alexander *et al.* 1954). This is also confirmed when looking at the result from geochemical modelling under section 4.4.1 when, for Åryd, $\text{Si(OH)}_3\text{O}^-$ is the most dominant species in relation to the total concentration of Si in the solution. For the other two glassworks, Flerohopp and Alsterbro, the result from geochemical modelling is similar, with the highest concentration of $\text{Si(OH)}_3\text{O}^-$ during the initial week of HCT (week 0), which corresponds to the week representing the highest pH. However, this result is not surprising considering that the pKa for Si(OH)_4 is 9,8 (Schróder *et al.* 2012) and hence $\text{Si(OH)}_3\text{O}^-$ would be expected to be the most dominant species at higher pH.

That pH is highest during the initial weeks might be explained by the rapid leaching of the alkali ion Na resulting in an increase of OH^- ions in the solution as presented in equation 4 under section 2.2.3 giving a more alkaline environment. These conditions create a destructive environment for the amorphous silica as stated by Alexander *et al.* (1954). An exception from this is seen for Flerohopp (Figure 11a), where the first week of the HCT shows the highest pH, yet the lowest concentration of Si. This is a surprising result considering the theory mentioned above.

5.1.3. Precipitation of Si and Al

To examine whether either Si or Al shows saturation in the leachate and hence are able to act as a protective layer to the glass surface (Mendel 1984) geochemical modelling was made. Looking at the result presented in Figure 19 and Figure 20 the SI values indicates that minerals containing either Si and/or Al may precipitate into the solution during the HCT. Yet, the results are not enough to evaluate how this might impact the durability and the leaching rate of the glass. One way to study this further would be to use a scanning electron microscope (SEM) to see what might occur at the surface and try to connect this with what happens in the leachate. This could give clues on whether or not a drop in

leachate concentration can be connected to formation of Si and Al containing minerals at the surface.

One thing that should be taken into consideration while studying the result presented in Figure 19 and Figure 20, is that for the HCT, deionized water is added to the sample. This non-mineral containing water makes the saturation process to happen much slower than, for example, natural ground water (Mendel 1984). What happens with the sample during the HCT may therefore not give an accurate picture of what SI value that would have been representative of the mineral in the field.

5.1.4. Leaching of Na and Ca against leaching of Si, As and Pb

When looking at the plots comparing the leaching pattern of Si with leaching of Na and Ca presented in section 4.3.3 and 4.3.4, no general conclusions can be drawn for either glassworks. The trends vary between parameter comparison and glassworks. Most similar pattern is shown in Figure 13a, where the leaching behavior of Ca and Si for Flerohopp is seemingly similar. The Na concentration in the leachate for Åryd, Figure 12b, is also similar to the variation in concentration for Si. Even so, the result is not evidence enough to make a statement regarding whether the leaching of Na and Ca impacts and controls the leaching of Si, yet if so, it could potentially be explained by a degradation of the glass network when glass containing modifier ions is exposed to water (Mendel 1984).

While comparing the leaching pattern between Na and As in Figure 14, a correlation can be seen for all glassworks. Looking at the result from the geochemical modelling in Figure 22, no mineral containing As had a SI around zero and hence determines the solubility of As from the glass. Consider both these results, one explanation to the correlation between As and Na could be explained by these substances being unlikely to form precipitates as secondary minerals. Instead, the released ions of both Na and As, from the glass network, can be expected as dissolved ions in the leachate. In comparison to the result for Na and As, the result regarding Pb seems to differ. Although Pb shows correlation with Na for two of the three glassworks, Figure 15, the similarity is less than when considering As. Looking at the result from the geochemical modelling in Figure 22, the mineral $\text{Pb}(\text{OH})_2$ show SI close to zero for all glassworks, which might indicate that this mineral controls the solubility of Pb in the solution. Which species that will dominate in the leachate depends on parameters such as pH and alkalinity, as well as the concentration of the metal. While looking at the distribution of Pb in Figure 21, the results show that Pb should likely be found in the form of PbCO_3 . This possible precipitation of Pb could be one explanation as to why no correlation between Pb and Na or Ca could be seen for some of the glassworks. Precipitation of secondary minerals might also be the explanation to why no correlation is seen when comparing the leaching pattern between Ca and As.

Another approach to describe this variability in similarity when comparing As and Pb against Na and Ca could be how the atoms are found in the glass structure. The results imply that the leaching of metalloids and metals such as As and Pb tends to follow the leaching of either one of the modifier ions (Na or Ca) where most of the samples in this case follows the alkali ion, Na. An explanation as to why the majority of the result looks like this might be connected to the leaching data over time for the different glassworks,

presented in Figure 10, showing that the leaching of Ca somewhat increases over the HCT period while Na instead decreases and reaches stable concentrations earlier in the HCT. This may further be explained by the literature defining Ca^{2+} as less mobile in comparison with Na^+ and furthermore the interaction between Ca^{2+} and its two connecting NBOs that is stronger than the bond between Na^+ and its single NBO (Le Bourhis 2014). The fact that no similarity is observed between Na and Pb but for Ca and Pb for the Alsterbro sample is interesting but a reasonable explanation to this reverse pattern is not obvious. As such, further analysis and more extensive studies are required.

5.1.5. Leaching of As and Pb from glass from a soil environmental perspective

Without further information regarding environmental parameters such as pH, redox, available particle surfaces and organic matter, it is hard to determine how either As or Pb would act on site for the three glassworks. But since Golder already has made risk assessments for all three, the focus of this study has not been to evaluate the result based on this perspective. It has rather been analyzing what compounds that may be expected from glass leaching to give further knowledge while evaluating the conditions in field. From what could be expected from the literature review, the result from the geochemical modelling with PHREEQC was not surprising. The most abundant oxidation form of As was found as As(V) which corresponds well to the high redox potential used when modelling. Considering Pb, one of the most dominant species which dominated the leachate solution was PbCO_3 (see Figure 21) which also is a common form during high pH (which the HCT data represented).

What also could be seen from this study is that As showed no SI close to zero indicating that, based on the geochemical modelling, there is no parameter close to equilibrium that is controlling the concentration of As in the solution. For Pb on the other hand, the SI for Pb(OH)_2 fluctuates close to zero which indicates that this element will be determining the solubility of Pb while looking at the glass leaching based on HCT.

5.2. USING HCT AS A METHOD TO DESCRIBE GLASS WEATHERING

That glass leaches elements when exposed to conditions represented by the HCT is something that is clear from this study. The reason for this can be connected to what both De Bardi *et al* (2015) and Shelby (2005) states, that an alteration of humid condition with dry condition may be devastating for the glass structure. This implies that the variations that the HCT process causes, might create a severe environment for the glass structure and hence result in a dissolution of the network.

In addition, the small fraction size that the glass sample is crushed to, before placing in the HCT cell, is probably another reason to why the leaching rate is so high. Crushing of samples enables new surfaces, that previous have been unexposed, to participate in reactions which increases the leaching rate. According to Lapakko (2003) this is also something that highly impacts the dissolution of neutralizing compounds such as CaCO_3 . The consequence of this might be that during the HCT process, the neutralization rate is

much larger than it would have been naturally, resulting in a higher pH than what might occur in field.

Lapakko (2003) also states as a major uncertainty with the HCT is the short duration time presented in the standard (20 weeks). The analysis made by ALS at Golder's request was conducted for 21 weeks and for the purpose of this study this time frame is considered enough. Although, it would have been interesting to see what would have happened after very long time of HCT, seeing if some components would have leached more after an even longer period. But overall, to get a primary idea regarding if and how glass leaches, 21 weeks is considered enough.

To conclude, the environmental changes out in the field may not be as continuous and frequent as simulated in the HCT and the fraction size used is not representative for how all glass waste appears on site. Yet, this test may be a good method to use to get an idea of the worst case leaching of glass waste after a long time exposed to natural conditions.

5.3. UNCERTAINTIES WITH THE PROJECT IN GENERAL

A major uncertainty in this project is the differences and variations of the samples from the three different glassworks. First, no consistency in sampling was made, instead a collection of both unfinished glass melts and finished glass was collected, which most certain is different considering both chemical composition and structure. Also, this project has not been evaluating the different environments at which the glass waste has been located. The production at the different sites have been conducted during a various amount of years, meaning that the duration for which the glass has been exposed to environmental conditions varies. Some of the glasses may have laid over 100 years while others around 50 years, some may have laid in a very humid environment underneath the ground for several decades while others might have laid above ground exposed to all kinds of weather changes.

All the above mentioned parameters will impact the result in several ways, for example when looking at the result from the total concentration, making it hard to distinguish whether the variations are caused by different chemical compositions, different samples representation (finished or unfinished glass) or that the glass has been exposed to different environmental conditions. The latter is a critical parameter to consider since this decides how much that has already been weathered and leached from the material in field. For example, the reason for the high Si content in Flerohopp may not exclusively depend on an initial high concentration of Si in the glass production. Instead, it might be affected by previous leaching of other components, resulting in a high Si content while looking at %dry matter. A better analysis would be to take glass samples just after production, before they have been put into landfills, to enable a proper analysis of different glass compounds ability to leach.

5.4. FURTHER STUDIES

One idea to further studies would be to analyze leaching of metals, based on HCT, from glass that has not been exposed to any environmental conditions as those sampled at the landfills at Flerohopp, Åryd and Alsterbro. To take it even further, it would also be interesting to separate glass into different categories, for example sort them by color or by different stages in the process (unfinished glass melt compared with finished glass). If differences in leaching patterns between different components or properties could be seen, this could be useful knowledge when first studying the site in field.

In addition, the literature explains well how Na and Ca bonds to NBOs in the glass network but information regarding how other components, for example As and Pb, bonds were not easy to find. Therefore, it would be interesting to study the glass sample in a scanning electron microscope (SEM) to get more knowledge about where and how these elements can be found in the glass structure.

Considering the HCT test and its effect on glass leaching, it would be interesting to look how a variation in contact time with the rinsing water might impact the concentration of components in the leachate and the saturation rate. The standard of 1 hours could for example be prolonged to 2 hours to see if something more happens during that extended time. This might also give a wider insight in to what extent the contact time of the rinsing water impacts the leaching relative what has already happened during the two three days periods of alternating air humidity. Something that also would be of interest is to do a proper comparison between the leaching result from HCT with result from another leaching methods, such as sequential leaching. This would give more knowledge regarding how severe the HCT might be in comparison to other methods.

For the geochemical modelling done in this study the input value for redox potential corresponded to an aerobic environment. This was based on the properties of the HCT where air is pumped through the sample continuously. What would be interesting to look further into is therefore a model representing reduced conditions to see what difference in speciation and solubility that may occur. For example, As can be expected to be found as As(III) at a larger extent in anaerobic environments and hence this would be a more crucial situation considering environmental and health risk with focus on As.

6. CONCLUSION

In this master thesis work, glass waste from three different glassworks in Sweden has been evaluated based on result from HCT and geochemical modelling with PHREEQC. In this section the conclusion, based on the aim and problem statements presented in section 1.2, is presented.

- *How does the glass waste perform from a chemical perspective?*

Depending on the glass type and the chemical composition, the durability of the glass differs. Previous studies show that when modifiers are added to the glass mass, this opens the structure and makes it less durable against exposure of, for example, water. This study has strengthened this and also shown that the leaching occurs at different rates depending on the ion which probably is due to the differences in bonding strength to the glass network.

- *What processes occur during the humidity cell tests that have been conducted on samples from the three different sites?*

Based on the literature review conducted for this study the water in contact with the glass surface during HCT causes hydration, hydrolysis and ion-exchange to occur at the surface of the glass structure. Furthermore, the environment that is created by HCT may be severe on the glass structure due to the variationally dry and humid condition causing the glass structure to be even more fragile and enhance the leaching of glass components. In addition, the pH increase caused by the cation leaching from the glass might increase the solubility of the silica matrix.

- *Can leaching of As and Pb be related to leaching of other, more dominant, glass components?*

This study has showed that the leaching behavior of As and to some extent also Pb is similar to that of Na. In contrast, no similar pattern was seen when comparing As and Pb with either Ca or Si. An explanation to this is based on previous studies saying that leaching of Na makes the glass structure vulnerable and hence additional glass components also becomes more easily accessed. Another explanation is that leaching of As and Pb is driven by different reaction mechanisms were As, in similarity to Na, is soluble in the leachate while instead Pb can be expected to precipitate as secondary minerals.

- *What species distribution of As and Pb can be expected and what precipitates may be present by taking results from humidity cell test into account?*

The most dominant form of As in the leachate from HCT, based on result from geochemical modelling with PHREEQC, is expected as As(V) and for Pb as $\text{Pb}(\text{CO}_3)_2^{-2}$. Regarding precipitates of the two elements, the result showed no tendency for As to fall out into the solution as a secondary mineral. For Pb however, the reaction mechanism can be expected to be controlled by $\text{Pb}(\text{OH})_2$.

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APPENDIX

APPENDIX A – GLASS THEORY

Table A1 Chemical formula and name for different glass components divided into different categories based on their role in the production (Shelby, 2005; Falk *et al.*, 2011; Hujova & Vernerová, 2017; Nationalencyklopedin, 2019)

Category	Chemical formula	Chemical name
Network formers <i>Forms the network</i>	SiO ₂	Silicon dioxide
	B ₂ O ₃	Boron trioxide
	P ₄ O ₅	Phosphorus pentoxide
Modifier oxides (flux) <i>Breaks up the network</i> <i>Decrease melt temperature</i>	Na ₂ O	Sodium oxide (soda)
	K ₂ O	Potassium oxide
	PbO	Lead oxide
	Li ₂ O	Lithium oxide
Property modifiers <i>Modifies the network</i> <i>Adds refractive index</i> <i>Adds gloss and luster</i>	KAlSi ₃ O ₈ -NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈	Feldspar
	CaCO ₃	Calcium carbonate (lime)
	CaMg(CO ₃) ₂	Calcium magnesium carbonate
	BaCO ₃	Barium carbonate
	ZnO	Zink oxide
	PbO	Lead oxide
Fining agents <i>Prevents bubbles</i>	As ₂ O ₃	Arsenic oxide
	Sb ₂ O ₃	Antimony oxide
	KNO ₃	Potassium nitrate
	NaNO ₃	Sodium nitrate
	Na ₂ SO ₄	Sodium sulfate
	NaCl	Sodium chloride
		Different fluorides and sulfates
Colorants <i>Adds color</i>	CeO ₃	Cerium oxide
	FeO	Iron oxide
	CdS	Cadmium sulfide
	CoO	Cobalt oxide
	Cu ₍₂₎ O	Copper(di)oxide
	Cr ₂ O ₃	Chromium oxide
	Mn ₂ O ₃	Manganese oxide
	S	Sulphur
	NiO	Nickel oxide
	TiO ₂	Titanium oxide
	U ₂ O ₃	Uranium oxide
	As ₂ O ₃	Arsenic oxide
	Sb ₂ O _x	Antimony oxide

APPENDIX B – COLLECTION OF DATA

Table B1(a-c) Data used in this report received from ALS after 21 weeks of HCT. Concentration is presented as dissolved elements in [mg/l], a) represents Flerohopp, b) Åryd and c) Alsterbro.

a) Flerohopp

Week	pH	Si [mg/l]	Na [mg/l]	Ca [mg/l]	As[mg/l]	Pb [mg/l]	Al [mg/l]
0	9,64	13,6	26,9	6,50	0,549	0,00179	0,0268
1	9,20	25,3	52,8	9,02	1,17	0,00193	0,0171
2	9,25	28,9	43,8	8,75	1,05	0,00140	0,0123
3	9,06	25,6	35,6	9,45	0,836	0,00156	0,0146
4	8,97	24,2	30,6	10,7	0,795	0,00112	0,0106
5	9,02	25,9	26,3	10,6	0,698	0,00121	0,0115
6	8,98	27,9	25,3	12,1	0,661	0,00100	0,00980
7	8,96	26,1	21,4	12,4	0,555	0,000987	0,00650
8	8,81	24,4	22,5	10,3	0,636	0,000667	0,00640
9	8,78	25,7	23,2	11,0	0,632	0,000729	0,00650
10	8,83	27,3	21,9	11,0	0,621	0,000840	0,00790
11	8,79	26,9	21,8	10,9	0,614	0,000735	0,00730
12	8,95	24,1	18,5	11,6	0,539	0,000759	0,00610
13	8,78	26,1	20,5	10,9	0,583	0,000837	0,00940
14	8,83	26,2	17,7	10,8	0,549	0,000445	0,00500
15	8,68	25,4	17,1	11,4	0,500	0,00124	0,0200
16	8,97	26,8	19,3	9,91	0,624	0,000437	0,00500
17	8,95	27,7	20,6	10,0	0,578	0,000750	0,00790
18	8,70	26,1	19,4	9,30	0,591	0,000562	0,00580
19	8,87	24,3	18,7	9,10	0,545	0,000468	0,00500
20	8,94	25,6	18,1	8,89	0,561	0,000472	0,00500

b) Åryd

Week	pH	Si [mg/l]	Na [mg/l]	Ca [mg/l]	As [mg/l]	Pb [mg/l]	Al [mg/l]
0	10,22	130	504	4,04	1,58	0,0154	0,0300
1	9,96	90,8	296	2,61	0,823	0,0127	0,0318
2	9,64	64,6	172	1,86	0,448	0,00765	0,0258
3	9,65	57,9	112	1,67	0,236	0,00670	0,0279
4	9,24	49,8	89,5	1,62	0,155	0,00414	0,0211
5	8,97	57,6	73,4	1,91	0,109	0,00412	0,0188
6	9,01	47,0	64,4	1,79	0,0821	0,0044	0,0158
7	9,17	44,7	49,0	2,02	0,0729	0,00347	0,0183
8	8,56	33,5	51,1	2,11	0,0709	0,00233	0,0147
9	8,79	39,9	42,5	2,55	0,0642	0,00210	0,0120
10	8,71	38,0	32,2	2,45	0,0674	0,00151	0,0092
11	9,07	38,2	31,8	2,89	0,0791	0,00188	0,0103
12	8,95	33,9	29,6	3,06	0,0937	0,00250	0,0137
13	9,10	35,1	27,8	2,89	0,0956	0,00249	0,0141
14	9,24	44,3	29,6	3,82	0,116	0,00304	0,0157
15	9,19	40,0	26,2	3,91	0,0999	0,00233	0,0117
16	8,91	25,3	21,5	3,47	0,0929	0,00169	0,0084
17	8,64	33,6	23,1	3,95	0,111	0,00292	0,0145
18	8,86	33,0	23,7	3,22	0,105	0,00180	0,0093
19	9,10	39,3	23,7	3,74	0,120	0,00197	0,0101
20	8,98	28,2	20,8	3,16	0,108	0,00340	0,0170

c) Alsterbro

Week	pH	Si [mg/l]	Na [mg/l]	Ca [mg/l]	As [mg/l]	Pb [mg/l]	Al [mg/l]
0	9,45	33,6	55,6	2,56	1,67	0,00223	0,0457
1	9,38	35,3	74,5	4,69	1,96	0,00247	0,0190
2	8,95	25,4	53,6	3,88	1,87	0,0028	0,0174
3	8,61	25,4	47,6	4,03	1,92	0,00386	0,0244
4	8,72	28,6	36,8	4,97	1,80	0,0033	0,0213
5	8,75	28,2	30,1	4,98	1,36	0,00402	0,0191
6	8,96	20,5	24,5	4,40	0,975	0,00328	0,0158
7	8,62	21,0	26,3	4,23	0,936	0,00400	0,0167
8	8,67	21,1	27,1	4,10	0,892	0,00394	0,0428
9	8,44	17,3	23,3	3,94	0,785	0,00429	0,0132
10	8,62	23,3	24,4	4,48	0,836	0,00454	0,0139
11	8,63	22,3	23,1	4,31	0,740	0,00419	0,0108
12	9,15	37,8	21,4	5,46	0,859	0,00548	0,0143
13	8,85	23,2	19,7	5,05	0,625	0,00383	0,0104
14	8,62	22,9	20,0	5,24	0,672	0,00483	0,0131
15	8,20	19,2	16,9	4,37	0,587	0,00527	0,0152
16	8,67	21,2	17,8	4,29	0,611	0,00413	0,0118
17	8,55	22,3	16,3	4,59	0,608	0,00472	0,0144
18	8,57	18,2	16,2	4,34	0,585	0,0039	0,0110
19	8,37	16,9	14,6	4,27	0,522	0,00322	0,00770
20	8,43	20,5	16,1	3,87	0,591	0,00357	0,00800

Table B2 Recieved result from total concentration analysis on glass sample from Flerohopp, Åryd and Alsterbro based on ICP-MS made at ALS lab.

ELEMENT	SAMPLE	Flerohopp	Åryd	Alsterbro
TS	%	96,7	99,9	*****
SiO2	% TS	82,3	68,8	56,1
Al2O3	% TS	1,69	3,54	0,34
CaO	% TS	4,85	13,1	5,26
Fe2O3	% TS	0,586	1,02	0,23
K2O	% TS	1,81	1,5	2,62
MgO	% TS	1,64	2,61	0,0305
MnO	% TS	0,0573	0,0992	0,0151
Na2O	% TS	11,8	9,19	12,4
P2O5	% TS	0,025	0,0355	<0,01
TiO2	% TS	0,105	0,0597	0,0339
Summa	% TS	104,9	100	77
LOI 1000°C	% TS	0,3	0,2	0,2
As	mg/kg TS	1850	58,3	7670
B	mg/kg TS	1150	<10	2440
Ba	mg/kg TS	262	123	114
Be	mg/kg TS	<0.5	3,37	<0.5
Cd	mg/kg TS	1	<0.05	110
Co	mg/kg TS	23,6	0,634	329
Cr	mg/kg TS	296	719	157
Cu	mg/kg TS	366	9,83	2360
Hg	mg/kg TS	<0.01	<0.01	<0.01
Mo	mg/kg TS	<0.5	0,508	<0.5
Nb	mg/kg TS	<5	1,46	<0.9
Ni	mg/kg TS	143	6,93	23,6
Pb	mg/kg TS	171	32,5	38000
S	mg/kg TS	133	504	204
Sb	mg/kg TS	2620	828	1080
Sc	mg/kg TS	0,999	1,84	<0.9
Sn	mg/kg TS	2,18	0,866	4,02
Sr	mg/kg TS	36,4	79,6	27,8
U	mg/kg TS		3,89	0,256
V	mg/kg TS	7,65	8,32	3,88
W	mg/kg TS	<50	<1	<0.9
Y	mg/kg TS	3,52	27,2	1,75
Zn	mg/kg TS	1430	7,76	241
Zr	mg/kg TS	50,1	37,4	16

Table B3 Volume water [ml] added (in) and the water released (out) on the seventh day of HCT after one hours rinsing for the three glassworks.

Time[Week]	Flerohopp		Åryd		Alsterbro	
	Vin [ml]	Vout [ml]	Vin [ml]	Vout [ml]	Vin [ml]	Vout [ml]
0	750	640	750	640,0	750	620
1	500	500	500	480,0	500	530
2	500	500	500	470,0	500	490
3	500	500	500	470,0	500	485
4	500	500	500	470,0	500	490
5	500	500	500	450,0	500	480
6	500	500	500	470,0	500	485
7	500	480	500	460,0	500	490
8	500	500	500	455,0	500	475
9	500	500	500	480,0	500	480
10	500	500	500	470,0	500	475
11	500	470	500	425,0	500	470
12	500	500	500	450,0	500	490
13	500	500	500	430,0	500	450
14	500	500	500	475,0	500	500
15	500	425	500	440,0	500	480
16	500	500	500	470,0	500	495
17	500	475	500	455,0	500	500
18	500	500	500	450,0	500	475
19	500	500	500	450,0	500	500
20	500	500	500	455,0	500	480

Table B4 Molar masses used for calculating mass of metal oxide from the concentration of metal as following equation 15.

Element	Molar mass [kg/mol]
Na2O	61,98
Na2	45,98
K2O	94,20
K2	78,20
CaO	56,08
Ca	40,08
Si	60,08
SiO2	28,08

APPENDIX C – GEOCHEMICAL MODELLING

Table C1 Chemical name, chemical and reaction formula and Log(K_{SP}) based on PHREEQCs database Minteq V4 for the minerals that from geochemical modelling showed a $SI \geq -2$.

Chemical name	Chemical formula	Reaction formula	Log K_{sp}
Boehmite	AlOOH	$AlOOH + 3H^+ = Al^{+3} + 2H_2O$	8,578
Cerussite	PbCO ₃	$PbCO_3 = Pb^{+2} + CO_3^{-2}$	-1313
Chalcedony	SiO ₂	$SiO_2 + 2H_2O = H_4SiO_4$	-3,55
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{+2} + 2H_4SiO_4 + H_2O$	32,2
Clausthalite	PbSe	$PbSe + H^+ = Pb^{+2} + HSe^-$	-27,1
Cristobalite	SiO ₂	$SiO_2 + 2H_2O = H_4SiO_4$	-3,35
Diaspore	AlOOH	$AlOOH + 3H^+ = Al^{+3} + 2H_2O$	6,873
Gibbsite	Al(OH) ₃	$Al(OH)_3 + 3H^+ = Al^{+3} + 3H_2O$	8,291
Greenalite	Fe ₃ Si ₂ O ₅ (OH) ₄	$Fe_3Si_2O_5(OH)_4 + 6H^+ = 3Fe^{+2} + 2H_4SiO_4 + H_2O$	20,81
Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{+3} + 2H_4SiO_4 + H_2O$	9,5749
Hercynite	FeAl ₂ O ₄	$FeAl_2O_4 + 8H^+ = Fe^{+2} + 2Al^{+3} + 4H_2O$	22,893
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{+3} + 2H_4SiO_4 + H_2O$	7,435
Pb(OH) ₂	Pb(OH) ₂	$Pb(OH)_2 + 2H^+ = Pb^{+2} + 2H_2O$	8,15
Quartz	SiO ₄	$SiO_2 + 2H_2O = H_4SiO_4$	-4
Sepiolite	Mg ₂ Si ₃ O ₇ .5OH:3H ₂ O	$Mg_2Si_3O_7 \cdot 0.5OH \cdot 3H_2O + 4H^+ + 0.5H_2O = 2Mg^{+2} + 3H_4SiO_4$	15,76

Table C2(a-c) Input data to geochemical modelling (based on HCT results from ALS), for the selection of HCT weeks.

a) Flerohopp

Flerohopp	W0	W5	W10	W15	W20
pH	9,64	9,02	8,83	8,68	8,94
pe (V)	0,8	0,8	0,8	0,8	0,8
Parameter	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
Alkalinity	89,00	104,00	91,60	83,70	78,60
NH4+	0,02	0,00	0,00	0,01	0,00
Br	0,00	0,00	0,00	0,00	0,00
Cl	0,00	1,27	1,20	0,95	1,09
F	0,45	0,42	0,39	0,29	0,30
NO3-	0,13	0,01	0,00	0,00	0,00
NO2-	0,05	0,00	0,00	0,00	0,00
SO4-2	0,55	0,00	0,00	0,00	0,00
Al	0,03	0,01	0,01	0,02	0,00
Sb	0,93	1,02	0,82	0,69	0,76
As	0,55	0,70	0,62	0,50	0,56
Ba	0,06	0,16	0,21	0,22	0,17
Be	0,00	0,00	0,00	0,00	0,00
B	0,22	0,45	0,38	0,35	0,36
Cd	0,00	0,00	0,00	0,00	0,00
Ca	6,50	10,60	11,00	11,40	8,89
Cr	0,00	0,00	0,00	0,00	0,00
Co	0,00	0,00	0,00	0,00	0,00
Cu	0,00	0,00	0,00	0,00	0,00
Fe	0,00	0,00	0,00	0,00	0,00
Pb	0,00	0,00	0,00	0,00	0,00
Li	0,00	0,01	0,00	0,00	0,00
Mg	0,96	1,33	1,99	1,99	1,36
Mn	0,00	0,00	0,00	0,00	0,00
Hg	0,00	0,00	0,00	0,00	0,00
Mo	0,00	0,00	0,00	0,00	0,00
Ni	0,00	0,00	0,00	0,00	0,00
P	0,41	0,00	0,00	0,00	0,00
K	8,48	7,45	5,61	4,29	3,88
Se	0,78	0,01	0,00	0,00	0,00
Si	13,60	25,90	27,30	25,40	25,60
Ag	0,00	0,00	0,00	0,00	0,00
Na	26,90	26,30	21,90	17,10	18,10
Sr	0,03	0,05	0,05	0,05	0,04
Tl	0,00	0,00	0,00	0,00	0,00
Sn	0,00	0,00	0,00	0,00	0,00
U	0,00	0,00	0,00	0,00	0,00
V	0,01	0,00	0,00	0,00	0,00
Zn	0,00	0,00	0,00	0,00	0,00

b) Åryd

Åryd	W0	W5	W10	W15	W20
pH	10.22	8.97	8.71	9.19	8.98
pe (V)	0.8	0.8	0.8	0.8	0.8
Parameter	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
Alkalinity	811,0	154,0	71,0	64.4	51.4
NH4+	0.0158	0,0	0,0	0,0	0,0
Br	0,0	0,0	0,0	0,0	0,0
Cl	5.9	0,0	0,0	0,0	0,0
F	127,0	13.4	4.69	2.44	2.03
NO3-	0.414	0,0	0,0	0,0	0,0
NO2-	0,0	0,0	0,0	0,0	0,0
SO4-2	24.5	0.45	0,0	0,0	0,0
Al	0.03	0.0188	0.0092	0.0117	0.017
Sb	1.33	0.936	0.47	0.424	0.283
As	1.58	0.109	0.0674	0.0999	0.108
Ba	0.0693	0.00681	0.00731	0.0106	0.01
Be	0,0	0,0	0,0	0,0	0,0
B	0.143	0.021	0.012	0.015	0.013
Cd	0,0	0,0	0,0	0,0	0,0
Ca	4.04	1.91	2.45	3.91	3.16
Cr	2.49	0.0788	0.0326	0.0211	0.0184
Co	0,0	0,0	0,0	0,0	0,0
Cu	0.0082	0.00072	0,0	0,0	0,0
Fe	0,0	0,0	0,0	0,0	0,0
Pb	0.0154	0.00412	0.00151	0.00233	0.0034
Li	0.06	0.0105	0.0041	0.0032	0.0027
Mg	0.098	0.0879	0.0892	0.113	0.091
Mn	0.0247	0.0177	0.00703	0.00678	0.00692
Hg	0,0	0,0	0,0	0,0	0,0
Mo	0.00191	0,0	0,0	0,0	0,0
Ni	0,0	0,0	0,0	0,0	0,0
P	0,0	0,0	0,0	0,0	0,0
K	11.7	4.51	2.47	1.97	1.38
Se	0.00034	0,0	0,0	0,0	0,0
Si	130,0	57.6	38,0	40,0	28.2
Ag	0.00004	0,0	0,0	0,0	0,0
Na	504,0	73.4	32.2	26.2	20.8
Sr	0.0182	0.00793	0.0119	0.0186	0.0137
Tl	0,0	0,0	0,0	0,0	0,0
Sn	0,0	0,0	0,0	0,0	0,0
U	0.000144	0,0	0,0	0,0	0,0
V	0.008	0.0017	0,0	0,0	0,0
Zn	0,0	0,0	0.0054	0,0	0,0

C) Alsterbro

Alsterbro	W0	W5	W10	W15	W20
pH	9.45	8.75	8.62	8.2	8.43
pe (V)	0.8	0.8	0.8	0.8	0.8
Parameter	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
Alkalinity	129,0	82,0	64,6	46,6	45,8
NH4+	0.0177	0,0	0,0	0,0	0,0
Br	0,0	0,0	0,0	0,0	0,0
Cl	0,0	0,0	0,0	0,0	0,0
F	0,045	0,0	0,0	0,0	0,0
NO3-	0,0133	0,0	0,0	0,0	0,0
NO2-	0.0045	0,0	0,0	0,0	0,0
SO4-2	2.49	1.16	0.48	0.54	0,0
Al	0.0457	0.0191	0.0139	0.0152	0.008
Sb	0.0695	0.0522	0.0457	0.0393	0.0369
As	1.67	1.36	0.836	0.587	0.591
Ba	0.0172	0.0738	0.114	0.141	0.144
Be	0,0	0,0	0,0	0,0	0,0
B	0.015	0.023	0.024	0.018	0.019
Cd	0.000138	0.00007	0.000032	0.000022	0.000012
Ca	2.56	4.98	4.48	4.37	3.87
Cr	0.00094	0,0	0,0	0,0	0,0
Co	0.00207	0.0011	0.0009	0.00078	0.00059
Cu	0.00757	0.00184	0.00124	0.00086	0.00059
Fe	0.034	0,0	0,0	0,0	0,0
Pb	0.00223	0.00402	0.00454	0.00527	0.00357
Li	0.0092	0.0032	0.0019	0.0012	0,0
Mg	0.103	0.143	0.112	0.0996	0.0887
Mn	0.0136	0.00845	0.00634	0.00577	0.00395
Hg	0.0000113	0,0	0,0	0,0	0,0
Mo	0.000202	0,0	0,0	0,0	0,0
Ni	0.00106	0,0	0,0	0,0	0,0
P	0.32	0,0	0,0	0,0	0,0
K	1.72	0.667	0.517	0.392	0.357
Se	0.00025	0,0	0,0	0,0	0.00014
Si	33.6	28.2	23.3	19.2	20.5
Ag	0.000038	0,0	0,0	0,0	0,0
Na	55.6	30.1	24.4	16.9	16.1
Sr	0.00669	0.0105	0.00798	0.00699	0.00564
Tl	0,0	0,0	0,0	0,0	0,0
Sn	0,0	0,0	0,0	0.00011	0,0
U	0.000335	0.00007	0.000036	0.000027	0.000019
V	0.0053	0,0	0,0	0,0	0,0
Zn	0.0085	0.0039	0,0	0,0	0,0

Table C3 Distribution of As(III) and As(V) for each of the selected weeks from the HCT as a result of geochemical modelling with PHREEQC for all glassworks.

Flerohopp	W0	W5	W10	W15	W20
TotAs [mol/kg]	7,3290E-06	9,3180E-06	8,2900E-06	6,6750E-06	7,4890E-06
As(III) [mol/kg]	1,7040E-17	3,0330E-15	1,3600E-14	4,0380E-14	4,9010E-15
As(V) [mol/kg]	7,3290E-06	9,3180E-06	8,2900E-06	6,6750E-06	7,4890E-06
Åryd	W0	W5	W10	W15	W20
TotAs [mol/kg]	2,1120E-05	1,4550E-06	8,9970E-07	1,3340E-06	1,4420E-06
As(III) [mol/kg]	4,2780E-19	6,8470E-16	4,2560E-15	1,1060E-16	6,9480E-16
As(V) [mol/kg]	2,1120E-05	1,4550E-06	8,9970E-07	1,3340E-06	1,4420E-06
Alsterbro	W0	W5	W10	W15	W20
TotAs [mol/kg]	2,2300E-05	1,8160E-05	1,1160E-05	7,8360E-06	7,8890E-06
As(III) [mol/kg]	2,1830E-16	6,0490E-14	1,1740E-13	3,4720E-12	4,5380E-13
As(V) [mol/kg]	2,2300E-05	1,8160E-05	1,1160E-05	7,8360E-06	7,8890E-06

Table C4 Saturation Index ≥ -2 for minerals containing Si or Al for the three glassworks over the five representative weeks of the HCT.

Flerohopp	W0	W5	W10	W15	W20
Boehmite	-1,6	-1,3	-1,3	-0,7	
Chalcedony	-0,3	0,12	0,17	0,15	0,13
Chrysotile		1,93	1,44	0,52	1,54
Cristobalite	-0,5	-0,1	-0	-0,1	-0,1
Diaspore	0,15	0,4	0,43	0,98	
Gibbsite	-1,3	-1	-1	-0,4	
Halloysite		-1,9	-1,7	-0,7	
Kaolinite	-1,1	0,26	0,4	1,47	
Quartz	0,13	0,57	0,62	0,6	0,58
Sepiolite		1,28	1,02	0,38	1,03
Åryd	W0	W5	W10	W15	W20
Boehmite		-1	-1,1	-1,5	-1,1
Chalcedony	0,31	0,47	0,32	0,28	0,16
Chrysotile		-1,4		0,11	-1,6
Cristobalite	0,11	0,27	0,12	0,08	-0
Diaspore	-0,4	0,66	0,62	0,24	0,62
Gibbsite	-1,8	-0,8	-0,8	-1,2	-0,8
Halloysite		-0,7	-1,1	-0,9	-1,4
Kaolinite	-1	1,48	1,08	0,26	0,77
Quartz	0,76	0,92	0,77	0,73	0,61
Sepiolite		-0,3	-1,7	0,33	-1
Alsterbro	W0	W5	W10	W15	W20
Boehmite	-1,1	-0,8	-0,8	-0,4	-0,9
Chalcedony	0,14	0,19	0,11	0,04	0,07
Chrysotile	1,09				
Cristobalite	-0,1	-0	-0,1	-0,2	-0,1
Diaspore	0,57	0,89	0,89	1,35	0,84
Gibbsite	-0,9	-0,5	-0,5	-0,1	-0,6
Greenalite	-2				
Halloysite	-1,5	-0,8	-0,9	-0,1	-1,1
Hercynite	0,54				
Kaolinite	0,63	1,37	1,21	2	1,02
Quartz	0,59	0,64	0,56	0,49	0,52
Sepiolite	0,76	-1,5			