Limitations and advancements of Sodium Silicate Inorganic Sand Binders; A Review

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Abstract

The use of Sodium Silicate as an inorganic eco-friendly sand binder is escalating. However, due to the inherent limitations the binder poses, it is not widely industrialized except in certain low-melting alloy casting. Curing performance, thermal stability, and moisture resistance are the main limitations currently addressed. This review aims to understand the fundamentals of these limitations and investigate the solutions proposed by researchers. Then we will analyse the applicability of these solutions in the high-tech area of 3D sand printing. From our analysis, we conclude that the curing mechanism is affected by the nature of the process (physical or chemical curing), the hardeners employed, the SiO_2/Na_2O molar ratio, and the pH of the medium. The thermal stability is directly affected by the curing mechanism, the morphology and the type of sand particles, and the presence of additives. Finally, moisture resistance is affected by the curing mechanism and is reduced in high-temperature humid environments and enhanced by promoters. Furthermore, the constraints of 3D sand printing concerning the print head and the recoater reduce our freedom in tackling these limitations.

Keywords: Curing, Crosslinking bridges, Syneresis, Thermal deformation, Hygroscopy

1. Introduction

According to the Environmental Protection Agency, 70% of metals are produced by sand castings. This makes sand casting one of the huge contributors to CO_2 and volatile organic compounds (VOCs) emissions. These emissions are mostly produced by the thermal decomposition of the binders involved. Consequently, efforts have been made to replace organic binders with ecological inorganic alternatives [1,2,3].

The superiority of organic binder resins and the poor environmental standards were the main factors slowing the development of the inorganic sand binders. Unlike inorganic binders, organic ones, mostly petroleum derivatives, are cheap, easy, and faster to apply.

Furthermore, they offer better thermal stability, higher strength, and longer shelf lives. However, inorganic alternatives produce fewer emissions, have better shakeout properties, produce fewer gas-related defects and have lower cleaning and filtering costs [4].

One of these promising inorganic binders is Sodium Silicate which bears the advantages of the availability and the low cost of raw materials [5]. However, silicate chemistry is complex but inevitable for the development of the binder [6]. Consequently, our aim in this paper is to understand the science behind the main limitations: curing performance, thermal stability, and moisture resistance. Then, we will identify the solutions proposed for each limitation and the compatibility of their use in the advanced field of 3D sand printing.

2. Limitations

2.1 Curing performance

Curing is the hardening process of the sand binder system that gives the mold the required strength. Before curing, the sand binder system has only the

green strength that gives the mold its required shape but not enough for the stresses developed during the casting process. Sodium Silicate curing involves polymerizing the polysilicic acid to form silica gel and give the sand binder system the hardness and strength required. Curing techniques include no-bake, cold box, and hot box systems. The no-bake and cold box systems are considered chemical curing means, while the hot box is considered physical curing.

The polymerization of the polysilicic acid is done by a condensation reaction within the silicic molecule where two hydroxide groups (Si-OH) condense giving off water and the Si-O-Si siloxane linkage. The process starts by adding Sodium Silicate $Na_2O.SiO_2$ to water. Depending on the molar ratio, SiO_2:Na_2O, the solution either contains soluble silica ($Si(OH)_4$) and silicate monomers (ratio 1:1 to 1:2) or three-dimensional particles with anhydrous silica in the internal structure and silanol (Si-OH) bonds at the surface, as shown in Fig. 1.a and 1.b. These particles are in equilibrium with the soluble silica monomer and form the nuclei for condensation polymerization into spherical particles as shown in Fig. 1.c and 1.d.
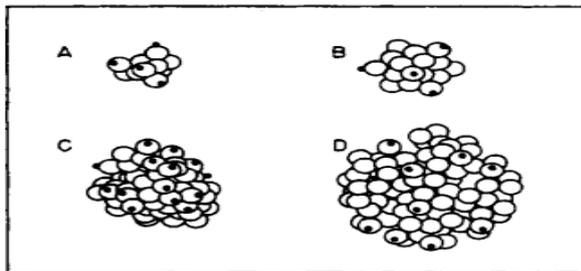

Fig. 1 Nucleation of the condensed colloids C and D from their silicic acids A and B according to R. K. Iler [8].
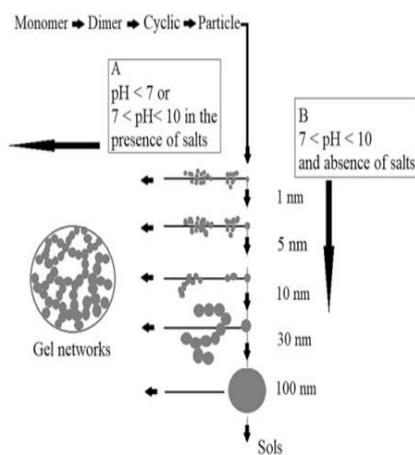

Fig. 2 Difference between chain growth and particle growth in acidic and alkaline media according to R. K. Iler [8].

The size and diameter of those spheres are highly pH dependent and their aggregation form chain-like gel networks. As shown in Fig. 2, the outcome of the condensation reaction is the growth of soluble silicates that bear a negative charge at basic pH values, pH > 7. On the other hand, when the pH is acidic, 5 < pH < 6, the particles become nearly neutral and agglomerate and precipitate in the form of gel networks. This hydrated gel has low strength that increases with water dehydration through a process called syneresis [5,6,7,8].

In addition to the pH value, hydrochloric acid, sodium hydroxide, and anions like Flouride decrease the polymerization rate due to the complex structure they form $(SiF_6)^{-2}$. Owusu also determined that the gelation rate is related to the water content, where lower content signifies faster gelation and causes the mold to become weak [5,6,7].

2.1.1 Cold box curing using pH change through CO_2 gas

The CO_2 gas flux causes a decrease in the pH of the sand resin system and the precipitation of silica gel that binds the coated sand particles together. The reaction between the Sodium Silicate solution and the Carbon Dioxide gas results in the formation of hydrated Silica gel polymer and Sodium Carbonate solution according to equation 1.a. As Owusu indicates, the formed Sodium Carbonate is the most effective hardener for CO_2 curing process with a less significant effect from the Silica gel polymerization. However, the basis of the Sodium Carbonate effect is not clearly stated in the literature.

2.1.2 Hotbox curing through thermal dehydration

As implied by its name, the Hotbox technique uses heat from hot air or microwaves to dehydrate the Sodium Silicate Solution, as in equation 1.b. The difference between this and the cold box technique is in the nature of the resulting silica gel which is hydrated in the cold box and semi- or dehydrated in the hot box technique. Furthermore, the Sodium Carbonate is not formed in the hot box technique.

Wallenhorst states that initially after thermal activation, particle growth and the formation of sol structures take place in the mold material mixture according to reaction path B in Fig. 2. Depending on the reaction temperature, either predominantly homogeneous network structures or structures with defects can be built up in this step. The number of defects has a direct effect on the other application properties, such as storage stability and moisture

resistance. This agrees with Owusu who stated that the rate of condensation polymerization is directly related to the rate of water loss which is directly related to the dehydration temperature. As stated in Fig. 3, the strength increases till the first peak at around 315°C is attributed to the loss of free water. The decrease after that is due to the evaporation of crystallographic-bound water which decreases the strength. This also helps in analyzing the flexural strength graph because the rate of water loss is the highest in the case of using microwaves which reflects the high strength of their cured molds.

To analyze the efficiency of both curing techniques, we need to compare the strength of the resulting bonding: the siloxane Si-O-Si linkage, the Sodium Carbonate bond, and the hydrogel bond. Out of the three bindings, the siloxane bond is the strongest and is the only dominant in the hot box technology which signifies the higher strength of the hot-cured sand molds. This result is also emphasized by Jelínek who measured the flexural strength of the molds cured by different techniques as shown in Fig. 4 [6,9,10].
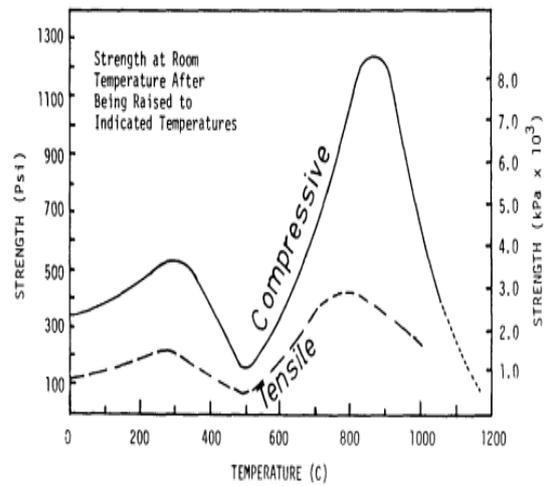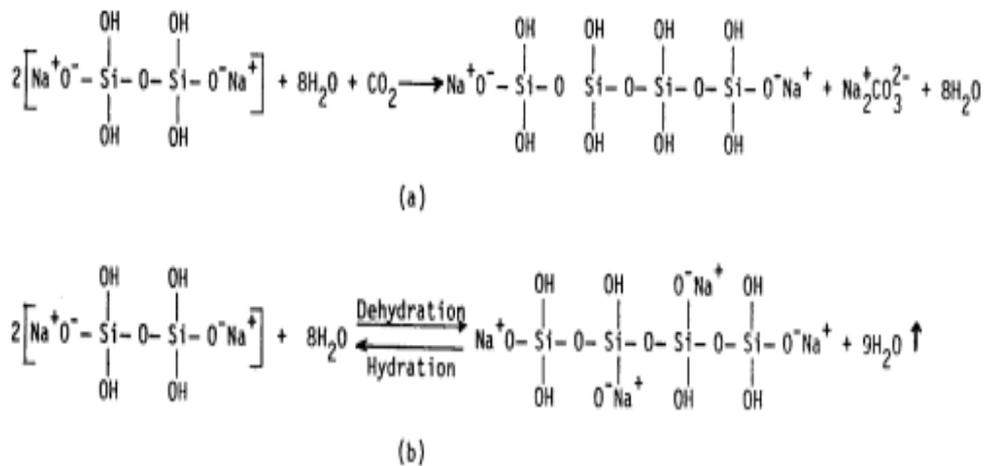

Fig. 3 Temperature effect on the Sodium Silicate bond strength according to Y. A. Owusu [6].

Eq. 1 Ionic Sodium Silicate reactions by (a) CO_2 gasification, (b) physical dehydration according to Y. A. Owusu [6].
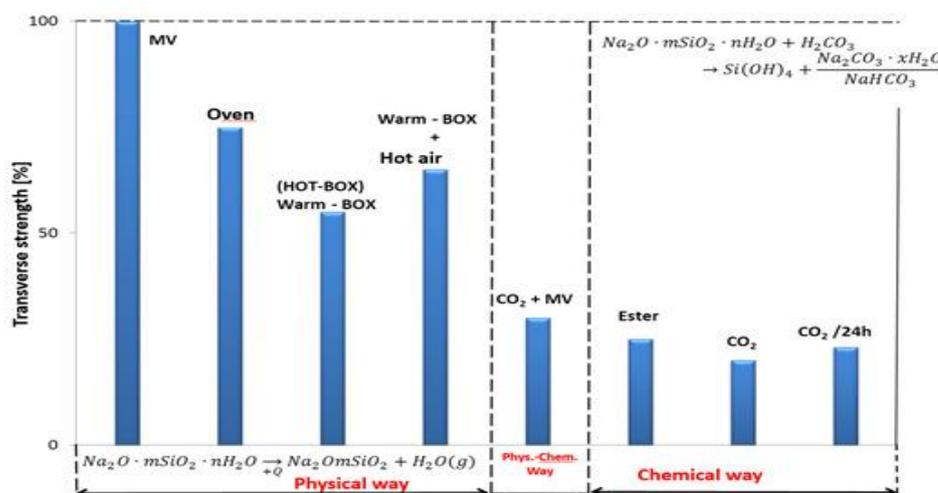
Fig. 4 Different transverse strengths for the different curing mechanisms according to P. Jelínek [10].
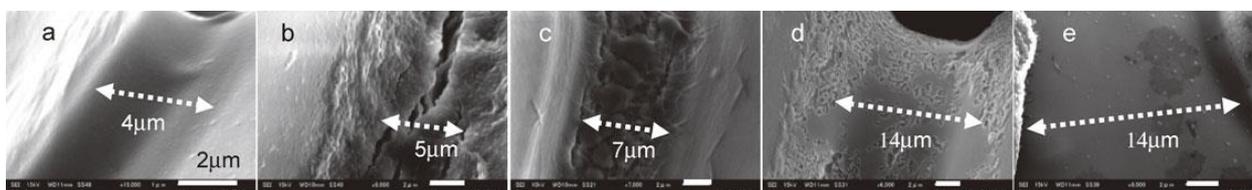

Fig. 5 Length and morphology changes of the crosslinked bridges at (a) unheated, and heated to (b) 1200C, (c) 3000C, (d) 4000C, (e) 5000C according to K. Kosuge et al. [12].

2.2 Thermal Stability

Thermal stability or thermal resistance is the ability of the mold to resist any deformation at high casting temperatures. Thermal stability does not necessarily mean the failure of the mold. The mold is designed with specific dimensions that directly affect the rejection of the product. One limitation that hinders the use of Sodium Silicate binders is their thermoplastic deformation. In the rest of this section, we are handling the heating transformations and how they affect the mechanical characteristics of the binder.

As stated in Fig. 4, which relates the temperature to the strength, the strength first increases by the dehydration of physical water. At around 315ºC, the chemical-bound water starts to dehydrate which decreases the bond strength. From 450ºC to 550ºC, the gel transforms into liquid. Beyond this temperature till 982^{0}C, glass formation occurs which has high viscosity and strength. However, the fall of strength beyond 800ºC is attributed to the formation of the liquid phase. This result is in strong agreement with the ASK Chemicals report on the advancements in inorganic binder systems which measured the heat resistance using heating microscopy. They recorded 778ºC as the softening temperature of the non-optimized sample versus 1310ºC for the thermally optimized one. The problem as stated in the report is that the softening or the plastic deformation of the mold causes deformations in the products along with poor surface and dimensional qualities [6,11].

Kosuge et al. investigated the collapse mechanism of the Sodium Silicate bond using SEM, Fig. 5. From the above SEM images, we can conclude that like the previous analysis, the crosslinked bridge between the sand particles was not homogenized till 400^{0}C (Fig. 5.d), where the dehydration occurs, but the gel is not yet transformed to liquid or glass. However, at 600^{0}C (Fig. 5.e), the glass phase is formed and causes homogenization in the crosslinking bridge. Furthermore, the length of the bridge increased from 4μm at the unheated state (Fig. 5.a) to 14μm at 600^{0}C (Fig. 5.e) [12].

Despite the agreement between these different studies, one thing is not clearly stated in the literature. As Owusu stated, the silica gel transforms to liquid between 450ºC and 550ºC before forming the glass state. The second liquid transformation occurs at a higher temperature. The softening temperature was detected to be 778ºC, which is at the second liquid transformation. This raises the question of the significance of the first softening temperature, the first liquid transformation, and whether there is another

mechanism that prevents the deformation of the mold at this temperature?

2.3 Moisture resistance

The short shelf life is a prominent limitation facing silicate bonded molds. The main reason for this short life is the depolymerization, hydrolysis, of the silica gel. The mechanism of the reverse hydration reaction starts by breaking the electrostatic bond between the sodium ion and silicon hydroxyl (silanol group), hydrating the Na+ ion (equation 2). Then, the water molecule attacks the siloxane, Si-O-Si, linkage (where O was previously bound to the Na^+ ion) causing the hydration of the siloxane linkage into two separate silicon hydroxyls according to the reactions of equation 3.
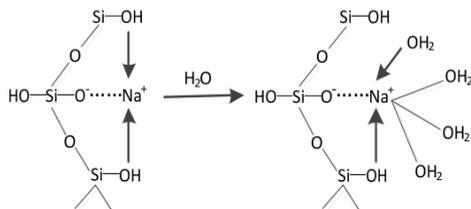
Eq. 2 Sodium ions hydration according to L. Tang [13].
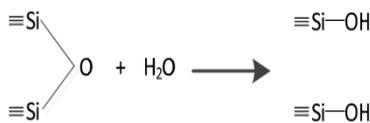
Eq. 3 Siloxane linkage hydration according to L. Tang [13].

The rate of this hydration reaction is strongly related to the mechanism of curing where the rate is higher in the case of the physically cured, thermal dehydrated mold, than the chemically cured, CO^2, mold. The reverse reaction is faster whereas Le Chatelier's principle in the first reaction states that water addition will favor the reverse reaction. Furthermore, the concentration of the siloxane linkages, where hydration occurs, is higher in the case of physically dehydrated mold. Moreover, the presence of chemical species, Sodium Carbonate, lowers the effect of water polarization and diffusion [6,13].

To sum up, even though physical dehydration imparts higher strength in the mold, it makes it more vulnerable to moisture. Consequently, research has been done to use the CO^2 / microwave curing

mechanisms by controlling air temperature, blowing time, microwave power, and heating time. This resulted in a 15.7% decrease in water absorption when the mold is tested at 83% relative humidity level for 24 hours. Another proposed solution was the utilization of additives that reduce the number of hydrophilic groups within the binder. Sond et al. identified that adding micro silica, polyvinyl alcohol solution, borax, and an agent called B agent in the ratio of 25: 20: 2: 1 increased the tensile strength more than four times (1.19 MPa vs 0.27 MPa) when tested after 4 hours in 90% relative humidity [13,14].

Another important limitation of the inorganic binders is the difficulty in applying water-based refractory coatings that are highly required especially for ferrous castings. The melting points of silica and iron are near which causes deformations and metal penetrations in the final product. However, the application of water-based coatings is hindered by the hygroscopic nature of the inorganic binder where the reverse dehydration will cause the strength of the mold to decrease especially when drying the coating because of the high temperature and humidity levels as Fig. 6 illustrates [11, 15, 16].
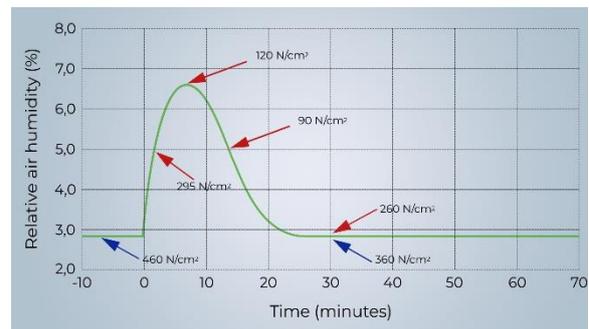

Fig. 6 Mold strength during furnace drying according to ASK Chemicals [11].

3. Application in 3D Sand printing

3D sand printing is a promising mold manufacturing technique, especially for complex designs. It poses a higher dimensional accuracy than conventional techniques. Furthermore, it reduces the lead times used for making patterns significantly. Furthermore, this assisted rapid manufacturing technique utilizes the advantages of additive manufacturing along with the advantages of sand casting as the high mechanical strength and the relatively low residual stresses.

In this review, we are focusing on the binder jet 3D sand printing using Sodium Silicate. As shown in Fig. 7, binder Jetting is done by forming layers of the powder material having a specific thickness using a recoater. After that, the fluid is applied through the

print head to bind the powder particles. After that, the powder is recoated again on top of the previously bonded layer by lowering the job box, and the process continues till the 3D structure is obtained [17,18].
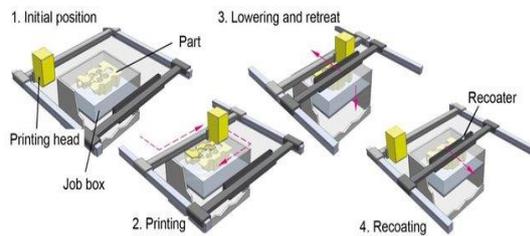

Fig. 7 Binder jetting 3D sand printing according to Ramakrishnan et al. [19]

The binder jetting process is affected by powder, binder, and process parameters. In this section, we are investigating the binder parameters and will relate these parameters to the Sodium Silicate binder system. However, there is a problem hindering the clear analysis. The problem is that there is no universal technique for introducing the binder to the system. In certain research, the dry binder powder was mixed with the sand powder to form the powder bed before the application of liquid hardener through the printing head. In other research, the sand powder was wetted with a sodium silicate solution and then dried before the application of the hardener from the printing head. A third technique involves dissolving the binder and ejecting the binding solution by the printing head on the sand powder bed. The problem is that each of these techniques has parameters that make it very hard to reach a conclusion that works for all of them. For instance, the wetting mechanism is different in each technique which results in different binder powder interactions causing different flexural strengths. Anwar et al. showed that liquid silicate binders generally have higher bending strengths than solid hydrated silicates. Furthermore, the surface roughness of the resulting molds is larger for molds hardened with solid silicates. However, they offer higher shelf life and moisture resistance than the molds binded with liquid silicates. Consequently, we can conclude that due to this variability in the initial binders form, there will be a disparity in the input parameters and hence in the output performance [18,19,20,21,22].

Despite the used technique, 3D sand printing poses restrictions that might hinder or at least limit tackling the challenges. For instance, the addition of ultrafine or nanoparticles as promoters is challenging because either adding them to the liquid binder in the printing head or mixing them with the powder in the recoater is not easy. For the print head, the nozzle is easily clogged by the agglomeration of the particles while the

problem in recoating the particles is that particles with different sizes travel different distances which cause a variation in concentrations within the mold depending on the recoater motion [18,23].

The previous discussion was analyzing the solid additives or promoters. Furthermore, the liquid additives must adhere to the limits of the printer used. One characteristic that should be considered is the viscosity of the binder and its surface tension. These factors are collectively evaluated using the Ohnesorge number (Oh) according to the following equation:

$$Oh = \frac{\mu}{\sqrt{\rho \sigma d}} = \frac{\sqrt{We}}{Re} = \frac{1}{Z}$$

- μ is the liquid dynamic viscosity
- σ is the surface tension
- ρ is the liquid density
- d is the droplet diameter
- We is the Weber number used for surface tension measurements
- Re is the Reynolds number used for viscosity measurements

Derby and Reis identified the $1 < Z < 10$ to be the values suitable for liquid binder jetting, Fig. 8.A. Their results are close to those of Pyeon et al. who identified the suitable range as $2.70 < Z < 15.09$. Values lower than this range is dominated by the viscous forces which require higher pressure than the printhead can provide while values above the range cause the formation of droplet tails which forms satellites that reduce the quality of the mold as shown in Fig. 8.B. To give the reader an estimate of this limiting range, we will compare the dynamic viscosity of the liquid binder used by Pyeon et al. which was 59.16 cP for the 50% solid content solution to that of Song et al. who modified Sodium Silicate solution using KOH, glucose, and sorbitol to reach a viscosity of 450 cP for the conventionally modified solution. This estimates how much dilution is required for the conventionally modified Sodium Silicate solution which means that lower binder content will be used, and this will consequently reduce the strength [20,24 ,25].
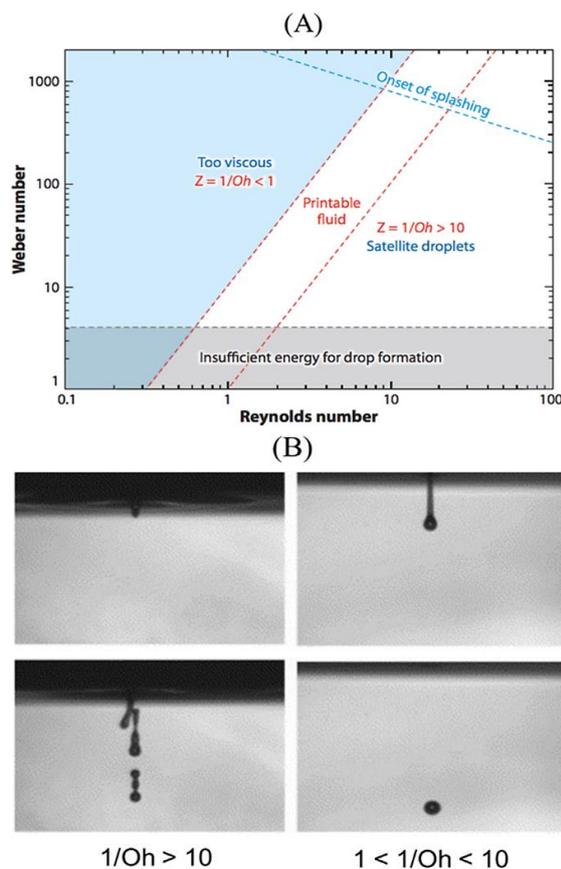
Fig. 8 (A) Jet table region for fluids, **(B)** ejection images of suspensions showing the effect of the ratio of (1/Oh) according to Mostafaei et al. [18]

4. Conclusions

The use of inorganic binders in sand castings is inevitable if we need to meet ecological standards. However, their use is challenging due to the limitations they possess. The limitations discussed in this review are the curing performance, thermal stability, and moisture resistance. Through our analysis we found that:

- There is a high interdependence between the limitations where the physical curing imparts better mechanical behaviour but poorer moisture resistance than the chemical curing.

- Furthermore, the thermal stability is lower compared to the organic alternatives. The softening temperature at 778^0C limits the use of sodium silicate in Aluminium castings (without optimization).

- It is very hard to use water-based coating with Sodium Silicate binders due to its poor moisture resistance. These coatings are inevitable for ferrous castings.

- One promising solution for increasing the bonding strength, delaying binder softening, and improving moisture resistance is the use of different promoters. However, promoters use is more restricted in 3D sand printing.

- In addition to the inherent binder limitations, 3D sand printing imposes further restrictions. The physical characteristics of the binder and its additives must adhere to the print head and recoater limitations which may hinder limitations tackling.

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