Inorganic foundry binders for sustainable sand molding

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Abstract

A good sand mold is an indispensable prerequisite to obtaining a good metal casting. Although sand casting is one of the oldest metal forming technique known to humans, research for alternative molding materials has never stopped, most notably to meet increasing demand for quality, better economics and to meet ever increasing environmental restrictions and regulations. The principal material of sand molds are the sand, binder and different additives depending on the application. Growing worldwide demands for sustainable manufacturing and an increased adoption of additive manufacturing across foundry industry are two underlying motivations for the search of alternative material in this dissertation.

Although different organic binders are popularly used in sand molding, there is concern over the volatile organic compounds (VOCs) emitted from thermal breakdown at elevated temperature. Also, the use of 3D printed sand molds is on the rise, which usually employ greater volume of binder than traditional method. It is therefore necessary to use more environmentally friendly binders. In recent times, the interest in inorganic binders have re-emerged due to their environmental friendliness. However, the performance of these need to be properly tested before widespread introduction to foundry practices. Additionally, although silica is the most widely used sand for sand casting, alternatives are sought for various reasons like worker health safety, increased scrutiny for silica sand mining etc.

This dissertation is a summary of 4 publications which explored many different sands, binders and additives. Inorganic binders were a focus of these tests while organic binders were also used in some tests to provide a fiducial reference point. The dissertation aims to facilitate the choice of mold materials with a more extensive outlook into their characteristics through a serious of sand, mold and casting quality test. Examples include sand flowability test, mold strength tests, loss on ignition tests, gas emission tests, SEM imaging of fracture surface, 3D scanning of mold and casts for mesh-to-mesh analysis, surface roughness of castings etc. Data from this dissertation will help in part the transition from the use of organic liquid binder to solid inorganic binder, enabling foundries to switch to more sustainable practices. Special emphasis is given to inorganic solid silicate binder, as it has the potential in the sustainability front as well as the simplification of 3D printing of sand molds. Effect of five different additives on solid silicate binder was found out that will aid in further development of the binder. Performance of a heat resistant 3D printed plastic pattern material was explored as well, which can be used with heat hardened inorganic molds.

Keywords sustainable molding; sand casting; inorganic binders; solid silicates; additive manufacturing

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Espoo, 20 February 2024
Nurul Anwar
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<th>Description</th>
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<tbody>
<tr>
<td>AM</td>
<td>Additive Manufacturing</td>
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<tr>
<td>AOR</td>
<td>Angle of Repose</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer Aided Design</td>
</tr>
<tr>
<td>CB</td>
<td>Cerabeads</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-Dispersive Spectroscopy</td>
</tr>
<tr>
<td>FDM</td>
<td>Fused Deposition Modeling</td>
</tr>
<tr>
<td>GP-E</td>
<td>Geopolymer binder, Ester cured</td>
</tr>
<tr>
<td>HR</td>
<td>Hausner Ratio</td>
</tr>
<tr>
<td>LOI</td>
<td>Loss on Ignition</td>
</tr>
<tr>
<td>MLS1</td>
<td>Modified Liquid Silicate 1</td>
</tr>
<tr>
<td>MLS2-E</td>
<td>Modified Liquid Silicate 2, Ester Cured</td>
</tr>
<tr>
<td>MLS3</td>
<td>Modified Liquid Silicate 3</td>
</tr>
<tr>
<td>Ra</td>
<td>Roughness Average of a Profile</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SLA</td>
<td>Stereolithography</td>
</tr>
<tr>
<td>SS</td>
<td>Solid Silicate</td>
</tr>
<tr>
<td>ULS</td>
<td>Unmodified Liquid Silicate</td>
</tr>
<tr>
<td>ULS-E</td>
<td>Unmodified Liquid Silicate, Ester cured</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compound</td>
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List of Publications

This doctoral dissertation consists of a summary of the following publications which are referred to in the text by their numerals.


Author’s Contribution

**Publication 1:** Comparative experimental study of sand and binder for flowability and casting mold quality.

In this study, first author contribution consists of conducting all the experiments, experimental design, data analysis and writing the first draft. Results were interpreted and commented together by all the authors.

**Publication 2:** Experimental study of inorganic foundry sand binders for mold and cast quality.

In this study, first author contribution consists of conducting mold and cast quality tests, experimental design, data analysis and writing the first draft. The results were interpreted and commented together by all the authors.

**Publication 3:** Effect of additives on heat hardened inorganic solid foundry binder.

In this study, first author contribution consists of conducting mold and cast quality tests, experimental design, data analysis and writing the first draft. Co-authors also took part in some of the experimental tests and data analysis. The results were interpreted and commented together by all the authors.

**Publication 4:** Evaluation of 3D-printed pattern material for heat-hardened inorganic moulds.

In this study, second author contribution consists of experimental design and conducting the experiments. Results were interpreted and commented together by all the authors.
1. Introduction

Metal casting is one of oldest metal forming method known to humans[1]. In simple terms, metal casting is a metal forming process where molten metal is poured into a cavity that conforms to the shape of the product wanted. After cooling and solidification of the metal, the part is taken out and post processed as per requirement. Casting can produce complex shapes with internal cavities, and it offers economic production of a large range of size, shape, and alloy. Over-time, major changes have taken place across the casting industry. One such example is the advent of automated process control systems which increased productivity and reduced labor costs. Another significant development was the need for high quality casts with demanding requirements. In most recent times, requirements of sustainable manufacturing, advent of additive manufacturing and digitilizations are playing major role in the direction foundry practices are going.

Sand casting is the most widely used type of casting in the world due to the flexibility, economics, and the wide range of different alloys that could be manufactured in this method[2]. Although sand casting has been around for a long time, the research for molding materials, i.e., sand, binder and additives had never stopped. Previously, the motivation towards these studies were principally driven by the ever-increasing product demands and requirements. The aim generally was to find molding material that offer improved mold and casting qualities or better economics. Environmental restrictions are slowly becoming tighter and search for alternative material is always going on even for very traditional foundry practices and materials[3]. In broad terms, sustainability ensures protection of the environment, guarantees social well-being, and maintains economic welfare. Measures that reduce the consumption of raw materials and energy, reduce generation of toxic substances, and improves economics of the industry all lead to manufacturing sustainability[4]. Improved quality control with digitalization is also part of sustainable practices as they help reduce number of defects and discarded products.

The preparation of sand mold begins by mixing sand, binder, and additives. The mixture is then poured over a pattern that conforms to the shape of the final product wanted. The sand and binder mixture is then rammed (in case of greensand) but with most chemical binders in use today hand molding is sufficient. Chemical reactions take place as the mold starts to set; bonding bridges are formed between sand particles that strongly hold it in position. Organic binders are very popular in sand casting due to the reliability and efficiency they offer.
However, thermal breakdown of these binders at elevated temperature is a source of concern for human health and the environment, which causes odour and harmful gas emissions\cite{5}. The gases produced also cause gas defects in castings. Silica sand is the most widely used aggregate material for sand casting. However, alternatives to silica sand are also being sought for numerous reasons. This dissertation showcases the performance of alternative materials through a series of tests that reveal the mold and cast quality. The principal motivation being sustainable mold manufacturing while also keeping in mind the concurrent rise in the use of additive manufacturing. Figure 1 shows the research context in the big picture.

**Figure 1.** Placing the research area into the big picture.

### 1.1 Background

A good sand mold is a compulsory perquisite to obtaining a good quality casting. Whenever there is discussion about possible new materials for sand molding, be it the aggregate, binder or additives, proper investigations must be done before introduction to foundry practices. Organic binders have been popularly used in sand casting foundries due to the ease, efficiency, and reliability it provides. However, there has been increasingly more concern about the release of VOCs (volatile organic compounds) from these organic binders due to breakdown at elevated temperatures. These fumes are detrimental to human health, as well as they cause gas defects in castings. In addition, the use of additive manufacturing of sand molds is on the rise across the foundry industry. The state-of-the-art sand printers mostly use modified organic binders (e.g., furan and phenol) for this process. One concerning aspect of this is that 3D printed sand molds usually employ more binder per unit volume compared to traditional sand molding method. It is therefore necessary to find alternate binders to mitigate these challenges. Inorganic binders, more specifically sodium silicate binder is being
thought of as the possible replacement of organic binders with the most potential.

Inorganic sodium silicate binder is thought to be the front runner in achieving green sand casting and achieving manufacturing sustainability[6]. These were first introduced in the mid-twentieth century but were not very popular due to certain challenges these had[7, Ch. 1]. However, these are making a comeback due to their environmental friendliness, reduced emission, and better worker health safety and hence a large amount of interest is generated towards the research of sodium silicate binders. Sodium silicate binders could be hardened in different ways, and some differences in mold and cast arise due to different hardening methods. Some of these differences was studied in this dissertation.

In addition to that, in this dissertation solid form of the sodium silicate binder is more closely studied as well. The solid form has enormous potentials due to its environmental friendliness, easier transportation, use and storage, and the simplification of 3D printing of sand molds[8]. Very little information about solid silicate exists in literature. Thus, every opportunity was used to improve this binder as well as learning about the challenges of working with it.

A good sand mold could be characterised to be one which is strong enough to withstand the molten metal pressure, has good dimensional stability, possesses sufficient permeability to the gases generated in the process, resists metal penetration, provides good collapsibility for easy shakeout and has a high reclamation rate. Usually, a higher binder content leads to greater mechanical strength of the mold [9]. However, if the strength is retained after pouring, it becomes difficult to break the mold after solidification of the metal. Also, a higher binder content leads to high gas generation [10] and high cost. A good mold, therefore, is a tradeoff between several different factors. But oftentimes economics of sourcing mold materials is a significant driver of the choice of material, and operationally viable material are chosen rather than the absolute best.

There is a significant push for change towards inorganic binders from the sustainability front, but a rapid switch is not viable from an operational perspective. Firstly, there are the challenges concerned with sodium silicates, for example, poor collapsibility, poor resistance to moisture and poor reclamation. Secondly, there are differences concerning the hardening method used for sodium silicate. Thirdly, although it is most frequently used as a liquid binder, there is concurrent interest in the solid form as well. However, not much is known about the performance of solid sodium silicate. On one hand is the serious push to switch to sustainable binders and on the other is the significant array of different decision making on the use with inorganic binders. Foundries must walk a fine line between the two, and the result from this dissertation would aid to some degree their plan and choice for short to long time future. The focus on this dissertation was to check the performance aspects of different inorganic binders and to facilitate the broader use of solid inorganic foundry binders which is a potential solution to further sustainability in sand casting.
1.2 Objectives, Scope, and Research Questions

A series of sand, mold and cast quality tests were conducted using different types of sand, binders (mostly inorganic) and additives to find answers to the research questions. Casting trials conducted were with ferrous alloys, as sodium silicate binders are known to have more challenges with ferrous casting. Figure 2 shows an executive summary of the tests conducted.

Research questions that this dissertation cater to are as follows:

- How do alternative sands perform compared to silica?
- How do different inorganic binders compare in terms of mold and cast quality?
- Could solid silicates become the norm of sustainable foundry binders?
- Exploring the prospects of inorganic molding and additive manufacturing assisted hybrid casting.

1.3 Outline of Thesis

This dissertation consists of four original research papers and this compiling part. Publication 1 consists of mold quality assessment of six different types of sand with three different types of binders (2 organic and 1 inorganic). Publication 2 focuses more on different types of inorganic binders and their achieved mold and cast qualities. Publication 3 then focuses solely on solid inorganic foundry binders and what effect different additives have on the mold and cast qualities. Publication 4 discusses in greater detail the dimensional consideration of a heat resistant 3D printed pattern material that was introduced in Publication 3 as a solution to metal pattern sticking to solid sodium silicate binder.
Figure 3 summarizes the content of different publications used in this dissertation.

As we go progress through the publications:
- Number of tested types of sand decreases (From 6 to 1)
- A shift in focus from organic to inorganic binder
- A shift in focus of the form of binder from liquid to solid
1.4 Main Contributions of this Thesis

Overall, this thesis supports in part the transformation from the use of liquid organic binders to that of solid inorganic binder as shown in Figure 4. However, it was done in several steps. Performance comparison of six different types of sand and three different binders (2 organic and 1 inorganic) was conducted in Publication 1. This was the starting point to compare an inorganic binder to two widely used organic binders. 6 different sands were tested. The mold quality tests aid in the selection of sand and binder combinations. When mold qualities of sands with different densities were compared, the volumetric binder addition rate was kept constant to give a better comparison, rather than keeping constant the binder addition rate by mass of sand. Also, keeping the binder and sand volume constant also makes this comparison more in par with 3D printing of sand mold.

The next step was to compare different inorganic binders in Publication 2. Extensive study to compare 5 different inorganic binders and their performance characteristics. Renewed interest in inorganic binders that perform very well environmentally must also meet the casting requirements. 5 different inorganic binders were tested, with 3 different types of sand in Publication 2.

Publication 3 then focused entirely on learning more about solid silicates. Effect of five different additives on solid silicate binder was studied. This provides a good starting point in the development of such binder for widespread deployment across the foundry industry.

Publication 4 is an extended study on the 3D printed plastic pattern material that was introduced as a solution to sticking problems with solid silicates and metal pattern. It was important to look at the dimensional aspects of high temperature resistant plastic patterns.
2. Theoretical Background

2.1 Sand Casting Technology

A good sand mold is a compulsory starting point to obtain a good quality casting. Sand molds consist of sand, binder, and additives. The binder holds together the sands in place, and additives are added depending on the desirable qualities sought for different applications. In greensand casting method, clay and water is used to bind the sands together to form the mold and ramming pressure is applied to consolidate the mold. Although greensand casting is quite popular, some challenges include the fact that it must be properly consolidated, else there could be a risk of mold distortion and inaccurate casts. However, there are now several different types of chemical binders that do not need to be consolidated much, that improves the process efficiency and reliability of the process as well as providing greater control over casting dimensions. Once the mold starts to set and able to hold its shape, the pattern is removed. Easy pattern removal is necessary to avoid damaging the mold surfaces, as any defects or damage on the mold surface ultimately gets transferred to the final casts made. Hollow internal cavities in final products are realized with the use of cores. After molten metal is poured into the mold, time is allowed for the metal to cool down. Afterwards, the mold is broken to take out the solidified metal and post processed. A good sand mold is also characterized by one that can be broken down easily after pouring (good collapsibility) and subsequently large portion of the sand could be reused for molding (good reclamation). Figure 5 shows a sand casting schematic diagram.

Figure 5. Sand casting schematic diagram.
2.2 Molding Material and Processes

2.2.1 Sand (Mold Aggregate)

Silica sand have been a very popular choice of mold aggregate because of its ready availability, low price, and high melting point. However, there are many factors that is driving the search for alternative sands. Firstly, long exposure to silica sand causes a disease named silicosis in foundry workers[11]. Secondly, silica sand expands at a range of 1.1-1.6% at a temperature of 573°C due to alpha to beta phase transition[12], which causes loss in casting accuracy. This problem is worse in ferrous castings when virgin silica sand is used. Thirdly, there are environmental concerns related to the mining of silica sand. A large amount of silica sand is mined from coastal areas, the environmental damage from which has a long recovery time[13]. Fourthly, in addition to sand casting foundries, silica is an essential raw material for many industries, including but not limited to glass, ceramics, construction and many silicon based chemical products[14]. While the demand is rising and mining opportunities coming under increased scrutiny, there is but one outcome: increase in price. All these factors are driving a search for alternative material for silica sand. However, silica is a good benchmark for comparison as there is widespread knowledge of the use of silica in foundries.

Zircon and chromite sand are more expensive and heavier sand compared to silica, but these do not share the expansion related problem like silica. These sands are characterized with low expansion and good thermal conductivity, consequently these are sometimes used as facing sands in silica molds for their excellent chilling properties[15, pp. 920–921]. Bauxite isn’t currently used much in foundries now, but it is an abundant mineral, and it has the prospect of overcoming some challenges faced with silica. It has lower thermal expansion than silica and compared to zircon and chromite, bauxite also has lower density. There is also interest for artificial sands, e.g., Cerabeads, which are engineered sand made by sintering of mullite granules having uniform spherical shapes and low thermal expansion[16, pp. 113–128]. Also, cerabeads cost less than chromite and zircon.

2.2.2 Chemical Binders

Chemical binders could be broadly divided into two categories, organic and inorganic binders. Example of organic binders include furan (furfuryl alcohol, catalyzed with sulphonic acid), alkaline phenolic, phenolic urethrane, etc. Chemical no-bake organic binders became popular in foundry practices because of a range of reasons including their ease of use, mold quality, process reliability, and good reclamation properties[5], [7, Ch. 2], [17]. But now there is a major drive in adopting more sustainable practices and materials worldwide. There is growing concern over volatile organic compounds (VOCs) emitted at casting temperatures due to thermal breakdown of organic binders[5]. Many researches were focused on the quality of acid hardeners used with organic binders, which were found to be a major cause of the the harmful gases [18], [19]. Aside from
the VOC emission, there is also concern over some of the organic binders being classified as possible carcinogen [20]. All these factors are causing an interest away from the use of organic binders and a renewed interest in inorganic binders is being experienced by the industry. Inorganic binders are discussed in more details in section 2.3.

2.2.3 Additive Manufacturing and Hybrid Casting

The advent of additive manufacturing (AM) is reshaping the manufacturing industry, sand casting is no exception. The versatility of additive manufacturing in terms of different techniques and material available has made it possible to be incorporated into metal casting in various ways[21]. Hybrid casting refers to casting with the help of additive manufacturing. The two principal ways of incorporating additive manufacturing with sand casting is through additive manufacturing of pattern and additive manufacturing of sand molds and cores[22].

In traditional casting, patterns could be made out of anything from plastic, wood or metal depending on the intended cycle of use. A few cycles of use do not necessitate much hardness of pattern material, hence wooden or plastic material could be used. However, if it is meant for hundreds of cycles, perhaps metal pattern would be more suitable. In certain cases, where the binder needs to be hardened with heat, heat resistant pattern material is required, e.g., metal patterns. 3D printing of pattern material could shorten the lead time as more time might be necessary in pattern production otherwise. Many different AM technologies are available that could be used in plastic pattern manufacturing, most notably Fused Deposition Modeling (FDM) and Stereolithography (SLA). The choice could be made depending on the surface quality of the pattern material wanted. Another notable issue with these both is the slow speed and small volume. For fabrication of large patterns, a potential solution could be Fused Granular Fabrication (FGF) of pattern material combined with finished machining[23].

3D printing of sand molds is gaining more interest across foundry industries. Sand molds can be directly printed from CAD data. Sand printers can print complex mold and cores which are ready for pour. Powder bed technology is most frequently used for 3D printing of sand mold[24]. The process utilizes binder jetting powder bed technology where foundry grade binders (modified) are selectively deposited over activator coated sand[25]. This process is repeated layer by layer according to the cross section of the 3D CAD model until the full part is printed. Full molds can be printed including gates and channels. However, it might be more cost efficient if those are done the traditional way and the complex parts are handled by the printer. The exceptional design freedom and topological optimization enabled by printed mold and cores mean that their popularity is increasing. Along with shortened lead time, this also means that pattern production and storage is not necessary. Compared to other AM techniques, high speed sand printers with big job box are already available[26]. On top of it, modular molds can be joined together to form a much larger mold than the printer job box. However, one concern of 3D sand printers is that these employ more binders per unit volume of sand compared to traditional molding and
most state-of-the-art 3D sand printers still use organic binders (furan or phenol)[27]. A high binder dosage amount also leads to more gas emission and gas defects. Another consideration of binder jetting 3D printers is that issues like clogging of nozzles and printheads arise over time due to the viscous binders. Schematic diagram of a binder jetting 3D sand printer is shown in Figure 6.

![Figure 6. Schematic diagram of state-of-the-art binder jetting sand printers.](image)

### 2.3 Inorganic Binders

#### 2.3.1 Sodium Silicate

Inorganic sodium silicate binders are not new inventions and have been used in foundries since mid-twentieth century[7, Ch. 1]. However, the popularity of these binders suffered due to certain challenges these had. For example, poor knock-out performance compared to organic binders, poor moisture resistance, reclamation difficulty, requiring heat or CO$_2$ for hardening, etc.[16, p. 219], [28, p. 204]. These paved the way for popularity of organic binders. However, due to increased focus on sustainable manufacturing in recent times, there is now a renewed interest of sodium silicate binders as these binders produce little to no fumes during pour, do not emit any toxic substances, no unpleasant odour either [16, p. 219], [28, p. 204]. Apart from reduced health hazards, there is economic benefit to foundries as inorganic binders cost less than organic binders[16, p. 219]. Air purification and exhaust equipment need less investment, as there is reduced presence of binder aerosols and casting fumes[29], [30]. When inorganic cores are used with die casting, the time required to clean the dies reduces as there is less tool contamination. Modified version of silicate binder is already being used in the casting of critical aluminum automotive parts[29]. Some steel foundries also benefit from the fact that, with the use of silicate binder, facing molds with expensive chromite sand is not necessary. This is a result of a high amount of latent heat being lost when free water and water of crystallization is removed from the binder. Thus, creating an effect similar to when good heat conducting sand like chromites are used as facing sands for faster cooling [15, p. 938].
2.3.2 Properties of Sodium Silicate

Foundries usually use sodium silicate binder of a module between 2-2.9 [16, p. 225]. This module is the ratio of number of moles of silicon dioxide (SiO₂) to that of sodium oxide (Na₂O). A higher module results in a higher viscosity at same binder density [16, p. 225]. Usual binder addition rate varies between 2 and 4% by mass of sand [16, Ch. 9]. Sodium silicate can be hardened reversibly by dehydration through heating, e.g., furnace heat or microwave. It can also be hardened irreversibly, by application of CO₂ or a mixture of esters.

Water is lost when heat is applied to sodium silicate binder, an anhydrous glassy film is formed joining matrix grains together. This process is reversible, which is why moisture affects the storability of heat hardend inorganic cores [29]. The process is also slow [29], resulting in long cycle time. Uniform heating of large molds poses operational challenges as well. In addition, issues of poor collapsibility and poor reclamation is present. Heating the cores using microwave offers good mechanical properties of the mold at lower binder addition of 1.5% already [31], and low binder addition in turn improves reclamation and collapsibility [32]. It was shown in [32] that, unit costs for cores reduces with the use of microwave compared to furnace heating. The stoichiometric equation for heat hardening is shown in Equation 1 [16, p. 230].

\[ \text{Na}_2\text{O}.n\text{SiO}_2.x\text{H}_2\text{O} + Q \rightarrow \text{Na}_2\text{O}.n\text{SiO}_2 \]  

(1)

The use of esters is another way of hardening sodium silicate binders that results in a semi-inorganic process. Hydrolysis of ester forms acetic acid, while the acetic acid dissociates to form acetic anions. The acetic anions then react with sodium silicate to form gel. Reclamation, both wet and dry, is hindered by formation of hydrated sodium acetate in this process [33], [34]. However, weak initial strengths and issues of collapsibility are also major challenges of this system. Hardening rates could be adjusted to a degree according to the need by using different blends of esters [16, p. 227]. This is a self-setting system which is the closest to organic self-setting systems, therefore offering obvious advantages as no heat or CO₂ gas is required. Example of esters use include glycerol diacetate, ethylene glycol diacetate, or glycerol triacetate depending on what speed of cure is desired, oftentimes a mixture of esters is also used [28, p. 211].

For CO₂ hardening of sodium silicates, molds and cores need to have high permeability so that carbon dioxide gas could pass through easily. Ensuring this means molds or cores can not be compacted like with other hardening methods or other binders and theoretical maximum strength of the molds cannot be achieved. Due to this, a higher binder addition rate was used for this hardening method. However, there are numerous recent studies that achieved good strengths of CO₂ hardened sodium silicate using 2-2.5% binder addition rate using different methods like blowing air after CO₂ blowing, using heated CO₂ or using different modifiers [35], [36], [37]. There are also issues with flowability, bad reclamation properties, long cycle times etc. The stoichiometric reaction for the hardening of sodium silicate binders with carbon dioxide is given in Equation 2 [38].
\[ \text{Na}_2\text{O} \cdot n\text{SiO}_2 + 2n\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + n\text{Si(OH)}_4 \]  

(2)

### 2.3.3 Modification of Sodium Silicate

One of the ways in which improvement of sodium silicate is attempted is through modification, to improve the challenges faced. This includes both physical and chemical modification. Physical modification includes tuning of temperature and conditioning time of silicate sodium glaze, the primary material[16, p. 234]; while chemical modifications include introduction of different chemicals into the polymer matrix. These include morphoactive organic compounds (with functional groups like –OH, –NH₂, –CONH, –COOH, etc.), ultrafine powders (containing ions like Mg²⁺ and Al³⁺), and nanoparticles of metal oxides (ZnO, MgO, Al₂O₃) in various alcoholic solutions[16, pp. 235–236]. Introducing nanoparticles creates new systems termed as nanocomposites, which influences the properties of the binder in the interface layers, leading to better mechanical and thermal properties[39]. In another study, authors managed to improve tensile strength, flowability, and collapsibility through the addition of potassium hydroxide, sodium hexametaphosphate, and white sugar modifiers [40].

Commercial brands of two-part heat-hardened sodium silicate binders are available now a days whose first part is a modified sodium silicate binder, and the second part is a solid promoter. This hardening involves both physical and chemical reaction leading to improved flowability and moisture resistance. Examples of such are already being used in the production of complex cores for high volume production of automotive parts[29].

### 2.3.4 Solid Silicates

Solid hydrous silicates are dry counterparts of liquid sodium silicates. Water is needed to dissolve the dry powder, after which the use could be like liquid silicate. Hydrous solid silicates are chosen instead of anhydrous solid silicates due to their faster dissolution rate. There is two-fold motivation for the use of the solid silicates in foundry industry. The first being the ease of storage and transport due to the reduced mass and volume of the material[8]. Also, modified liquid silicate binders could contain water soluble additives which gives rise to storage issues like binder separation, lumping and thickening etc[8]. The second advantage is the potential of solid silicates in the simplification of 3D printing of sand molds. 3D printing of sand mold and cores enables exceptional design freedom and reduction of lead time for small series products[41], [42]. More and more foundries are adopting the use of additive manufacturing of sand molds and there is a heightened concern as most state-of-the-art 3D sand printers are using organic binders, and a higher binder amount is usually required with 3D printing of sand mold compared to traditional molding, and a higher binder content usually leads to more gas defects[43], [44], [45]. Therefore, it is increasingly becoming more important to shift away from organic binders. In addition to that, jetting binders through a printhead causes issues
like clogging of printhead nozzles. The use of solid silicates could provide a solution to both these challenges. Firstly, it is inorganic with a reduced harmful gas emission and secondly, if only thickened water is jetted through the printhead over a mixture of solid silicates and sand[46], the difficulty associated with the blocking and cleaning of nozzles could be overcome. Longer lifetime, low maintenance and thereby low running cost of the printheads will ease more adoption of 3D sand printer by foundries. Figure 7 shows the schematic diagram of a 3D sand printer that uses solid silicate binder.

![Figure 7. Schematic diagram of 3D sand printer that uses solid silicate binder.](image)

Ablation casting is a new emerging sand-casting technology where water soluble foundry binder is used[47]. Heat hardened hydrated sodium silicate binders perform very well in ablation casting as was shown in [48]. Therefore, molding with heat hardened solid silicates could also be a good candidate for ablation casting. There are two different ways in which solid silicates could be used in sand molding. The first is to use solid silicate powder mixed with silica sand and the other is to use silicate coated sand. When foundries are required only to add water to a premixed sand and solid silicates blend or to sodium silicate coated sand, foundry operations simplify. However, before introducing solid silicates as main line foundry binders, or their widespread use in 3D printing, more data and trials are needed to identify any potential challenges and to overcome challenges already known. Silicate coated sand was not investigated in this dissertation, rather solid silicate powder was mixed with the sand.

### 2.3.5 Geopolymers

Geopolymers are inorganic materials that belong to the group of alkaline aluminosilicates. The polymer consists of chains of SiO$_4$ and AlO$_4$ tetrahedrons and the properties of the binder system could be changed to some degree by changing the ratio of Si:Al[7, Sec. 3.4]. The Si:Al ratio of about 10:1 is found in binders currently in foundry use[49]. Geopolymers are manufactured artificially from slag or fly ashes, but these are not the result of geological process as the name might suggest. The naming is used because their composition imitate that of natural rocks very closely[50]. Commercial brands of geopolymer binder exists, where the binder is already a polymer with low polymerization, and degree of
polymerization increases during the hardening reaction[51]. Geopolymer binders are hardened by three ways, very similar to the way sodium silicate is hardened. These include self-hardening mixtures with the use of esters, hardened by gaseous carbon dioxide for both mold and cores or hot box technology for cores only[16, p. 278]. It is reported that geopolymer binders achieve high strength, good flowability, and permeability[52]. These also perform better in terms of collapsibility and reclamation of sand compared to sodium silicate binders[16, p. 278]. Geses produced on pouring consists mainly of water vapor and contains little to no hazardous fumes or unpleasant smell[53]. Reduced gas emission also reduces gas defects in castings. The interest in geopolymer binders in foundries is therefore increasing due to these favorable characteristics.

2.4 Summary of Literature Review

Global push for sustainable manufacturing has intensified the search for alternative molding materials for sand casting. Inorganic binders are making a comeback due to their environmental friendliness, and these are deemed to have the most potential to facilitate sustainable sand casting. Of these, the most promising inorganic binder is sodium silicate binder. However, it could be seen from the literature review that the switch from organic to inorganic binder is not a straightforward matter. Sodium silicate binders could be hardened in different ways, it could exist in both solid and liquid forms, and there are other related binders, e.g., the sodium aluminosilicates (geopolymers). All these different possibilities present unique challenges and foundries considering a switch need more information how inorganic binders compare with organic binders. Also important is to know how the inorganic binders hardened in different ways, different types and forms of inorganic binders differ in terms of mold and cast quality, so that foundries are well informed about the potential challenges and possible remedies to some. While searching an answer for these, several alternative sands were also researched, and some prospects of inorganic molding and hybrid casting were explored.
3. Experimental Methods and Materials

3.1 Materials

3.1.1 Sand

Silica is the most widely used sand for sand casting. Due to the widespread use and prevalent knowledge about silica, it provides a good benchmark for comparisons with other sands. Apart from silica, other sands used in the experiments were bauxite, Cerabeads 400 (CB 400), Cerabeads 1450 (CB 1450), zircon and chromite. Bauxite is heavier sand than silica, mainly consisting of aluminum oxide. Chromite sand is a mixture of several oxides consisting mainly of chromium oxide, followed by iron, aluminum and magnesium oxides. Zircon sand usually consists of very small, rounded grains, and with a high bulk density close to that of aluminum[15, p. 921].

3.1.2 Binders

Slightly different naming convention is used for the binders in this dissertation summary and in the original publications. The terminology used differently is explained in Table 1. In Publication 1, three different binders were tested, organic furan and phenol, and a modified inorganic sodium silicate binder (MLS1). In Publication 2, five different inorganic binders were tested. These included four binders in liquid form, and one in solid form. In Publication 3, the focus was entirely on solid silicates and the effect five different additives have on it. Inorganic binders that were cured with esters, are identified with a suffix ‘-E’ in this dissertation. In publication 4, mainly solid silicate binder was used.

Table 1. Naming convention used for all the binders in the dissertation.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Name used in this dissertation</th>
<th>Name used in publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol (Self-setting)</td>
<td>Phenol</td>
<td>Phenol (Publication 1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Binder F (Publication 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol (Publication 3)</td>
</tr>
<tr>
<td>Furan (Self-setting)</td>
<td>Furan</td>
<td>Furan (Publication 1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Binder G (Publication 2)</td>
</tr>
<tr>
<td>Modified Liquid Silicate 1</td>
<td>MLS1</td>
<td>MSS (Publication 1)</td>
</tr>
<tr>
<td>Commercially available foundry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>binder (Heat hardened)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unmodified Liquid silicate</td>
<td>ULS</td>
<td>Binder A (Publication 2)</td>
</tr>
<tr>
<td>(Heat Hardened)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unmodified Liquid Silicate</td>
<td>ULS-E</td>
<td>Binder B (Publication 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Addition rate of different binders is given in Table 2.

**Table 2. Addition rate of different binders**

<table>
<thead>
<tr>
<th>Binder Name</th>
<th>Binder</th>
<th>Activator/co-reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>1.5% by mass of silica sand</td>
<td>25% by mass of binder.</td>
</tr>
<tr>
<td>Furan</td>
<td>1% by mass of silica sand</td>
<td>33% by mass of binder.</td>
</tr>
<tr>
<td>Modified Liquid Silicate 1, MLS1</td>
<td>2% by mass of silica sand</td>
<td>6% promoter by mass of sand. Then heated for 3 hours at 160°C.</td>
</tr>
<tr>
<td>Unmodified Liquid Silicate, ULS</td>
<td>3% by mass of sand</td>
<td>Heated for 1 hour at 160°C.</td>
</tr>
<tr>
<td>Unmodified Liquid Silicate, ULS-E (Ester Hardened)</td>
<td>3% by mass of sand</td>
<td>15% by mass of binder.</td>
</tr>
<tr>
<td>Modified Liquid Silicate 2, MLS2-E (Ester Hardened)</td>
<td>2.5% by mass of silica sand</td>
<td>12% by mass of binder.</td>
</tr>
<tr>
<td>Geopolymer, GP-E (Ester hardened)</td>
<td>1.8% by mass of sand</td>
<td>16% by mass of binder.</td>
</tr>
<tr>
<td>Solid Silicate, SS (Heat Hardened)</td>
<td>0.83% by mass of sand</td>
<td>1.17% of water by mass of sand. Heated for 1 hour at 160°C.</td>
</tr>
<tr>
<td>Modified Liquid Silicate 3, MLS3 (Heat Hardened)</td>
<td>2.5% by mass of sand</td>
<td>Heated for 1 hour at 160°C.</td>
</tr>
</tbody>
</table>

### 3.1.3 Additives Tested with Solid Silicates

Modification of liquid sodium silicate binder with the addition of different promoter/additive is a popular contemporary research topic to improve the challenges faced, e.g., poor collapsibility, poor moisture resistance etc. This idea was now carried forward in this dissertation to solid silicates. 5 different additives were shortlisted to study their effect on solid silicates. These were: glucose, sucrose, boric acid, aluminum oxide and iron(III) oxide. The content and naming convention used is shown in Table 3. The additives tested were applied at a constant rate of 15% by mass of the solid silicate binder. The hydrous sodium disilicate powder used had a mean particle size of 70 µm, crystallized water content of 16-20% and a module of 2.0.

**Table 3. Content and naming convention used for solid silicate molds with and without additives.**

<table>
<thead>
<tr>
<th>Name</th>
<th>Binder</th>
<th>Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>Solid Silicate.</td>
<td>No Additives.</td>
</tr>
</tbody>
</table>
3.2 Sand Tests

3.2.1 Sieve Analysis

Sieve analysis was done according to test procedure AFS 1105-12-S[54], to reveal particle size distribution of the sand used. Mass of sample measured for each analysis was determined by bulk density. Higher mass of sand was used for sand type with higher bulk density.

3.2.2 Sand Flowability Tests

Sand with good flowability is required to ensure that it flows properly around a pattern which results in uniform mold density and hardness. However, flowability plays an even more crucial part in the additive manufacturing of sand molds where sand must be deposited uniformly in each layer in a repeatable manner [55]. Flowability also plays a part in how easily sand is spread in additive manufacturing and is also considered in the design of hoppers, mixers, and silos. Flowability is often defined simply as the ability of powder or bulk material to flow [56]. Predicting accurate flowability of powder using a single test is very difficult as powder flow does not only depend on intrinsic powder properties, but also how the powder interacts with the equipment or apparatus it is contained in [55]. As there are differing views on how well a flow test could accurately predict flowability of powders for different applications but many of these are relatively simple and easy to carry out. Hence, three flowability tests were done to assess the comparative results, namely Hall flow, Hausner Ratio (HR) and static Angle of Repose (AOR).

Hall Flow Test

Hall flow test utilizes a hall funnel designed according to standard ISO 4490[57], which is used for flow tests of metal powders. In this test a particular amount of powder is allowed to fall through the funnel and the time taken is measured. The funnel has an orifice diameter of 2.5 mm. The standardized test for metal powders measures the time taken for 50g powder to fall through the funnel. However, this process is best suited for powders which have very similar densities. A high-density difference between powders results in this test favoring the powder with higher density. Therefore, a constant volume of sand was used rather than a constant mass. 25 ml of the sand was allowed to flow through a hall funnel made of aluminium and the time taken was measured. For each sand, the test is carried out three times and the average calculated.

Hausner Ratio (HR)

Hausner Ratio is the ratio of tapped density to bulk density[58]. Loose sand has many void spaces, which reduces on tapping as the particles pack closer together, reducing the volume and increasing the density. This change in volume
of bulk materials is a result of many different characteristics like powder morphology, surface area, inter particle attraction, moisture content, etc. Hausner Ratio was measured using a 100 ml graduated cylinder, filled with a carney funnel between the 80 ml and 100 ml mark which was then vibrated using a sieve shaker for 1 min. The new tapped volume was recorded. As the mass remains constant, the ratio of initial apparent volume to the final tapped volume gives Hausner ratio. The experiment was done three times and average value calculated. The lower the value of Hausner Ratio, the better the particle flows[55].

Angle of Repose (AOR)
An adapted version of standard ASTM C1444[59] was used for measuring the angle of repose with some changes in the apparatus used. The angle of repose was measured by allowing the sand to flow through a carney funnel with an outlet diameter of 5 mm. The outlet sat 48 mm above a white paper, which had straight lines etched at different angles, that cross at the center. The funnel was first filled with sand with the stopper in place. The stopper was then removed, and sand was allowed to fall onto the paper, until sand rose to the height of tip of the funnel. On the straight lines of the paper, the diameter was marked with a pen as close to the sand pile as possible. For each trial, 3 dia were marked on different lines on the paper. For each sand, the test was carried out three times and the mean calculated correct to 1 decimal place. The angle of repose was measured using Equation 3.

\[
\text{Angle of repose} = \tan^{-1} \left( \frac{2H}{D - d} \right)
\]  

(3)

where H (48 mm) is the height of sand pile, D is the average of three diameter measurement of sand pile and d (5 mm) is the internal diameter of the funnel. The lower the angle of repose, the more flowable the powder is[60].

3.3 Mold Quality Tests

3.3.1 Sand Mixture Preparation for Test Samples
In the AFS test procedures [54] for preparing sand mixture, the binder is taken as a mass percentage of the sand. However, because different types of sand are used in this dissertation which has different densities, and a fair comparison cannot be done if the amount of binder used is based on the mass of sand. In that way, sands with higher densities receive more binder per unit volume, resulting in misleading conclusions. Hence, the volume of sand and volume of binder was kept constant. As most commercial binders are optimized for silica sand, the binder was calculated for the mass of silica. For all the other types of sand, the same volume of binder was added to same volume of sand as silica. This process ensures a constant unit volume of binder per unit volume of sand, therefore, ensuring a proper comparison in Publications 1 and 2 where different sand types were used.
For mixing purposes, a standard laboratory mixer was used. Most of the binders tested were two-part binder systems. In such cases, the sand was first mixed properly with the first part of the binder (which was usually the catalyst, promoter or activator, depending on the binder type), followed by a thorough mixing with the second part, the main component. The mixture was then molded into different shapes, depending on the specimen requirement for different test types. Some examples are shown in Figure 8. In case of solid silicate binder, the sand was first mixed with the binder, followed by addition and mixing with water. For tests that were conducted with additives, the additives were first mixed with the sand before the solid binder.

Figure 8. Test samples; a. Bending strength test bars, b. cuboids cut out for Loss on ignition (LOI) tests, c. standard Ø50mm x 50mm cylindrical specimens.

3.3.2 Bending Strength

The Morek Multiserw Universal Strength Tester LRu-2e/w was used for the bending strength measurements on standard bars measuring 22.4 mm × 22.4 mm in cross section and a length of 172 mm. In a 3-point bending strength test, the bar rests on two supports from below and an increasing pressure is applied at the midpoint from above. The tester then records the pressure required to break the bar. Three samples were tested, and the mean presented. The strength test results show if the mold is strong enough to withstand the various pressure from molten and solidifying metals. An optimum strength depends heavily on the application; however, a balance must be struck on the strength. If it’s too weak, it fails and if the mold is too strong then breaking the mold after solidification becomes very difficult. For self-setting binders, the tests were carried out from 24 h of mixing and nothing additional was done to accelerate the curing by heat or other methods, as is the practice with no-bake binders.

3.3.3 Loss on Ignition (LOI)

Loss on ignition test measures weight loss of a sample when fired to a high temperature. The loss is the combined effect of weight loss from gases emitted, loss
of chemically bound water and some weight gain from oxidation. Cuboid samples were cut from test bars having a mass of 20g-30g. The difference in weight of the samples before and after heating, expressed in percent of initial weight is the loss on ignition. As the heat hardened inorganic binders were heated to 160 °C, the test was modified to acquire comparable results with all the binders. Hence, all the samples were first heated at 160 °C for 1 h in a drying oven followed by at 915 °C for 2 h in a muffle furnace. Measurement was taken before and after putting the samples in each oven and loss of ignition was calculated with the difference in weight before and after taking it out of the 915 °C muffle furnace. Smaller loss on ignition value is desirable as it means smaller amount of gas generation.

### 3.3.4 Permeability

Permeability is a measure of how much gases can pass through the porous structure of cores and molds. Permeability depends on several different factors. For example, the sand particle size and shape distribution, how and to what degree mold was compacted and also, the binder amount. Smaller particles reduce the interparticle space and the presence of binder bridge between particles is expected to reduce permeability of molds as well[24]. Standard Ø50mm x 50mm cylindrical specimens were used in this test and the permeability measured using a Digital Absolute Permmeter. The reading ranged between 0 and 999; the higher the number, the higher the permeability the mold possesses. By definition, the permeability number indicates the volume of air that passes through a test tube of 1 cm$^2$ cross section and 1 cm in height when the air pressure is kept constant at 1 g/cm$^2$ [61]. The test was carried out in duplicate, and the average value reported.

### 3.3.5 Hot Distortion

Hot distortion (thermal deformation) parameters were investigated using a DMA apparatus by Morek Multiserw. 114mm x 25.4mm x 6.3mm samples were used in this test. One end of the sample is fixed in the jaws of the device, while a tilt sensor rests on the free end of the sample. Additionally, a temperature sensor is provided for more accurate temperature reading. The sample is then heated in the middle from below, with two halogen lamps of total power 500 W. The heating temperature ranges from room temperature up to 900 °C. The apparatus provides deformation readings as a function of both time and temperature. Maximum deformation reading was set at 6mm. A schematic diagram of hot distortion test is shown in Figure 9.
3.3.6 Gas Emission

Gas emission was estimated (or rather indicated) through the Loss on Ignition tests (LOI) in Publications 1 and 2. However, in Publication 3, emission measurement was conducted according to Polish standard BN-76/4024-05, which measures the actual volume of emitted gas when heated to 1000°C. After reaching a temperature of 1000°C, a corundum boat with a weighed sample of 2g is introduced into the quartz tube. The pipe is closed tightly to prevent any leakage. The other end of the pipe is connected to a peristaltic pump, which is turned on to create a negative pressure. When the measurement starts, and the quartz tube is moved to the position where the sample is in the heating zone. Placing the sample in the heating zone causes the release of gases that are products of the reactions taking place. This increases the pressure in the system. The pump is automatically turned on to remove the generated gases. The recording of the volume of released gases continues until the pressure stabilizes to the initial value[63]. The test is carried out until no further gases are generated.

3.3.7 Collapsibility

One of the challenges of working with sodium silicate binder is the poor collapsibility. However, there is difficulty as well in designing a test that’s an accurate representation. One way of collapsibility assumption is to measure the retained strength after heating to very high temperature. Retained bending strength was measured in Publications 2 and 3. However, in Publication 3, the collapsibility test carried out was according to Polish standard PN-85/H-11005, which uses standard Ø50mm x 50mm cylindrical specimen made from the tested sand. The specimens are placed as cores in a mold cavity and cast with grey cast iron. The cast is then taken out and the core is rammed using a device to push the core out. The number of hits it takes to completely push out the core is taken as a measure of collapsibility. The smaller number of hits it takes, the more collapsible the sample is. Total work done to remove the core is measured as per Equation 4 [38].

\[ L = 1.63 \times n (J) \]  

Where, 1.63 is the work done by one hit of the weight, in Joules(J); n is the number of hits of the weight until the core is pushed out of the casting.
3.3.8 SEM Imaging

To see the fractured surface, Scanning Electron Microscope (SEM) imaging was done on fractured mold surface to study fracture mechanism of some select samples in Publication 3. The equipment used was Tescan MIRA4 GMU Scanning Electron Microscope, which can observe non-conductive samples without any processing as it is equipped with two imaging detectors: secondary electron (SE) and backscatter (BSE) detector, and an additional GSD detector of secondary electrons (SE) designed to work in low vacuum mode. This meant no coating material was necessary to make the mold surfaces conductive before SEM imaging. Figure 10A shows a representation of two bonded sands with a force applied. The way fracture occurs depend on the values of cohesive forces within binding material and adhesive forces between the binding material and the sand surface. Figure 10B shows an instance where the cohesive force is greater than the adhesive forces and the binder material separates from the sand surface. Such case is desirable for good collapsibility and mechanical reclamation. When the force of adhesion is stronger than the force of cohesion, the fracture takes place within the binding material, as shown in Figure 10C. When the force of cohesion and adhesion are balanced, the fracture could take place anywhere within the binding material or the surface of the sand. Sometimes both cohesive and adhesive strength is more than the strength of sand grains, and destruction of the sand grains take place as shown in 10D.

![Fracture mechanism representation](image)

**Figure 10.** Fracture mechanism representation, Adapted from [64], [65].

3.3.9 3D Scanning

Use of 3D scanners is increasing across the manufacturing industry mainly as a tool for inspection and quality control. It is an excellent tool for reverse engineering as well specially when it comes to remanufacturing of old patterns. A 3D scanner was used in Publications 2, 3 and 4 which works based on structured light process, with a manufacturer claimed accuracy of up to 0.05 mm, and a resolution of 0.13 mm. Scans were taken of the patterns, molds and final castings. From the 3D scans, measurements could be made in each stage of the casting process, from pattern to mold and mold to final castings and deviations.
could be found out. 3D scans also allow mesh-to-mesh analysis. Mesh-to-mesh analysis is a good visual representation of the overall deviations. The scans were also instrumental during defects analysis where they could be referred, to understand from which stage particular defects resulted from. An anti-reflective spray was sometimes used while scanning the pattern and most of the castings to overcome the limitation of structured light technology on shiny surfaces.

### 3.4 Cast Quality Tests

Casting trials were conducted in Publications 2 and 3. The cast alloy used in Publication 2 was EN GJS-500-7 and small molds were made using an aluminum metal pattern as shown in Figure 11. The small molds were then combined in a large phenolic mold so that the trial could be conducted at once, as shown in Figure 12.

![Figure 11. Metal pattern used in Publication 2.](image)

In publication 3, the cast material used was EN-GJL-300 and small molds were made using a 3D printed heat resistant plastic pattern as shown in Figure 13. Two molds were combined in a phenolic mold for casting trial, an example is
shown in Figure 14. This pattern was also used in publication 4 to study its dimensional variation of the molds made.

![Figure 13. 3D printed plastic pattern used in publication 3 and 4.](image1)

Figure 13. 3D printed plastic pattern used in publication 3 and 4.

![Figure 14. Two molds combined in a big phenolic mold in Publication 3 (left SSGC and right SSFE).](image2)

Figure 14. Two molds combined in a big phenolic mold in Publication 3 (left SSGC and right SSFE).

Publication 4 also makes use of a 3D printed metal pattern, as shown in Figure 15. This was used as a control for publication 4 to demonstrate the differences with the 3D printed SLA pattern (Figure 13).
3.4.1 Surface Roughness Analysis

Although most casts go through some form of post processing to improve surface finish, having a good as-cast surface finish reduces the work required on the casts and thereby reduces operational costs and lead time. Common methods of assessing as-cast surface conditions include the use of Gar Microfinish comparator C-9 or the SCRATA plate (as per ASTM A802 standard) [66], [67]. The operator visually compares castings with these reference plates. In literature, there are also suggestions of using point clouds from 3D scans to analyze surface quality of the whole castings rather than a small representative surface[68]. However, a 3D optical profilometer was used to measure surface roughness in this dissertation. 2mm-by-2mm area was inspected for the measurements. For each location, profile parameters were noted as well as a surface micrograph taken. There are other surface texture parameters, e.g., $S_a$ which quantify surfaces from an area viewpoint rather than line profile viewpoint (for example, $R_a$ and $R_s$). The $S_a$ parameter is the closest to the $R_a$ parameter, although they are fundamentally different. However, if a large number of $R_a$ values are averaged, it tends to be closer to the $S_a$ parameter, as reported in[69]. The profilometer software (Vision64) provides an $R_a$ reading which is an average roughness of the entire region being measured. Therefore, the $R_a$ values reported in this dissertation are also very close approximation of $S_a$ parameters.

Since the area of measurement does not lie in a planar surface, a compensation was applied by the built in function of vision 64 software. This compensation converts curvature to a planar surface before calculation. This is very important, especially in case of castings, as even planar surface by design could deviate for reasons like mold wall displacement and shrinkage differences[67]. Surface roughness values were then noted as reported by the software.
4. Results

This chapter summarises the results of the four publications that were done during this thesis. Findings from this dissertation broaden the knowledge about inorganic binders, the challenges to work with them and possible remedies. First, Publication 1 studies six different sands and three different binders (2 organic and 1 inorganic). Publication 2 then focuses extensively on different inorganic binders only, four of which are in liquid form and one in solid form. Publication 3 focuses entirely on solid silicate binder and how some additives affect its performance. In the end, Publication 4 looks a bit more closely at the 3D printed pattern material used in Publication 3 and briefly presented in publication 2 as a potential solution to metal pattern alternative for heat hardened binders. A recap of the binders used, and naming convention is given at the start of each section for easier understanding.

4.1 Sand Flow and Mold Quality (Publication 1)

Table 4 shows the name and content of the binders used in Publication 1. Six different sands were used: silica, bauxite, CB 400, CB 1450, chromite, and zircon.

Table 4. Name and content of the binders used in Publication 1.

<table>
<thead>
<tr>
<th>Name</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>Self-setting alkaline phenolic binder.</td>
</tr>
<tr>
<td>Furan</td>
<td>Self-setting furfuryl alcohol binder.</td>
</tr>
<tr>
<td>MLS1</td>
<td>Modified Liquid Silicate 1. Heat Hardened.</td>
</tr>
</tbody>
</table>

The size distribution of different sands used is shown in Figure 16, along with the mean particle size. Bauxite and chromite had a wider distribution, while chromite also had the largest mean particle size of 0.387 mm. CB 1450 had the lowest mean particle size of 0.130 mm, followed very closely by zircon at 0.132 mm. Silica had a mean particle size of 0.264 mm. Very little or no dust was present in the sand samples. The silica represented here was used in Publication 1. In Publications 2, 3 and 4, the silica used was from same manufacturer, but different particle size.
Figure 16. Sieve analysis of the sands used.
Results from AOR tests is shown in Figure 17. Chromite sand exhibited the highest AOR (34.7°) and the two lowest were CB 1450 (30.2°) followed by zircon (31.9°). Silica exhibited quite high AOR of 33.8°. It should also be emphasized that all the sands were within ‘free flowing’ range according to AOR test. Results for Hausner Ratio is shown in Figure 18. Like AOR test, the two lowest values were from zircon and CB 1450. Unlike AOR, bauxite had the highest HR value, followed by chromite. Silica had a moderate HR value of 1.133. All the sands were within the ‘good’ flow range according to HR values.
The least time for 25 ml sand to flow through Hall flowmeter funnel was taken by CB 1450 (56.43 s), followed very closely by zircon (56.91 s). Silica and bauxite needed similar times at 72.12 s and 74.11 s respectively. The highest time was taken by chromite sand (85.13 s). The lower the time, the more flowable the sand is. From the results it was seen that the higher the mean particle size, the higher was the time taken.

Results from the bending strength tests, permeability tests and the loss on ignition tests are shown in Figures 20, 21 and 22 respectively. Furan failed to harden with both Cerabeads type with the addition rate used in the publication. For phenolic binder, only zircon exhibited more strength than silica. The rest were
less than silica, while the least was obtained with CB 400. With all sand types, MLS1 produced the highest strength compared to furan and phenol. Zircon achieved the highest strength, followed by chromite.

The difference in permeability for different binders on the same sand was little as can be seen in Figure 21. Only zircon and CB 1450 exhibited lower permeability than silica. The highest permeability was seen with CB 400. Bauxite and chromite showed similar permeability. Bauxite, chromite and CB 400 had higher permeability than silica, CB 400 being the highest. With the binder addition rate used in the study, different binder did not have much effect on the same sand type. Therefore, mold permeability values were not prioritised in the subsequent publications.
Results

Figure 22. Loss on ignition of sand and binder combinations.

Furan produced the highest loss on ignition, with all sand types as can be seen in Figure 22. The highest loss across all tests was the combination of silica and furan. A negative loss on ignition was obtained with the chromite sand, when combined with phenol and MLS1. This is due to the oxidation of chromite, and a negative loss means that the sample gained more weight due to oxidation than it lost from gas release, thereby confirming the very little emissions produced by inorganic sodium silicate binders.

4.2 Study of Different Inorganic Binders (Publication 2)

Binders used in the publication is listed in Table 5. Figure 23 shows stereo microscope images of the three different sands used in the publication: silica, bauxite, and CB 400. Table 6 lists the base properties of the sands used.

Table 5. Recap of the binders used in Publication 2.

<table>
<thead>
<tr>
<th>Name</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULS</td>
<td>Unmodified Liquid Silicate. Heat hardened.</td>
</tr>
<tr>
<td>ULS-E</td>
<td>Unmodified Liquid Silicate. Ester cured.</td>
</tr>
</tbody>
</table>


Figure 23. Stereo microscope images of the sand used in the Publication 2.

Table 6. Base properties of the sands used.

<table>
<thead>
<tr>
<th></th>
<th>Mean particle size</th>
<th>AFS GFN</th>
<th>Grain Shape</th>
<th>Bulk Density (g/cm³)</th>
<th>Permeability</th>
<th>LOI (%)</th>
<th>Calculated Specific Surface Area (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>240 µm</td>
<td>62.8</td>
<td>Sub-angular</td>
<td>1.48</td>
<td>90-100</td>
<td>0.20</td>
<td>153.3</td>
</tr>
<tr>
<td>Bauxite</td>
<td>300 µm</td>
<td>51.1</td>
<td>Rounded</td>
<td>1.99</td>
<td>103-106</td>
<td>-0.01</td>
<td>85.9</td>
</tr>
<tr>
<td>CB 400</td>
<td>380 µm</td>
<td>40.8</td>
<td>Rounded, compound</td>
<td>1.49</td>
<td>300-330</td>
<td>0.15</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Figure 24. Bending strength of all the sand and binder combinations.

Figure 24 shows the bending strength achieved with the different inorganic binders and three sand types. ULS produced the highest bending strength with all types of sand. Specifically, bauxite and ULS produced bending strength as high as 448.5 N/cm². For all binder types, CB 400 had the least strength. This was anticipated as CB 400 produced low strengths with organic binders as well, owing to its large and uniform particle size (as per results from Publication 1). Solid Silicates (SS) produced intermediary results with all sand types, which is deemed sufficient for most applications. Residual bending strength of the sand
and binder combinations were also measured at 160°C, 450°C and 900 °C. The results are shown in Figure 25. LOI values are shown in Figure 26.

![Graph showing residual bending strength of binders with silica sand](image1)

**Figure 25.** Residual bending strength of the binders with silica sand.

![Bar graph showing loss on ignition of sand and binder combinations](image2)

**Figure 26.** Loss on ignition of the sand and binder combinations

For all inorganic binder types, the loss on ignition was less than loss on ignition obtained with organic furan and phenol binders. Solid silicate and bauxite had the least loss on ignition, while silica and ester-cured liquid silicate (ULS-E) had the highest loss on ignition.

The effect of storing the solid silicate in closed containers is shown in Figure 27A. Solid silicate was stored as a mixture with silica sand in closed containers. After the indicated time, water was added, and bending strength test was carried
Results

out. The bending strength remained above 200 N/cm² over the period of 4 weeks confirming good storability of silica and SS binder as a mixture up to 4 weeks before use. Storage in open containers was also studied, up to 8 days and bending strength more than 250 N/cm² was achieved (Figure 27B).

![Graph A](image)

![Graph B](image)

**Figure 27.** Storage tests of silica and solid silicate (SS) mixture. A closed container and B, container open to air.

Figure 28 shows the 3D scan of silica and phenol mold. Very smooth surfaces were seen with little to no defects. In contrast, Figure 29 shows the 3D scan of solid silicate and silica mold, where very rough surfaces were seen.
Results

Figure 28. 3D scan of mold made using silica and phenol binder (Sil-Phenol).

Figure 29. 3D scan of mold made using silica and solid silicate binder (Sil-SS).

Example photos of some of the castings are shown in Figure 30 and surface roughness of the castings are showed in Figure 31. Prefix ‘Sil’ refers to molds made with silica, ‘BX’ refers to molds made with bauxite and ‘Sil-BX’ refers to molds made with 50% silica and 50% bauxite by volume. It can be seen from Figure 31, the metal pattern used had an average $R_a$ of 4.92 $\mu$m. The best surface finish was achieved with phenolic binder (Combination Sil-Phenol) at 8.06 $\mu$m, followed very closely by the furan at 10.51 $\mu$m. Commercially used ester-cured sodium silicate (Sil-MLS2-E) produced an $R_a$ of 12.04 $\mu$m and that by geopolymer (Sil-GP-E) 11.95 $\mu$m. Very high surface roughness was seen with solid silicates, at 55.45 $\mu$m. This improved to 36.91 $\mu$m when a mold release agent was
utilized (Sil-SS-MR). The worst surface roughness in the experiment was seen with Bx-SS (61.9 µm). However, a promising result was obtained when 50% of silica and 50% of sintered Bauxite was used as a molding mixture (Sil-BX-SS), and the roughness dropped to 28.12 µm, very much less than when only either silica or bauxite was used with solid silicates. Some select micrographs taken with optical profilometer are shown in Figure 32.
Figure 30. Select castings with visible differences in surface condition.
Figure 31. Surface roughness of castings (average of 3 Ra).

Figure 32. Select optical micrographs of the castings made.
Mesh-to-mesh analysis of the casts was done against the pattern used. The software tracked differences in pattern and casting produced after a best-fit alignment of the separate scans. Range of scale used were −1.00 (blue) mm to +1.00 mm (red). The blue color represents a place where the casting is smaller than the pattern, and red color where the casting is bigger than the pattern and with other gradual changes in color in between as shown in Figure 33 for Sil-Phenol casting. Comparable results were obtained with both organic binders phenol and furan. Contractions seen on the outsides of both the flanges, whereas small expansion was noticed to areas on both flanges on the inside. This is the expected casting contraction. Rest of cast remained within green to yellow zone, demonstrating little dimensional differences with the pattern.

In comparison, geopolymer binder (Sil-GP-E) showed less contraction on the outside. With Sil-MLS2-E, although the outside showed similar contraction, the inside of the flanges showed some expansion compared to the pattern, as shown in Figure 34. With Solid silicate binder (Sil-SS), much rougher surface was noticed as can be seen in Figure 35. There was less contraction on the outside and much larger deviation on the inside of both flanges and small contractions can be seen on the top of the top flange. The situation was improved both in terms of surface roughness and deviations in mesh-to-mesh comparison when a mold release agent was used with SS (Combination Sil-SS-MR). Dimensions like flange-to-flange distances were compared for all the casts, and deviations were also found in pattern to mold and mold to casting stages. Interested reader is referred to Publication 2 for those results. In addition, mesh-to-mesh analysis of all the casts can be found as supplementary file 2 of Publication 2.
4.3 Effect of Additives on Solid Silicate Binder (Publication 3)

The effect of five different additives on solid silicates was studied through different mold and cast quality tests and compared against a modified liquid sodium silicate. Content of the binders is shown in Table 7. Sieve analysis of the silica sand used is shown in Figure 36.
Table 7. Name and content of binder used in Publication 3.

<table>
<thead>
<tr>
<th>Name</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLS3</td>
<td>Modified Liquid Silicate 3. Heat hardened.</td>
</tr>
<tr>
<td>SSGC</td>
<td>Solid silicate with glucose additive.</td>
</tr>
<tr>
<td>SSSC</td>
<td>Solid silicate with sucrose additive.</td>
</tr>
<tr>
<td>SSBA</td>
<td>Solid silicate with boric acid additive.</td>
</tr>
<tr>
<td>SSAM</td>
<td>Solid silicate with aluminum oxide additive.</td>
</tr>
<tr>
<td>SSFE</td>
<td>Solid silicate with iron(III)oxide additive.</td>
</tr>
</tbody>
</table>

Figure 36. Sieve analysis of sand used in Publication 3 (Mean particle size: 0.33mm).

Results of strength tests are shown in Figure 37. Good bending strength more than 260 N/cm² was obtained with the solid silicates without any additives. With boric acid, it decreased to around 200 N/cm² and with glucose, there was a further decrease to 170 N/cm². Addition of sucrose, aluminum oxide and iron oxide have all increased the bending strength more than 300 N/cm². However, maximum strength was obtained with liquid silicate (MLS3), more than 380 N/cm² (Same day maxima: 414.3 N/cm²; same day minima: 365.3N/cm²). Similar to the bending strength, the lowest tensile strength achieved was with SSGC and the highest with MLS3 (Same day maxima: 212.4 N/cm²; same day minima: 174.3 N/cm²). Residual bending strength at 900°C, were not so different. It should be emphasized that the same day measurements were taken 30 min after the samples were removed from furnace. A wear resistance test was also conducted on the samples which showed MLS3 had the most wear resistance (Friability 0.66%). SS had a friability of 1.4%. Other additives were similar to SS, except for SSGC which had a friability of 2.78%, meaning it possessed the least wear resistance. The reader is referred to Publication 3 for the detailed results of wear resistance test.
Figure 37. Strength test results of molding sand with liquid silicate (MLS3), solid silicate (SS) and solid silicate with different additives.

Figure 38. Gas emission results.

Figure 38 shows the result of gas emission tests. The lowest emission was seen with MLS3, SS and SSBA at 16.5 cm$^3$/g. Addition of sucrose and glucose increased the emission to some extent but those were still lower than phenol binder, that produced 23.5 cm$^3$ of gas per gram of molding sand.
Thermal deformation results with respect to both temperature and time are shown in Figures 39 and 40 respectively. The results were very close to expected deformation with sodium silicate molding sands[62] with a small (less than approx. 0.3 mm) deformation in the opposite direction to the heat source. Molding
sands demonstrated good heat stability, showing little to no thermal deformation between 0-200° C range. Deformation was seen after that until eventually the samples were damaged. The samples made from molding sand with sodium silicate began to degenerate after about 50 sec. The best thermal stability was with SS and SSGC. Additionally, a longer time was necessary for the destruction of SSGC specimen.

Collapsibility test results are shown in Figure 41. The best result was obtained with liquid silicate (MLS3), which was anticipated as this was a modified liquid silicate for good collapsibility. Solid silicate (SS) without any additives had lower collapsibility (11.41J of work required to push core out) than MLS3. Collapsibility was reduced by the addition of aluminum oxide and iron(III)oxide but improved very close or equal to that of MLS3 by the addition of glucose, sucrose and boric acid.

Figure 41. Collapsibility test results.

Figure 42. A. SEM fracture image of solid silicate (SS), B and C. EDS layered image representing presence of sodium (Na).
Some example photos of fracture surface are shown in Figures 42, 43 and 44. The bonding bridges are marked in red, remains of binder in yellow and arrows used to show broken sands. Mostly broken sands and not broken bonds was noticed with SS, as shown in Figure 42 A. Elemental analysis with EDS (Energy-Dispersive Spectroscopy) was used to distinguish sand from remains of broken bonding bridge. This was mainly done by tracking presence of sodium as shown in Figures 42B and 42C.

With MLS3, fractures were seen both on the surface of the sand and some destruction of sand as shown in Figure 43. Fracture of the bonding bridge rather than within the sand body itself was noticed with glucose as shown in Figure 44A. This was expected from the low strength of SSGC. Addition of sucrose revealed a similar Fracture to SS, as sand shearing was seen, and many intact bonds as shown Figure 44B. This confirms the high strength values of the bonds with SSSC. No undissolved solid silicate on the surfaces of sand were seen.

![Figure 43. SEM fracture image of liquid silicate (MLS3)](image)

![Figure 44. SEM fracture image of A. SSGC and B. SSSC.](image)
All the molds produced with the 3D printed SLA pattern had very smooth surfaces, with little to no visible damage. This was also confirmed from the 3D scans of the molds. One such example of SSSC mold scan is shown in Figure 45.

![Figure 45. 3D scan of mold SSSC.](image)

Figure 45. 3D scan of mold SSSC.

Figure 46 shows the casting obtained with SS. Sand particles can be seen embedded to the cast in the top flange, and even more in the middle of the casting due to penetration. The heaviest penetration was seen in the region between top flange and middle. No penetration was seen on the right and left flanges. Figure 46 also shows a stereo microscope image of the right flange and surface micrograph taken with optical profilometer for the left flange. Similar penetrations were seen with all castings in the top flange, middle area, and areas in between. Hence, only left and right flange surface roughness were measured as shown in Table 8.

![Figure 46. Casting obtained with solid silicate and no additive (SS), pouring temperature: 1350 °C.](image)
Table 8. Surface roughness values of the castings (Target pouring temperature 1350°C)

<table>
<thead>
<tr>
<th>Description</th>
<th>Left Flange, Rₐ (µm)</th>
<th>Right Flange, Rₐ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLS3</td>
<td>29.69</td>
<td>31.14</td>
</tr>
<tr>
<td>SS</td>
<td>19.91</td>
<td>23.92</td>
</tr>
<tr>
<td>SSGC</td>
<td>15.21</td>
<td>20.01</td>
</tr>
<tr>
<td>SSSC</td>
<td>12.83</td>
<td>10.23</td>
</tr>
<tr>
<td>SSBA</td>
<td>18.37</td>
<td>22.11</td>
</tr>
<tr>
<td>SSAM</td>
<td>25.90</td>
<td>33.39</td>
</tr>
<tr>
<td>SSFE</td>
<td>11.59</td>
<td>18.49</td>
</tr>
</tbody>
</table>

As can be seen in Table 8, except for SSAM all the other additives resulted in better surface roughness readings compared to SS. The best was obtained with SSSC. Liquid silicate also resulted in higher surface roughness values compared to SS and also suffered more penetration compared to SS. Some repeat casts were then attempted with solid silicate alone (no additives) as the understanding of the authors was that fluidity of the molten metal and elevated temperature were in part factors that increased penetration, and penetrations could be reduced by changing some conditions. Hence, 4 casts were repeated with SS: using higher pouring temperature of 1400 °C but graphite coating applied (SS1), same pouring temperature but higher amount of binder (SS2), lower pouring temperature of 1320 °C (SS3) and even lower pouring temperature of 1300 °C (SS4). Surface roughness values were measured again and shown in Table 9 for these recast trials.

Table 9. Surface roughness obtained with repeat casting trial with solid silicate and altered conditions.

<table>
<thead>
<tr>
<th>Description</th>
<th>Rₐ Left Flange (µm)</th>
<th>Rₐ Right Flange (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS1 With coating, pouring temperature 1400 °C</td>
<td>10.27</td>
<td>11.06</td>
</tr>
<tr>
<td>SS2 With higher amount of binder (25% more)</td>
<td>39.11</td>
<td>24.49</td>
</tr>
<tr>
<td>SS3 Pouring temperature 1320 °C</td>
<td>10.9</td>
<td>8.90</td>
</tr>
<tr>
<td>SS4 Pouring temperature 1300 °C</td>
<td>12.68</td>
<td>10.60</td>
</tr>
</tbody>
</table>

Improved results were obtained with SS1, SS3 and SS4 with very reduced penetration. A higher amount of binder did not improve the surface quality (SS2). SS1 along with a surface micrograph using optical profilometer is shown in Figure 47. Average of the roughness values for all the measured specimens is shown in Figure 48.

![Figure 47: Photo and surface micrograph of SS1.](image-url)
4.4 Additively Manufactured Plastic Pattern for Heat Hardened Molds (Publication 4)

The 3D printed heat resistant plastic pattern used in Publication 3 released easily, produced molds with good surfaces, confirmed both visually and also from the 3D scans. However, it was also necessary to test the dimensional variation of the produced molds. Tests were conducted with same silica sand used in Publication 3. Mesh-to-mesh analysis of the 3D scans of molds made were compared against the CAD model of the pattern, the differences were tracked in a scale from $-1.00$ mm to $+1.00$ mm.

Figure 49 shows the mesh-to-mesh analysis of furnace heated SS mold with 3D printed plastic pattern. Mold cavity deformation or
loss of sand from the surface is very minor. The result is very similar to the microwave heated sample. Figure 50 shows the combination of solid silicate binder used with 3D printed plastic pattern and microwave heating. Very little deformation and sticking was seen in this combination, with a small defect in the sharp corners of the cavity.

Figure 50. Mesh-to-mesh analysis of microwave heated SS mold with 3D printed plastic pattern.

An additively manufactured metal pattern with same dimensions was also used in this publication. Similar to Publication 2 metal pattern, this metal pattern also stuck strongly to the mold, making pattern release very difficult. As a result, a very rough surface could be seen in the 3D scans and mesh-to-mesh analysis, as shown in Figure 51. High roughness of the sand mold surface was also clear in visual inspection.

Figure 51. Mesh-to-mesh analysis of microwave heated SS mold with 3D printed metal pattern.
5. Discussion

The chapter discusses the results of Publications 1-4, the experimental method and equipment used and the practical implications of the findings of this dissertation.

5.1 Inorganic Molding: Performance, Potential, Challenges

Stricter environmental laws and global trend for sustainable manufacturing is bringing about rapid changes across the whole manufacturing industry, foundry industry being no exception. Silica sand will remain popular for sand casting for years to come, although there will be changes in demand as other alternatives start to be more widely used. Many of the sands tested here have exhibited good properties on the parameters tested. However, it must be emphasized that bauxite, chromite, and zircon sand are all much heavier than silica sand which brings about other challenges like mechanical handling of the sand. Much stronger robots might be necessary as well as silos strengthened. Another consideration is the higher wear rate of pattern and tooling material when denser aggregates are used in traditional casting. Cerabeads have a similar bulk density to that of silica and the fact that they have very round and uniform shapes make them ideal for use in 3D printing of sand molds as well. Of the tested sands, only cerabeads have a comparable density to silica and these also have a lesser expansion related problem compared to silica. The increased cost of cerabeads is justified in 3D printing of sand mold, where other sustainable measures could be taken through steps like complex design and topological optimization to offset the cost. However, for heat hardened inorganic binders, sands with higher heat diffusivity could play a major role in more efficient and sustainable systems. This means sands with higher heat conduction rate and lower heat capacity must be prioritized when they are meant to be furnace hardened. In publication 1, the highest strength achieved with heat hardened inorganic binder was with zircon, followed by chromite sand. The very high strength achieved also signifies the fact that binder addition rates could be further reduced to get the strength in the optimum range.

Inorganic binders are being heavily researched as green binder systems, and there is a compelling push on foundries for adoption of inorganic binders due to their environmental friendliness. However, their introduction to widespread
replacement of organic binders is not without challenges. Ester cured sodium silicate (MLS2-E) and ester cured geopolymer (GP-E) both approximate the ease of use of self-setting organic binders like furan and phenol. This is a good intermediate step before complete switch to fully inorganic binders could be possible. Good mold quality parameters were seen with the ester cured inorganic binders. The pattern release was very smooth using metal patterns and very good surface qualities were obtained with ferrous casting, which were very close to the best results obtained with the organic binders. Some challenges were observed with heat hardening of sodium silicate binders. Metal pattern release was difficult, which resulted in abrasion of the mold surface, resulting in poor surface quality of the casts made. This was even more profound with the use of heat hardened solid silicates, where the mold stuck strongly to the metal pattern surface. This challenge needs to be overcome if molds need to be heated in furnace with the pattern inside. Three different solutions were attempted with varying degree of success. One of those was the use of a mold release agent which was sprayed on the metal pattern, reducing Rₐ value from 55.4 µm to 36.9 µm. The other attempt with some degree of success was the use of a mixture of 50% silica and 50% bauxite sand that improved the surface roughness of the casts even better to 28.1 µm. The last attempt was the use of a 3D printed heat resistant plastic pattern. The pattern was tested at 160 °C and satisfactory end results were obtained. Pattern release was possible without damaging the mold surface. This resin printed heat resistant pattern holds a great promise for inorganic molds and cores that must be heat hardened, additionally also because this pattern material enables microwave hardening, which is limited with the use of metal patterns. The same material could be used for coreboxes as well. Apart from that, there is a number of potential advantages of using SLA printed pattern over, e.g., additively manufactured metal patterns. SLA prints are generally known to have very good surface quality that should result in better mold surface, these are lighter as well as less energy intensive to produce.

Storability of the solid silicates in a mixed form with silica sand was tested for up to 4 weeks in closed container and for 8 days in container open to air. Good results were obtained in both these cases, shedding light on the fact that solid silicates mixed with silica is a good opportunity for suppliers to explore. Of course, further research is required to find out how much longer could it be stored in mixed form. If in-house water is supplied by the foundry, and foundry buys a mixture of sand and solid silicates, or silicate coated sands, the process simplifies to a great deal the storage and transportation of the binder. With the tested levels in this dissertation, the mass of solid silicates used was 37.6% less compared to 2 part furan binder, 55.7% less compared to 2 part phenolic system, 70.36% less compared to 2 part ester cured modified sodium silicate (MLS2-E), and 66.8% less compared to a heat hardened sodium silicate (MLS3, used in publication 3) when the water component could be supplied in house in the foundry.

Two reasons were identified for high surface roughness with solid silicates. The first being the use of metal patterns that sticks very strongly to the solid silicate binder, the remedy to which has already been discussed and addressed.
The second is the penetration issue which is a challenge of casting gray iron with sodium silicates. One of the remedies explored in the dissertation, is the use of graphite coating which reduced penetration to a great extent. The use of coatings is a common practice for casting with high temperature alloys. Also, in the case of organic binders, a gas builds up near the surface of the mold applies opposing pressure to the approaching liquid front, and thus plays a part in reducing penetration. Gas generation from the solid silicates was much lower. Hence, a less permeable molding material (e.g., sand with smaller particle size) could potentially be explored to reduce penetration, for example zircon or CB1450 that were used in the earlier publications. Low melting point alloys, for example, aluminum was not attempted as aluminum is known to work without much challenges with sodium silicate binders.

One major motivation towards the use of solid silicates was the additive manufacturing of sand molds. Of course, 3D printing of sand molds mean a patternless casting process, thereby the issues encountered with the release of metal pattern and solid silicates are irrelevant. However, it is to be emphasized that the result from this dissertation puts solid silicates as a strong contender for main line foundry use as well. If the same binder is in use for both traditional molding and for 3D printing of sand molds, it would accelerate the adoption even faster for foundries. There are studies already that used solid silicates for 3D printing of sand molds, and also about post processing of such molds[46], [70]. The additives tried in this dissertation would help binder manufacturing companies in developing a more optimized blend of additives that improve the casting performance of solid silicates even further. Having all the additives and the binder itself in solid form significantly improves the storage prospect of the binder. When liquid silicate binder is modified with different additives, they tend to separate over time, reducing their shelf life. Other issues that could occur include binder lumping, thickening, and crusting. Solid silicate binder could mitigate all these issues with binder storage.

Despite the additional advantages of solid silicates compared to liquid silicates, it is also necessary to discuss their safety considerations. When these powders are in use, adequate ventilation must be ensured, and all foundry workers must have access to proper PPE and special protective masks. However, the requirements are expected to be similar to foundry practices in use for silica sands[8]. The best-case scenario is of course when foundries are buying blends of sand and solid silicate or silicate coated sand already produced by a manufacturer at a special facility. In that way, solid silicate dusts would have minimal exposure to air and humidity at foundry premises and foundries will only add water to the ready blends at their premises, simplifying their operation to some extent.

5.2 Comments on Experimental Method and Equipments

The test specimens used in the molding tests were all hand molded. Although these are not as accurate with each repetition when compared to for example, core shooters, it is worthwhile to mention that it is closer to the real foundry
operation. This obviously introduced some differences and errors; however, the experiments were conducted with sufficient safeguards in place in an attempt to reduce the variations and credible trends were found out. Of course, to get very accurate data on each criterion and/or combination, more samples will be required which could be topic for further experimentations. A lot of digital techniques were used throughout the dissertation. The suitability of 3D scanner for dimensional analysis of the molds and casts were clearly demonstrated. 3D scans of the molds were successfully used in the defects analysis as well, where the scans were referred to understand whether the defects arose from molding phase or casting phase. The structured light 3D scanner performed generally well in scanning the molds, however some particular cases were more challenging, e.g., the molds that had a mixture of 50% silica and 50% bauxite, due to the alternate dark and bright appearance of the mold.

The use of optical profilometer provides a more accurate surface roughness analysis compared to using discrete results plate Gar Microfinish Comparator C-9 and SCRATA plates. With these plates, distinguishing accurately between two surfaces which are close is very difficult, results might also vary from one operator to other. The use of optical profilometer performs very well as documented in this dissertation. The non-contact process gives very accurate surface roughness measurements and all parameters like $R_a$, $R_z$ and $S_a$ can all be measured accurately. The provision of straightening out curvature planes by the built-in software also enables accurate roughness determination of curved surfaces.

3D printed patterns were used in this dissertation, one in the form of 3D printed heat resistant SLA pattern (mainly in publications 3 and 4), and a 3D printed metal pattern in Publication 4. The ability of printing pattern directly from CAD files gives a lot of freedom to the foundries for digital pattern storage and also reprinting any patterns that might need some design changes. Of course, the use of sand printers renders a pattern totally unnecessary, and it is worthwhile to mention again that one of the motivations for experimenting with solid silicates in this dissertation was the easing of 3D printing of sand molds and cores.

5.3 Practical Implications of the Findings

Drastic changes to industrial operations are often not realistically possible. A lot of considerations must be given to new equipment that might be necessary as well as material supplies and suppliers. New practices must also be validated and standardized before becoming the norm. Although changing to inorganic binders might look straightforward, this is a tremendous undertaking for many foundries. The vision initially introduced in this dissertation was a change in the use from liquid organic binder to solid inorganic binder. However, to go the end vision, intermediate steps might first be necessary, like the use of semi organic binders or use of organic additives with inorganic binders. One should not shy away from viable intermediate steps which are a bit more sustainable from the original practice, even though it might not be the end point one would like to be.
The results presented in this dissertation will aid foundries in selecting sand and binder combination for different applications. The results presented in Publication 3 is a promising start to developing further the solid silicate binder and it should be helpful for foundry binder manufacturers. However, the findings should generate interest in both foundries and binder manufacturers alike as solid silicates have excellent potential both for 3D sand printing and to be main-line foundry binder. The introduction of heat resistant 3D printed plastic pattern is also a promising solution to the need of heat resistant patterns where heating is used. One added advantage of such material is the possibility of using it with microwave ovens as most metallic patterns will be useless in microwave hardening process due to the reflection of waves.
6. Conclusions

Search for mold materials for sustainable production will continue for foreseeable future as all manufacturing will continue streamlining for more sustainable practices. Sustainability is a continuous endeavour where every chance should be taken to continuously improve the manufacturing practices. Inorganic binders are deemed to be the most promising foundry binder for sustainable casting and continuous research is required to optimize the process and overcome the challenges. To conclude the dissertation, we reflect on the research questions we began with.

6.1 Reflecting on the Research Questions

RQ1. How do alternative sands perform compared to silica?
All the sands tested achieved good mold strength. The only combination that failed to harden were furan with both type of cerabeads. The permeability did not depend much on different binders, but rather on the sand type and distribution. This could be a good thing for foundries considering a switch to different binders. High permeability is generally considered a good mold property as it allows gases to pass. However, if little gas is generated that provides an opposing pressure to the advancing liquid metal front, molds with low permeability will perform better at preventing penetration. It might be worthwhile to prioritize sands with low density and also to use sands with higher heat diffusivity for heat hardened inorganic binders. The two highest strengths measured in this dissertation were with zircon and chromite with MLS1. Mixture of different aggregates, at different proportions should be a topic of new research. In this dissertation, a mixture of 50% silica and 50% bauxite achieved better surface roughness values with solid silicates compared to 100% silica or 100% bauxite which shows potential of aggregate mixtures in overcoming some challenges.

RQ2. How well do inorganic binders perform compared to organic ones?
Inorganic binders have all demonstrated very good mold strengths, especially with heat hardening. These binders produce very little fumes (low LOI values seen in Publicaion 1 and 2 and low volume of emitted gases in Publication 3) compared to organic ones. Difficulty was experienced in metal pattern release
with heat hardened binders, resulting in mold damage and less than optimal surface of the mold. Especially with solid silicate binders, it was even more difficult as the pattern sticks very hard to the mold. Organic binders produced the best surface finish, but commercially available ester cured sodium silicate (MLS2-E) and geopolymer binder (GP-E) produced results very close to the organic ones. The ester cured inorganic binders approximate the closest the ease of use experienced with self-setting organic binders, which may mean that foundries currently using the self-setting technology will find it easiest to change to ester cured inorganic binder technology. In terms of strength, all the inorganic binders worked quite well with all the different sands tested, at the binder addition rate used in this dissertation, which is a good indication as it gives more choice to the foundries for the sands used. Solid silicates produced very rough castings, the remedy of which is discussed in more detail in Research question 3. Inorganic binders also worked well with alternative sands tested in this dissertation. Operational differences are to be expected which could necessitate use of new tooling, e.g., heat resistant core-box or patterns when heating is involved.

RQ3. Could solid silicates become the norm of sustainable foundry binders?

Solid silicates were shown to have enormous potential to be a sustainable main-line foundry binder as well as simplify 3D printing of sand molds. When in house water is supplied in the foundry, the solid silicate weighs significantly less than the liquid organic/inorganic binders. This makes the transportation and storage of solid silicates much easier. Solid silicates were also tested for storage as a mixture together with silica sand both in close containers and open to air. Some challenges were identified with the use of solid silicates, of them notably is the sticking issue with metal pattern and producing very rough castings. One improvement in surface roughness was achieved through a mixture of 50% silica and 50% bauxite sand. The surface roughness was much better than either all silica mold or all bauxite mold with solid silicates. Other sand or sand mixtures could be investigated as well. Another potential solution was also presented in the form of a heat resistant, additively manufactured plastic pattern which did not have any sticking issue. The pattern release was much easier compared to metal pattern. This pattern material also allows for the microwave heating of solid silicates unlike metal patterns. This can play an enormous role in the reduction of energy consumed through faster and efficient heating. Another thing to note is the fact that, additive manufacturing of sand molds is a patternless process and hence issues related to pattern release could be irrelevant. The additives tested also had some encouraging results in terms of the improvement of the collapsibility of solid silicates. Additives were also found that increase and decrease the strength of the mold, that would aid in achieving the desired strength of the mold.

Penetration was seen at casting trials with solid silicates; however, a lot of improvements were also achieved in numerous ways through the control of pouring temperature and use of coatings. To be a truly more sustainable replacement
of organic binders, inorganic binders have to match reclamation efficiency of the organic binders. Of course, wet reclamation is a potential way of improving reclamation efficiency for inorganic binders. One truly circular process would be if a process of wet reclamation could be developed that would also allow a sizable amount of reclamation of the solid silicate binder.

**RQ4. Statement: Inorganic molding and additive manufacturing assisted hybrid casting.**

Switch to sustainable inorganic binders could be a lengthy process. The solid silicates experimented in this dissertation could simplify the 3D printing of sand molds enormously. However, it is not just about the 3D printing of sand molds, but also that 3D printing could be used for tool making like patterns and core-boxes. The SLA printed pattern presented in this dissertation was tested to a temperature of 160°C, it overcomes the sticking issue of solid silicates to metal patterns, thereby improving the surface roughness of the casts. This pattern also makes it possible to heat inorganic molds using microwave, which could be much faster and more efficient than furnace heating. The dimensional changes were also investigated to a degree, but it remains to be seen how it performs in larger size or over longer cycles of use. This material will also pave the way of non-metallic core boxes, that could be both furnace heated or microwave heated and aid in the heat hardening of inorganic molds. The ability of printing patterns directly from CAD data also enables foundries in digital storage of patterns rather than physical storage, which is particularly helpful for foundries with space constraints and for patterns that are not used regularly.

### 6.2 Recommendations for Further Research

Building on from this dissertation, further tests regarding solid silicates could be to carry out orthogonal test to find out an optimum blend of additives that elevate all the desirable characteristics and diminish the undesired ones. One of the motivations of investigating solid silicates was the fact that it has the potential to simplify 3D printing of sand mold, it is necessary to investigate further the parameters of 3D sand printing with solid silicates, which was not conducted in this dissertation. Apart from the cast and mold quality tests conducted in this dissertation, it is also important to find out the reclamation efficiency of solid silicates. If the reclamation efficiency is very poor and the industry need to mine a lot of virgin sand, then that’s detrimental for overall sustainability of the process. Wet reclamation process is generally known to work well with sodium silicate binders. To that effect it could be worthwhile to research if a process could be developed whereby even the dissolved sodium silicate binder could be reclaimed along with the sand. This would ensure a true circular economy where both the sand and binder could be recycled.

The heat resistant 3D printed plastic pattern presented in this dissertation could potentially solve a transformation hurdle when foundries need to move to heat hardened inorganic binders. The pattern material performed well in the
small size and series tested here, however it must be researched further to see how it performs over large size and long cycle of use. This material combined with microwave hardening could play a role in efficient heat hardening of inorganic binders. This also shows a true potential for additive manufacturing to aid in hybrid casting, not just in the 3D printing of sand molds but also enabling a range of materials suited for patterns and coreboxes.
References


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References


Global push for sustainable manufacturing has intensified the search for alternative molding materials for sand casting. Inorganic binders are making a come back due to their environmental friendliness, and these are deemed to have the most potential to facilitate sustainable sand casting. Of these, the most promising inorganic binder is sodium silicate binder. However, the switch from organic to inorganic binder is not a straightforward matter. Sodium silicate binders could be hardened in different ways, it could exist in both solid and liquid forms, and there are other related binders, e.g., the sodium aluminosilicates (geopolymers). All these different possibilities present unique challenges and foundries considering a switch need more information how inorganic binders compare with organic binders and also how the inorganic binders hardened in different ways, different types and forms affect mold and cast quality.