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Research, application and development of inorganic binder for casting process

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Abstract: Inorganic binder used in casting process has the advantages of low odor, labor-friendly conditions, and relatively low cost, which is one of the main development directions for casting molding materials in the future. However, compared to organic binders (such as resin binders), inorganic binders exhibit lower bonding strength and are more sensitive to environmental humidity. This sensitivity poses challenges, particularly in the reclamation of used sand, thus limiting their broader application. In this paper, the research and application status of inorganic binders (mainly silicate inorganic binders) and their curing methods are summarized. In addition, the research and application of phosphate inorganic binders and 3D printing inorganic binders that are being developed are introduced. Meanwhile, a detailed comparative analysis is conducted on the challenging issue of "reclamation for used sand" in the application of inorganic binders. Finally, the development direction of inorganic binders is clarified.

Keywords: inorganic binder; silicate system; phosphate system; 3D printing; used sand reclamation; development trend

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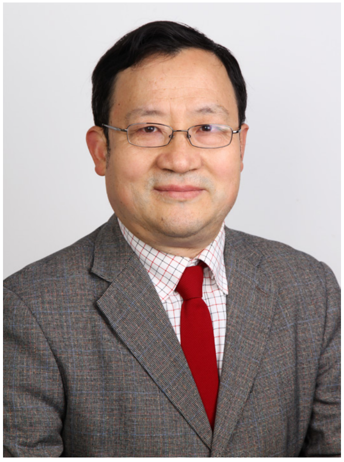

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1 Introduction

Sand casting is the primary casting process for the manufacturing of castings such as steel, iron, and non-ferrous metals, accounting for approximately 70%–80% of the total castings output [1-3]. Binders play a crucial role in the sand casting process, serving to bond the raw sand or reclaimed sand through a curing method to form the sand mold or sand core. According to their type and application, sand casting process can be classified into clay green sand mold process, resin organic binder sand mold process, and silicate inorganic binder sand mold process [4-6].

The clay green sand casting process is characterized by low material cost, simple process, and short production cycle. It is widely used in the production of iron castings and small steel castings [7-8]. In the 1940s, resin binder was introduced into the foundry industry and has rapidly developed due to its high strength, excellent surface quality of the sand mold (core), and good reclamation performance of used sand, which are widely used in the production of steel, iron, and non-ferrous metal castings [9-10]. Besides, the silicate inorganic binder sand process began to be applied in the 1950s and has received widespread attention due to its low cost, minimal odor, labor-friendly conditions, and simple operation, which is mainly used in the fabrication of steel castings [11, 12].

During the organic binder (resin) sand casting process, the mixing, molding, and core making stages generate irritating and harmful gases, thereby polluting the environment and posing health risks to foundry workers. As environmental regulations become increasingly stringent, foundries are under pressure to enhance the development and adoption of environmentally friendly inorganic binder sand casting technology. Particularly, there is a focus on improving and refining silicate inorganic binders with the aim of replacing the organic binder with more environmentally sustainable alternatives [13-15].

The development of silicate inorganic binder has generally undergone four stages: CO_2 cured sodium silicate sand process, powder cured sodium silicate sand process, ester cured sodium silicate sand process, and new silicate inorganic binder sand process [1]. Currently, the CO_2 cured sodium silicate sand process and the ester cured sodium silicate sand process are mainly used in the production of steel castings, while the new silicate inorganic binder sand process is mainly applied in aluminum alloy castings [16, 17].

In recent years, researchers have studied the application of phosphate inorganic binder sand process due to its excellent properties and application potential [18]. Similarly, the development and application of inorganic binders for 3D printing has become a research hotspot, aiming to replace the currently mature organic binders such as furan resin and phenolic resin [18].

At present, silicate inorganic binders remain the most successful environmentally friendly binders applied in sand casting process. This paper focuses on the research and application status of silicate inorganic binders and their curing methods, while also summarizing the progress in research and application of phosphate inorganic binders and 3D printing inorganic binders. Additionally, the reclamation of used sand, which is the key challenge of inorganic binder sand, is compared and analyzed. Finally, the future development direction of inorganic binders for casting process is discussed.

2 Silicate system inorganic binder

Currently, the inorganic binders used in the foundry industry mainly refer to sodium silicate binders [1]. According to different curing methods and a wide range of applications, silicate inorganic binders have undergone four development stages, as shown in Fig. 1. Among them, CO_2 cured sodium silicate sand process and ester cured sodium silicate sand process are mainly used in the manufacturing of steel castings in industries such as railway, shipbuilding, and engineering machinery. However, the new silicate inorganic binder sand process cannot withstand high temperatures and is mainly used for aluminum alloy casting.

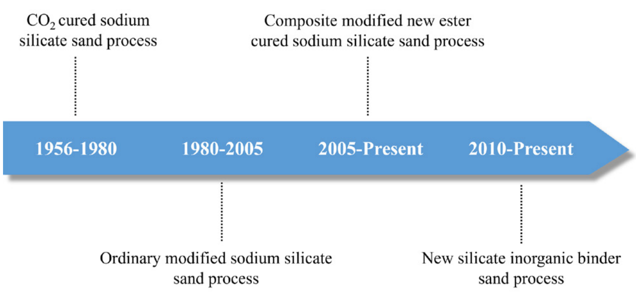


Fig. 1: Development of silicate inorganic binder

2.1 CO_2 cured sodium silicate sand process

2.1.1 Development of CO_2 cured sodium silicate sand

The CO_2 cured sodium silicate sand process involves blowing CO_2 gas into the sodium silicate sand to harden the sodium silicate binder, thereby achieving the bonding strength. This process has the characteristics of rapid curing speed, short production cycle, and high efficiency, and is widely adopted in the manufacturing of steel castings.

However, the problems of the conventional CO_2 cured sodium silicate sand process are also obvious, such as a high dosage of sodium silicate binder (6.0%–8.0%), poor collapsibility of the molding sand, and difficulty in used sand reclamation. In order to address these challenges, in 1982, Japanese researcher Kobayashi Kazunori invented a vacuum replacement hardening process (VRH method), which reduced the sodium silicate content to 3.0%–4.0%, improved the collapsibility property, enabled the dry reclamation of used sand, and decreased CO_2 gas consumption by 1/2–2/3 [1]. In addition, researchers have also made significant efforts in improving the blowing process and collapsibility of CO_2 cured sodium silicate sand. For example, the air-diluted CO_2 hardening (mixed gas of "10% CO_2+90% air"), heated CO_2 hardening (heating CO_2 gas to 30 °C–60 °C), pulsed CO_2 hardening, adding collapsing agent into the molding (core) sand, and utilizing modified sodium silicate binders [1, 19]. These techniques are considered improvements to the CO_2 cured sodium silicate sand process, and both conventional and improved CO_2 cured sodium silicate sand processes are collectively referred to as the "first-generation sodium silicate sand process".

2.1.2 Application of CO_2 cured sodium silicate sand

Since the 1960s, the CO_2 cured sodium silicate sand process has been widely used in the production of steel castings across various industries including metallurgy, mining, rail transportation, engineering machinery, coal mining machinery, pumps, and valves.

The ratio and properties of traditional CO_2 cured sodium silicate sand are listed in Table 1 [1]. Due to the use of ordinary sodium silicate binder, a high dosage of sodium silicate (6%–8%) is required during the application process, resulting in poor collapsibility of the molding sand, difficulty in cleaning of castings, poor reusability of reclaimed sand, and large discharge of used sand.

In the early 21st century, with in-depth research in the structure and curing mechanism of sodium silicate binders, new modified sodium silicate binder gradually replaced traditional sodium silicate binder, and combined with improved air blowing technology, a new CO_2 cured sodium silicate sand process was developed. For example, the new RC series modified sodium silicate sand, the K220 series modified sodium silicate sand, the Qiangli 2000 multi-modified sodium silicate sand, the Solosil-433 modified sodium silicate sand, and the organically modified sodium silicate sand [1, 20-25]. These new CO_2 cured sodium silicate sand processes reduced

Table 1: Ratio and properties of traditional CO_2 hardened sodium silicate sand [1]

Molding sand formula (mass ratio, %)					Compression strength (MPa)	Application
New sand		Sodium silicate	Bentonite or kaolin	Water		
Particle size	Content					
–	100	8–9	4–5	4–5	>1.5	Surface sand for large steel castings
40/70	100	6.5–7.5	–	4.5–5.5	–	Steel casting mold (core) sand
–	100	7	3	4.5–5.5	>1.0	
50/100	100	4–4.5	–	<3.5	>1.0	
40/70	100	5	–	–	>1.3	

the dosage of sodium silicate binder (4%–5%) and improved the collapsibility of the molding sand and the regenerability of used sand.

Currently, the ordinary CO_2 cured sodium silicate sand process still has a large application market in the production of steel castings due to its simple process operation, low cost, rapid hardening speed, and strong adaptability. However, with increasingly strict environmental requirements, the adoption of new CO_2 cured sodium silicate sand processes, such as modified sodium silicate binder combined with gas-blowing processes like pulse method and heating method, further reduces the dosage of sodium silicate (<3%), and improves the bonding strength and heat collapsibility. This is expected to be the development trend of the CO_2 cured sodium silicate sand process.

2.2 Ester cured sodium silicate sand process

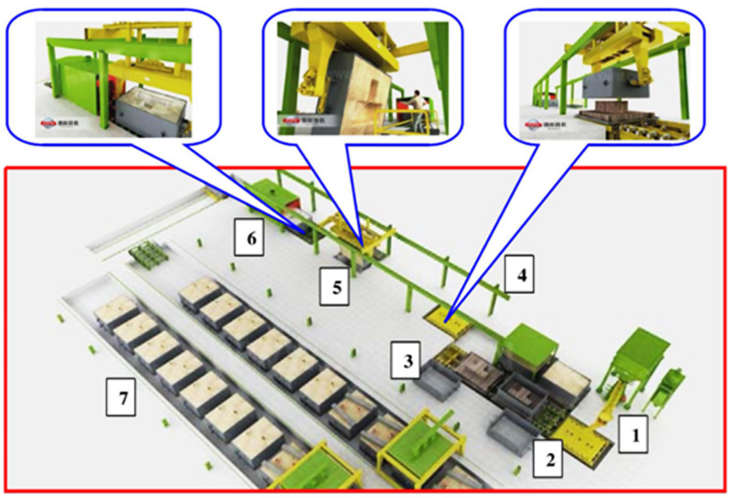
2.2.1 Development of ester cured sodium silicate sand

The ester cured sodium silicate sand process, recognized as the second-generation sodium silicate sand process, originated in the early 1970s in the United States and gradually gained popularity in China after the 1990s [1]. Ester cured sodium silicate sand has the comprehensive advantages of sodium silicate sand and resin self-hardening sand, such as high bonding strength, adjustable curing speed, convenient operation, good working environment. Furthermore, the dosage of sodium silicate binder can be decreased to 3.5%–4.5%. The schematic diagram of ester cured sodium silicate sand process production line is shown in Fig. 2.

For the ordinary ester cured sodium silicate sand process, the amount of binder added is relatively high, and the curing hardening performance and permeability of the molding sand are generally significantly affected by the ambient humidity and temperature. The collapsibility of the molding sand needs to be improved, and the dry reclamation rate of used sand is relatively low (approximately 50%–60%).

In response to the persistent challenges faced by the sodium silicate sand process, particularly in terms of poor collapsibility and reclamation properties, Chinese foundry workers have conducted extensive research on the modification technology of ester cured sodium silicate based on the actual production needs of railway thin-walled steel castings, such as bolsters, side frames, couplers. As a result, significant enhancements have been achieved in the bonding strength of modified sodium silicate sand, accompanied by a further reduction in the dosage of binder to less than 3.0% [1]. This improvement greatly enhanced the collapsibility and reclamation capabilities of used sand. Particularly noteworthy is the use of ultra-low modulus sodium silicate (with M=1.5–1.9), which has significantly extended the working time of dry reclaimed sand, effectively enabling the recycling of reclaimed sand as a single sand source through the dry reclamation method.

For example, Huazhong University of Science and Technology has developed the DFH series sodium silicate modifiers [1]. By incorporating 10%–15% of DFH modifiers into ordinary sodium silicate binders with varying modulus and concentrations, different modified sodium silicate variants with exceptional properties can be achieved. Moreover,



1. Continuous sand mixer; 2. Vibrating compaction machine; 3. Transfer trolley; 4. Mold taking station; 5. Flip flow coating station; 6. Drying oven; 7. Pouring roller conveyor

Fig. 2: Schematic diagram of ester cured sodium silicate sand process production line [26]

Shenyang Huiyatong Foundry Materials Co., Ltd. uses organic and inorganic composite modifiers to enhance the sodium silicate binder, resulting in the creation of a range of new modified sodium silicate products along with matching organic ester hardeners. These products feature a low sodium silicate addition (1.8%–3.0%) and achieve a high used sand recycling rate (about 80%) through the dry reclamation method [27, 28].

The ester-cured modified sodium silicate sand process, along with its associated materials and equipment, has gained widespread adoption in China. It is considered the second major breakthrough in the development of sodium silicate sand technology since the invention of CO_2 sodium silicate sand technology. It represents an important contribution of Chinese foundry workers to the advancement of sodium silicate sand technology. Ester cured modified sodium silicate sand not only overcomes the shortcomings of high cost, strong odors, and poor working conditions of resin self-hardening sand, but also retains the advantages of resin self-hardening sand. Moreover, it has basically overcome the shortcomings of high dosage, poor collapsibility, and low reclamation rate of ordinary sodium silicate sand, thus achieving the recycling of sodium silicate used sand.

2.2.2 Performance and application of ester cured sodium silicate sand

The new ester cured modified sodium silicate sand process has been widely adopted in China. Table 2 shows the performance of new ester cured sodium silicate sand under different temperatures and humidities [1].

A coal machinery manufacturing company utilized the new ester cured sodium silicate sand process to produce steel castings for coal machinery, mining, engineering machinery, etc [25]. The dosage of modified sodium silicate binder was 2%, and the organic ester curing agent was 0.3%–0.4%. The working time of the sodium silicate sand was around 15 min, and the demolding time was 45–70 min. The 24 h tensile strength was greater than 0.4 MPa. Similarly, a valve casting production company employed the new ester cured sodium silicate sand process to manufacture valve steel castings. The addition of modified sodium silicate was 2.8%–3.0%, and the organic ester curing agent was 0.45%–0.55%. The working time of the sodium silicate sand was approximately 5 min, and the demolding time was around 45 min. The 24 h tensile strength was 0.4–0.6 MPa [25]. Figure 3 illustrates the pictures of typical steel castings produced by new ester cured sodium silicate sand process.

At present, the new ester cured sodium silicate sand process is gradually replacing ordinary sodium silicate sand process and part of resin self-hardening sand process in the actual production of steel castings for industries such as metallurgy and mining machinery, rail transit, engineering machinery, coal mining machinery, and pump valves, etc. With the continuous improvement of this process, as well as the technical and equipment levels of modified sodium silicate materials, the new ester cured sodium silicate sand process has become the preferred technology for the production of steel castings.

2.3 New silicate inorganic binder sand for aluminum alloy

2.3.1 Development of new silicate inorganic binder sand

At the beginning of the 21st century, German company HA developed the Cordis system inorganic binder, and the ASK company invented the INOTEC system inorganic binders, which are both suitable for aluminum alloy castings [18]. This process uses a modified alkaline silicate binder (1.8%–2.5%, based on sand weight) and a metal oxide powder (approximately 50%, based on binder weight), and it is cured under hot air (150 °C–200 °C) conditions. Figure 4 shows the comparative results of tar content and harmful gas emissions in the core making process [25]. It can be seen that inorganic binder does not contain tar condensate and has no benzene emissions. Due to the absence of organic components, the use of the INOTEC system binder does not result in the buildup of condensate, which in turn reduces the amount of cleaning involved. Investment in air treatment measures is also saved, making INOTEC a cost-effective alternative. Figure 5 shows the comparison of glass tube cleanliness between cold box and INOTEC inorganic process, and Table 3 lists the performance comparison of cold box and INOTEC process [29].

Table 2: Performance of new ester cured sodium silicate sand under different temperatures and humidities

Molding sand formula (mass ratio, %)			Environmental conditions		Compressive strength (MPa)		
Sodium silicate	Hardener	Raw sand	Temperature (°C)	Humidity (%)	1 h	6 h	24 h
3.0	0.3 fast ester	100 (Yueyang sand)	15	87	0.26	1.13	1.78
3.0	0.3 fast ester		8	85	0.8	0.69	1.45
3.0	0.3 medium ester	100 (Duchang sand)	16	87	0.64	1.89	2.52
3.0	0.3 medium ester		16	85	0.56	1.52	1.81
3.0	0.3 medium ester	100 (Haicheng sand)	8	85	0.07	0.72	1.45
3.0	0.3 medium ester		18	93	0.61	1.62	1.88
3.0	0.3 slow ester		28	92	0.68	1.72	1.83

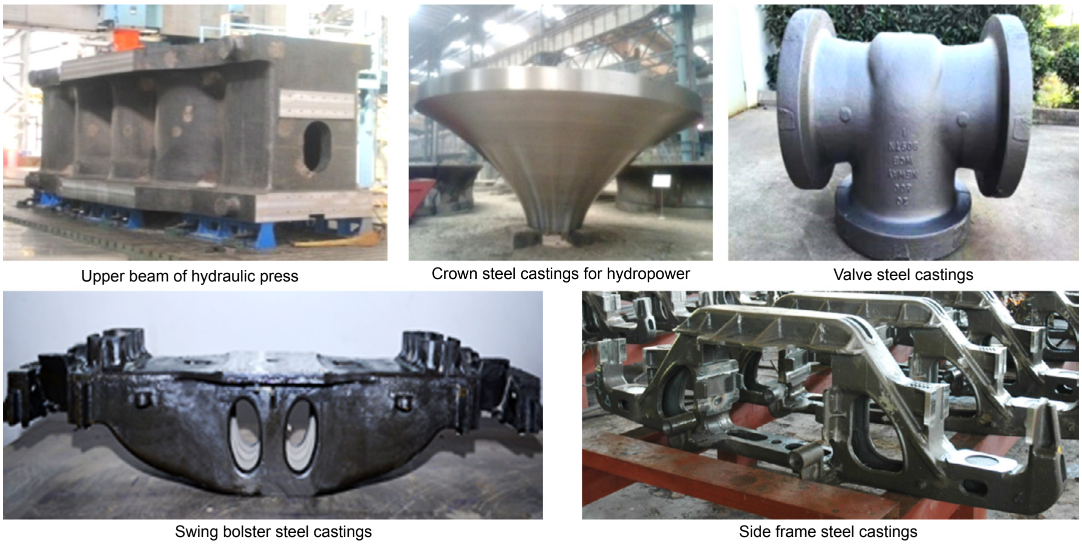


Fig. 3: Pictures of typical steel castings produced by new ester cured sodium silicate sand process [25]

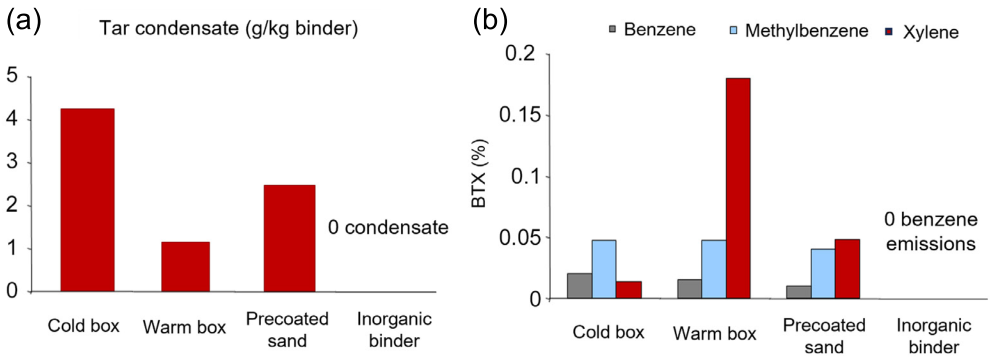


Fig. 4: Comparative results of tar content and harmful gas emissions in the core making process [25]

Fig. 5: Comparison of glass tube cleanliness between cold box and INOTEC inorganic process [29]

Table 3: Performance comparison of cold box and INOTEC process [29]

Casting performance	Cold box	INOTEC
Solidification time (min)	6	5.5
Mold reusability without cleaning (times)	15	257
Cleaning time required within 24 hours (min)	320	20
Cast part output (unit/h)	7.8	10.8

The new silicate inorganic binder sand process was first applied to the core making for automotive aluminum alloy castings. German companies Volkswagen and Daimler adopted the Cordis system binder, while BMW adopted the INOTEC system binder products from ASK company. These products completely replace the traditional organic cold box and warm box process. After verification by three companies, this process has been proven to be competitive in terms of casting quality, production efficiency, and sand shakeout performance compared to the traditional methods. Therefore, it has been rapidly adopted in mass production of automotive aluminum alloy castings.

In 2010, HA China company pioneered the introduction of Cordis series inorganic binders and collaborated with China FAW to manufacture complex cylinder head water jacket cores on the inorganic shooting core machine produced by Laempe Company. This was successfully applied in the production of aluminum alloy cylinder heads. In 2013, the INOTEC system inorganic binder also began to enter China. The successful application of inorganic binder process in the production of automobile aluminum alloy castings has great social benefits and economic value in reducing pollution and achieving green production in the foundry industry and has a good application prospect.

In the past decade, Chinese foundry material manufacturers and research institutions have successively developed various new silicate inorganic binder materials based on modified sodium silicate and conducted production trials. They have achieved good results in several areas, including the inorganic binder warm box process, composite blow air cold box process, and inorganic coated sand process [30, 31].

2.3.2 Application of new silicate inorganic binder sand

The new silicate inorganic binder sand process is mainly used in the production of aluminum alloy castings such as automobile cylinder blocks and cylinder heads. In 2010, this process was introduced to China for the fabrication of automotive aluminum alloy cylinder blocks, cylinder heads, and motor casing castings.

In 2017, a joint venture in Shanghai used HA company's Cordis series inorganic binder process to produce sand core for manufacturing aluminum alloy cylinder heads. This resulted in a casting yield rate exceeding 97%, thereby attaining the standards of cold core technology. Additionally, the factory accomplished zero emissions of sand core casting process, and the relevant production process data are delineated in Table 4 [25].

In 2018, an automotive parts enterprise in Jiangsu adopted a new silicate inorganic binder sand process to prepare sand core for producing motor shell castings, as shown in Fig. 6 [25]. The sand core weighed 1.5 kg, with a thin-wall section measuring 3.5 mm, and achieved a casting yield exceeding 90%. Currently, the new silicate inorganic binder process can replace the traditional cold box and hot box processes in the field of automotive aluminum alloy castings, with a certain improvement in product quality [25].

Since 2012, Chongqing Changjiang Materials Company has developed a new silicate binder sand process. This process uses a modified sodium silicate binder (1.8%–3.0%, based on sand weight) and an inorganic powder reinforcement agent (35%–50%, based on binder weight). It cures under hot air (130 °C–180 °C), which is known as the inorganic coated sand process. At present, this process has been applied in the production of automotive subframe aluminum alloys and brake disc cast iron components [25].

FOSECO employs the SOLOSIL TX inorganic binder, which consists of modified sodium silicate (with a modulus of 2.0–2.4) and fine powder containing various minerals. This binder cures under hot air (150 °C), resulting in the production of high-quality aluminum cylinder head water jacket cores for passenger cars. Notably, this process can completely eliminate reactions between metal and sand, as shown in Fig. 7 [19].

Besides, Chinese foundry material manufacturers and research institutions have also successively developed new silicate binder sand process and conducted trial on aluminum alloy castings. Currently, both domestic and international developed new silicate inorganic binder sand processes (cured by hot air) are mainly used for producing aluminum alloy castings or other low-temperature alloy castings. Only a few companies have reported applications for the production of iron or steel castings.

Table 4: Relevant production process data of Cordis series inorganic binder process

Project	Customer field data
Binder dosage	Inorganic binder 1.8%–2.2%, inorganic additives 0.8%–1.1%
Core making efficiency	Cold box cores ~40 s/mold, shell cores ~60 s/mold
Core yield rate	95%–99%, averaging 98%
Automation	Automated core retrieval and core repair
Core storage	Longest core storage time up to 5 days
Casting yield rate	>97%
Reclamation of used sand	Recycling rate exceeds 90%

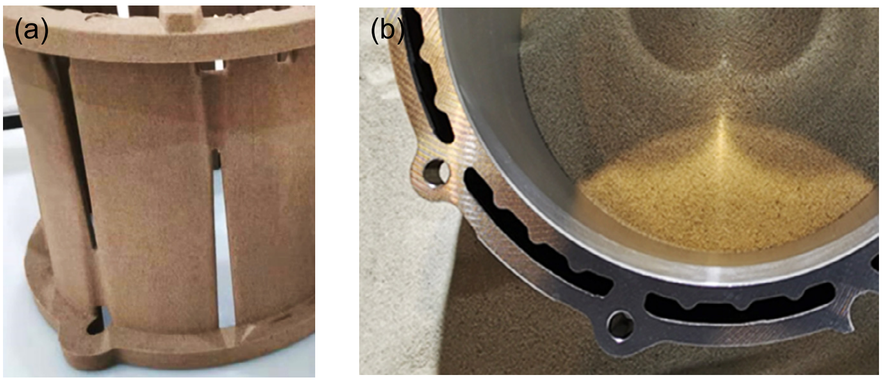


Fig. 6: Pictures of inorganic sand core (a) and motor casing castings (b) [25]

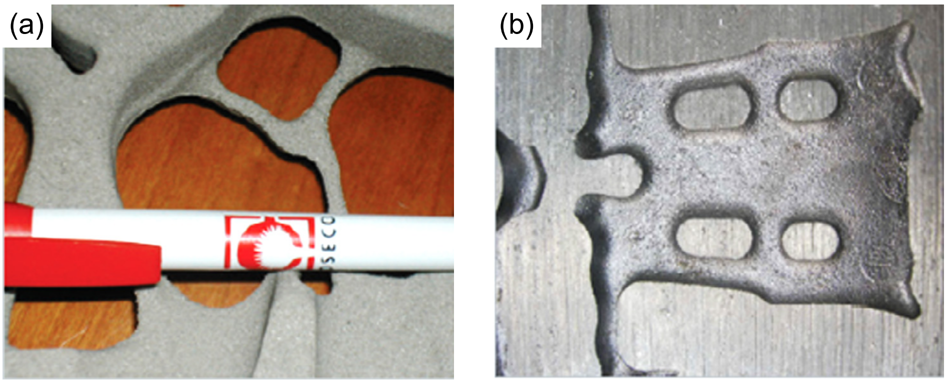


Fig. 7: Water jacket core bridge (a) and aluminum alloy castings (b) produced with SOLOSIL TX binder [19]

3 Phosphate inorganic binder

Phosphate inorganic binder enters the foundry industry in the 1970s. Due to its excellent high-temperature strength, low residual strength, and good collapsibility, phosphate inorganic binders once attracted great attention in the foundry industry. However, due to the unstable nature and strong hygroscopicity of phosphate inorganic binders, they have not been widely applied [18].

The curing methods of phosphate inorganic binders are divided into self-hardening, gas hardening, and heat hardening. Self-hardening phosphate bonded sand usually uses alkaline metal oxides hardener such as iron oxide powder, magnesium oxide powder, fused magnesia powder, and slag. Gas-hardened phosphate bonded sand is typically cured by ammonium chloride blowing, while heat-hardened phosphate bonded sand is cured by heating (150–200 °C). The formulation and properties of phosphate inorganic bonded sand are shown in Table 5 [18].

The former Soviet Union and United States are the earliest to conduct research on phosphate inorganic binders for foundry applications [32]. The former Soviet Union used orthophosphate as an inorganic binder, with iron oxide and magnesium oxide powder as curing agents, for the production of large cast iron and steel parts. The largest steel casting produced reached 40 tons with a wall thickness of 40–150 mm. The American company Ashland Chemical invented a cold-set boron aluminum phosphate binder suitable for foundry production, named Inoset. Poland added chromic acid CrO_3 to heat-cured aluminum phosphate binders to improve the stability and viscosity of the binder. The drying temperature was 180 °C. This binder absorbed moisture before curing, became insoluble in water after curing. It exhibited high refractoriness, and was named “Fosterm”. In the UK, research was conducted on the effect of magnesium oxide curing agents on the performance of self-hardening aluminum phosphate sand. It was found that the chemical activity of newly precipitated magnesium oxide was too high, resulting in excessively rapid curing of the self-hardening sand. It was recommended to use sintered magnesia or fused magnesia powder with lower chemical activity as curing agents. Additionally, the effective mass fraction of magnesium oxide as a curing agent should be greater than 90%.

China starts its research on phosphate binders relatively late. In the 1980s, Huazhong University of Science and Technology successfully developed a boron-aluminum-magnesium phosphate binder suitable for both self-hardening and heat-hardening

Table 5: Formulation and properties of phosphate inorganic binder sand

Molding sand formula (mass ratio, %)			Working time (min)	24 h compressive strength (MPa)	Curing method	Application
Silica sand	Binder	Curing agent				
96.5–96.9	Orthophosphate 2.0–2.2	Magnesia powder 1.1–1.3	35–40	5.0–6.0	Self-hardening	Large steel castings Wall thickness 300–600 mm
95.2–96.3	Orthophosphate 2.5–3.2	Magnesia powder 1.2–1.6	14–16	3.0–3.2	Self-hardening	Medium steel castings Wall thickness 80–150 mm
87–89	Orthophosphate 5.0–6.0	Iron ore powder 6.0–7.0	10–12	2.7–3.0	Self-hardening	Large iron castings Wall thickness 50–120 mm
85.5–96.3	Phosphate 2.0–8.0	Steel slag 1.7–6.5	10–25	Tensile strength 1.36–1.5	Self-hardening	–
88–94	Phosphate 4.0–7.0	Steel slag 2.0–5.0	18–26	2.64–3.2	Self-hardening	–
96	Phosphate 4.0	–	–	Tensile strength 1.35	Heat hardening	–

processes [32]. The binder dosage was 3%. During self-hardening, the tensile strength ranged from 1.2 to 4.0 MPa, while during heat-hardening, the tensile strength exceeded 2.0 MPa. Hubei University of Technology conducted extensive research on the synthesis, modification, and curing of phosphate inorganic binders to address issues such as stability, moisture resistance, and strength properties of phosphate inorganic binder sands [33-35]. Chongqing Changjiang Materials Company developed phosphate inorganic coated sand, which exhibits good fluidity. The prepared sand cores had a bending strength exceeding 3.5 MPa at room temperature, and still demonstrated good collapsibility properties at the temperatures above 1,300 °C. It can be used in the production of ferrous castings, as shown in Fig. 8 [36, 37].

Liutyi et al. [38] studied the performance characteristics of sodium phosphate inorganic binders synthesized by H_3PO_4 with Na_2CO_3, NaCl, and $Na_5P_3O_{10}$, respectively. The results showed that sodium pyrophosphate ($Na_2H_2P_2O_7$) binder synthesized by $Na_5P_3O_{10}$ and H_3PO_4 has high bonding strength, good thermal stability, and excellent collapsibility of sand cores. Therefore, it can be used to produce high-quality cast iron parts.

Liu et al. [39] proposed a heat-cured phosphate inorganic binder. The optimal ratio of binder components is phosphate: water:aluminum hydroxide:magnesium oxide:boric acid=300:70:60:9:8. The addition of polyvinyl alcohol (PVA) solution to modify the phosphate inorganic binder during the sand mixing process can significantly improve the 24 h tensile strength of the sand sample, meeting the general requirements of foundry production.

Compared with silicate inorganic binders, phosphate inorganic binders exhibit superior high-temperature resistance and collapsibility properties, and their environmental friendliness has also been recognized, showing promising application prospects in the foundry industry [40]. However, phosphate inorganic binders still face many challenges, such as high hygroscopicity, poor stability, and relatively high prices. Insufficient understanding of their bonding and curing mechanisms also hinders their widespread application, unlike silicate inorganic binders. Additionally, the recycling of used phosphate inorganic binder sand emerges as a crucial area for future research and application advancement.

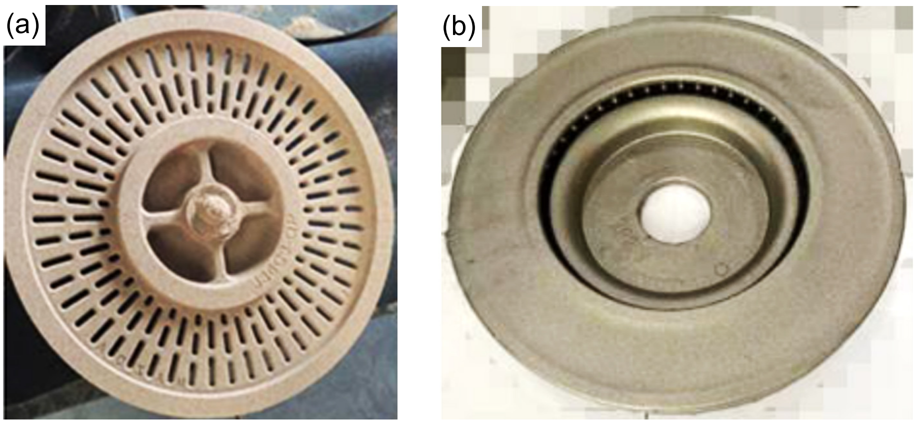


Fig. 8: Phosphate inorganic coated faceplate sand core (a) and faceplate iron castings (b) [36]

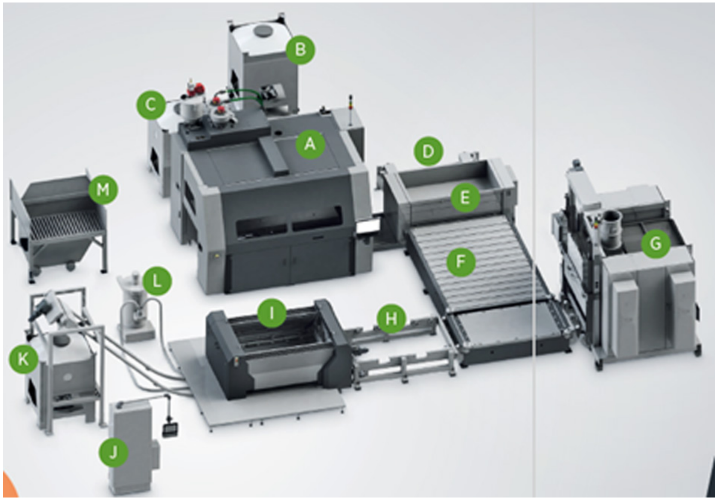
4 Inorganic binder for 3D printing process

The utilization of 3D printing technology enables rapid manufacturing of complex sand mold without flasks, reducing the production time of sand mold and shortening the R&D cycle of complex casting products, thus having a significant application market in the foundry industry. Currently, the most maturely applied 3D printing technologies in sand mold are selective laser sintering (SLS) and binder jetting (BJ) processes [41].

Selective laser sintering for preparing sand mold typically utilizes resin coated sand. Laser irradiation layer by layer on the surface of resin coated sand induces the curing reaction of the binder on the sand grains, resulting in bonding strength. Currently, the resin coated sands used in SLS all employ thermoplastic or thermosetting resin binders coated on the surface of sand grains. For binder jetting of sand mold, sand material is layered on the worktable, and a binder is jetted onto the sand layers by the print head. After the BJ process finished, the binder is cured under the action of curing agent or heat treatment to obtain bonding strength [42]. Currently, the binders used in BJ technology are mainly furan resin and phenolic resin.

To overcome the issues such as the irritating odor generated by resin binders during the 3D printing process, environmental pollution, and the large gas emission from sand mold (core), developing an inorganic binder for 3D printing with performance equivalent to organic resins and environmentally friendly characteristics has become an industry consensus. In recent years, foreign companies such as ExOne and Voxeljet AG, as well as domestic companies like Ningxia Gongxiang, have conducted some research and application on inorganic binders for 3D printing.

ExOne Company has successfully applied inorganic binders to BJ technology. The inorganic binder is derived from a modified sodium silicate binder, with a pH of 12 and a density of 1.3 g·cm^{-3}. It uses a microwave curing process, and the strength of the sand mold is 250–400 N·cm^{-2} [43]. Figure 9 illustrates the schematic diagram of inorganic binder 3D printing system in ExOne Company. This process involves transferring the 3D printed workbox from the "printing station" to the "microwave heating station", followed by curing of the sand mold, and then transferring to the desanding module and finishing area. Figure 10 shows the pictures of inorganic binder 3D printing, microwave curing, and sand core samples.



A. S-Max Pro; B. Transport container (new sand); C. Transport container (recycled sand); D. Transfer station; E. Job box; F. Conveyor; G. Microwave; H. Transport module; I. Desanding module; J. Control cabinet; K. Collection hopper with recycling bin; L. Industrial dust collector; M. Finishing area

Fig. 9: Schematic diagram of inorganic binder 3D printing system in ExOne company [43]

At the GIFA2023 trade fair held in June 2023, Voxeljet AG introduced a cold-curing inorganic binder (Cold IOB) 3D printing technology. This technology allows the formation of sand mold (core) without the need for microwave curing, as shown in Fig. 11. Additionally, Voxeljet AG also demonstrated the results of its collaboration with Loramendi for BMW's core printing (ICP) industrialization project. This project involves printing sand mold (core) using an inorganic binder and then employing the microwave curing process, which is a hot-curing inorganic binder (Hot IOB) 3D printing technology, as depicted in Fig. 12 [44].

Ningxia Gongxiang Company has developed an inorganic binder for BJ technology, primarily using a sodium silicate-based binder. This binder undergoes a curing reaction with a compatible curing agent material under normal or heated conditions to form the sand mold (core). The performance indicators of the inorganic binder are shown in Table 6 [45]. Additionally, they have developed a two-component thermosetting inorganic binder material for BJ technology. Component A of the binder material consists of deionized water, phosphoric acid, and the surfactant alkyl dimethyl betaine, forming a transparent aqueous liquid with a viscosity of 8–12 mPa·s at 20 °C. Component B is composed of lightweight magnesium oxide, lightweight zinc oxide, and aluminum dihydrogen phosphate, with an average particle size of 300 mesh [46].

Fig. 10: Pictures of inorganic binder 3D printing (a), microwave curing (b), and sand core samples (c) [43]

Fig. 11: 3D printing with cold-curing inorganic binders [44]

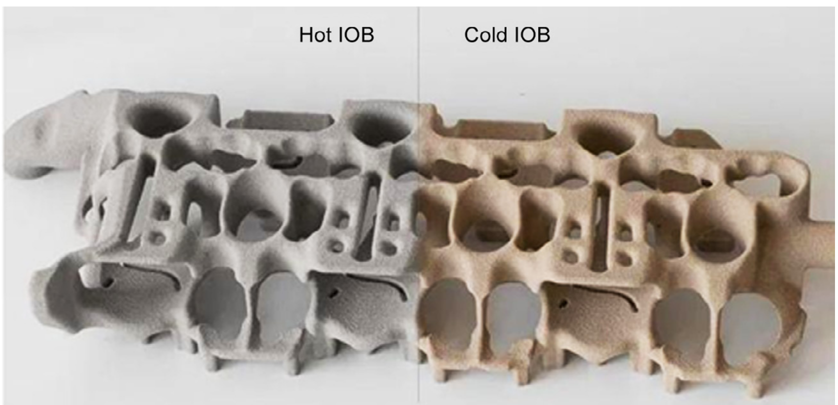


Fig. 12: Comparison of 3D printing with heat-curing and cold-curing inorganic binders [44]

Table 6: Performance indicators of 3D printing mold/core using sodium silicate binder [45]

Project	Label and index	
	3DS-2.9	3DS-2.5
Modulus (M)	2.6–2.9	2.2–2.5
Density, g·cm^{-3} (25 °C)	1.20–1.40	
Viscosity, mPa·s (25 °C)	6.0–14.0	
Surface tension, mN·m^{-1} (20 °C)	≤40	
Water insoluble content (%)	≤0.06	

Wang et al. [47] uniformly mixed sodium silicate powder with sand particles and printed sand mold by spraying a water-based solvent through a nozzle to overcome the issue of high gas generation in sand mold manufactured using traditional organic BJ processes. The manufacturing process is illustrated in Fig. 13. Through a systematic investigation of the BJ process, the optimal process parameters were determined: a binder saturation of 50%, a sodium silicate powder addition of 10wt.%, and a layer thickness of 0.2 mm. The prepared sand samples exhibited excellent performance, with a tensile strength of 4.5 MPa and a maximum gas emission of 8.1 L·kg^{-1}.

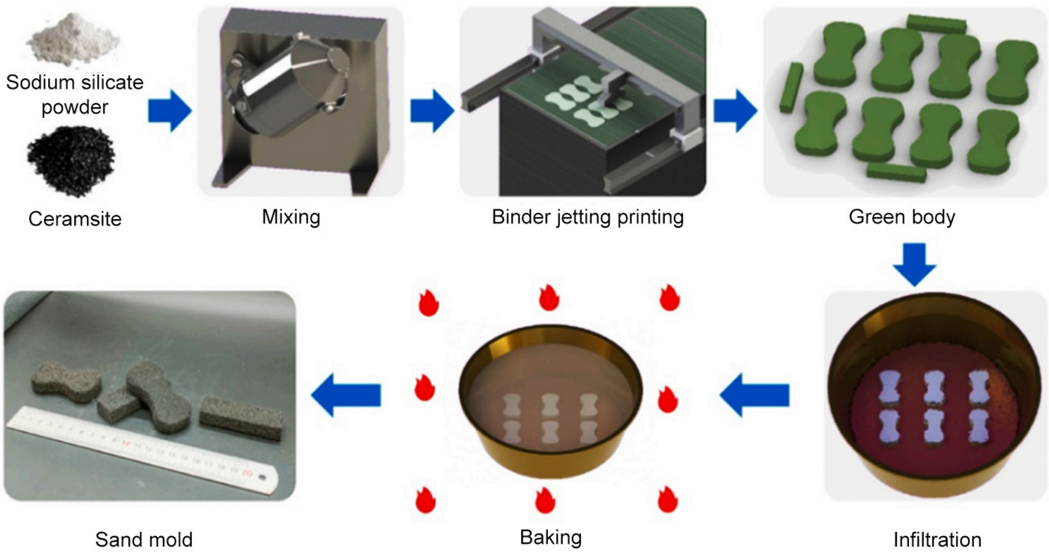


Fig. 13: Schematic diagram for manufacturing sand mold by BJ technology [47]

5 Used sand reclamation technology and equipment

The reclamation and recycling of used sand are important for achieving green and environmentally friendly practices in inorganic binder sand process. It is also a crucial component of sand casting production. There are various methods for reclaiming used sand in inorganic binder casting process, including dry reclamation, medium-temperature heating combined with dry reclamation, and wet reclamation [1].

(1) Dry reclamation method

Dry reclamation involves using pneumatic or mechanical power to accelerate the used sand particles, relying on collision and friction between the sand particles or the equipment to remove the residual binder on the surface of the used sand particles, thereby achieving the reclamation of the used sand.

There are various forms of dry reclamation, and the equipment used for the dry reclamation includes vertical counter-flow frictional reclamation machines, mechanical centrifugal impact reclamation machines, horizontal centrifugal mixing friction reclamation machines, and airflow impact reclamation machines. The reclamation mechanism of these devices all involve "collision-friction". The greater the intensity of collision-friction, the better the stripping effect and the higher reclamation rate, but this also exacerbates the phenomenon of sand particles breakage. Currently, the most widely used dry reclamation equipment in China is the centrifugal impact dry reclamation system. The schematic diagram and actual picture of this equipment are shown in Fig. 14.

Dry reclamation equipment is simple and relatively low-cost, but it cannot completely remove residual binder from the surface of used sand. The reclamation de-skinning rate of used sand is typically between 5% and 25%, resulting in a low quality of regenerated sand. To improve the reclamation de-skinning rate of used sand in dry reclamation, Wang et al. [48] used a “freeze-mechanical” method to regenerate used sodium silicate sand. The results showed that low-temperature freezing causes the residual binder on the surface of used sand freeze to become brittle and crack, making it easier to remove. When the freezing temperature reached −40 °C, the de-skinning rate reached 40.4%. Under natural low-temperature freezing conditions (−10 to −15 °C), the de-skinning rate reached around 32%. Danko et al. [49] employed −70 °C to freeze the used sodium silicate sand, significantly improving the quality of reclaimed sand. However, when the mechanical reclamation time exceeded 5 min, it could easily lead to sand particles crushing and generating a large amount of dust.

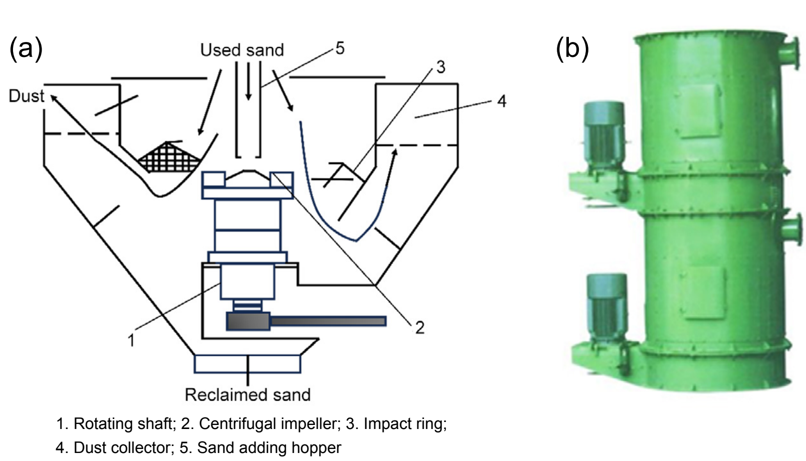


Fig. 14: Schematic diagram (a) and actual pictures (b) of centrifugal impact reclamation equipment [1]

(2) Medium-temperature heating combined with dry reclamation method

Medium-temperature heating combined with dry reclamation is a reclamation method developed to address the shortcomings of dry reclamation. The surface binders of used sodium silicate sand are prone to moisture absorption. The binder film firmly bonds to the surface of sand particles and possesses a certain degree of toughness, making it difficult to remove under the force of collision-friction. Pre-heating treatment before the reclamation of used sand makes the binder film on the surface of sand particles brittle, making it easier to be removed by the force of collision-friction. This method can improve the quality of reclaimed sand, with a reclamation de-skinning rate reaching 25%–40%.

Fan et al. heated the used sodium silicate sand to 300 °C–350 °C before dry reclamation. They found that heating the used sand to 300 °C–350 °C could reduce or eliminate the effects of water to residual binders in the used sand. For ester-hardened sodium silicate sand, this temperature range can decompose and remove the residual ester, significantly improving the quality of dry reclaimed sand, which can be used as a single sand. Xinan Casting Machine Company in Wuxi has developed a “medium-temperature heating combined with dry reclamation equipment system”, and the schematic diagram is shown in Fig. 15 [1].

Recently, some companies have adopted a “mechanical grinding + thermal calcination (650–700 °C)” technique for the used sand reclamation in new silicate inorganic binder sand process (as shown in Fig. 16). This process involves removing residual binders on the surface of sand grains through mechanical grinding and then using high-temperature calcination to passivate (vitrify) the remaining binders. However, this reclamation process leads to the accumulation of residual binders on the surface of the reclaimed sand, thereby reducing its refractoriness. As a result, after multiple cycles of usage, it is inevitable that a certain amount of used sand needs to be discharged and replaced with new sand. Furthermore, this reclaimed sand can only be used for the production of aluminum alloy castings.

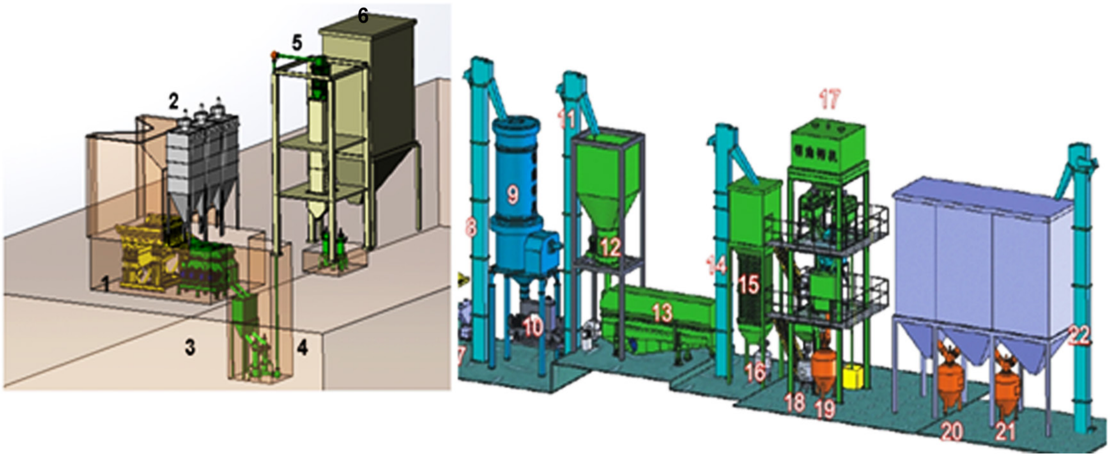
There have been relatively few reports on the reclamation of used sand in phosphate inorganic binder sand casting process. Zhang et al. [50] investigated the reclamation and reuse of self-hardening sand with phosphate inorganic binders via heating combined with mechanical friction. The results showed that the curing speed of regenerated sand at different treatment temperatures was faster than that of new sand. Additionally, the strength of the regenerated sand was comparable to that of new sand. Furthermore, the performance of the sand mold did not deteriorate with an increase in the number of recycling cycles of the reclaimed sand.

(3) Wet reclamation method

Wet reclamation utilizes the dissolving and scrubbing action of water to remove the residual binder film from the surface of used sand. China has developed a multi-stage intense scrubbing wet reclamation system, which achieves a high reclamation de-skinning rate (greater than 90%) for sodium silicate used sand. The properties of the regenerated sand are close to that of new sand, making it widely applicable. The multi-stage intense scrubbing wet reclamation system is shown in Figs. 17 and 18. After being crushed and sieved, the used sand particles are mixed with clean water in a certain proportion, and undergo primary (intense scrubbing) wet reclamation, secondary (intense scrubbing) wet reclamation, followed by wet sand dehydration, drying, and other processes to obtain regenerated sand.

Wet reclamation of sodium silicate used sand achieves a high reclamation de-skinning rate (≥90%) and results in high-quality regenerated sand. However, the wet reclamation systems are relatively large, require sewage treatment, and entail higher costs. Currently, research on the wet reclamation process for sodium silicate used sand primarily focuses on minimizing water consumption during reclamation and the recycling of sewage.

Wang et al. studied the ultrasonic-assisted wet reclamation of sodium silicate used sand (as shown in Fig. 19) and found that the mechanical, cavitation, and thermal effects of ultrasound can accelerate the dissolution of residual sodium silicate from the surface of the used sand. Under the condition of low water consumption, a high reclamation de-skinning rate can be achieved. When the total water consumption for 1 ton of used



1. Vibration sand dropper; 2. Dust collector; 3. Crusher; 4. Screening machine; 5. Pneumatic conveyor; 6. Used sand hopper; 7. Feeder; 8, 11, 14, 22. Bucket elevator (or double tank sending tank); 9. Medium-temperature calcination furnace; 10. Rubbing reclamation machine; 12. Centrifugal reclamation machine; 13. Vibrating fluidized cooling bed; 15. Sand temperature regulator; 16, 18, 19, 20, 21. Pneumatic conveying system; 17. Chromite sand separation system

Fig. 15: Schematic diagram of medium-temperature heating combined with dry reclamation system [1]

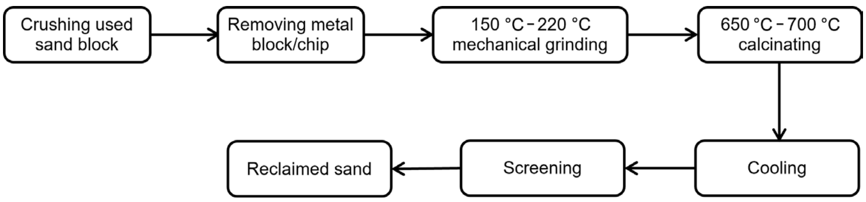
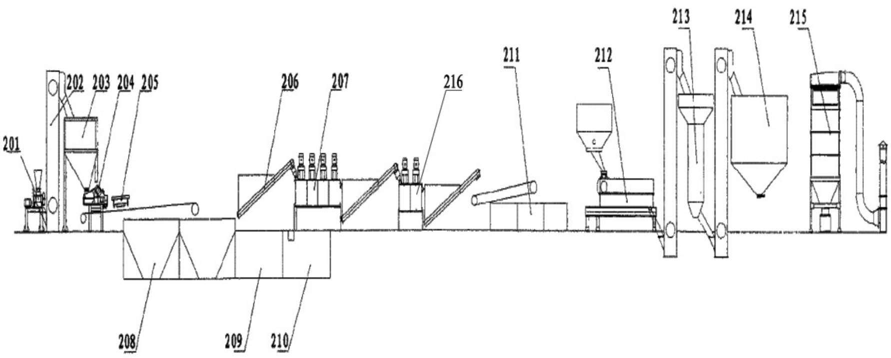


Fig. 16: Flow chart of used sand reclamation in new silicate inorganic binder sand process



201. Jaw crusher; 202. Bucket elevator; 203. Used sand hopper; 204. Screening machine; 205. Magnetic separator; 206. Sand-water separator; 207. Primary reclamation machine; 208. Soaking tank; 209–210. Sewage tank; 211. Wet sand tank; 212. Drying equipment; 213. Cooling equipment; 214. Reclaimed sand hopper; 215. Dust collector; 216. Secondary reclamation machine

Fig. 17: Multi-stage strong scrubbing wet reclamation equipment system [1]

sand was 0.9 tons, the reclamation de-skinning rate can reach 90.58% [51, 52]. In addition, the recovery of sodium silicate from the sewage generated during the wet reclamation of sodium silicate used sand was investigated, as shown in Fig. 20. The results found that the strength of the recovered sodium silicate binder is similar to that of commercial sodium silicate, making it a potential substitute for commercial sodium silicate [53, 54]. Further development and application of these research findings are warranted.

Gong et al. [55, 56] developed a roller-type wet reclamation and dehydration integrated equipment for sodium silicate used sand, which has both reclamation and dehydration functions. This equipment consumes 30% less water during each reclamation cycle, and after three wet reclamation cycles, the de-skinning rate can reach 90.04%. He et al. [57] conducted systematic research on the treatment of sewage generated during wet reclamation of used sand using a water solution of polymeric aluminum chloride (PAC) and polyacrylamide (PAM) as a flocculant. The results showed that the minimum treatment cost for directly discharging treated sewage was CNY0.51/ton of sewage, while the lowest treatment cost for recycling the sewage was CNY1.62 per ton.

Kim et al. [58] employed KOH solution for the wet reclamation of used sand containing a new silicate inorganic binder used in aluminum alloy casting. The used sand was initially grinded and regenerated in a 0.2 M KOH solution to remove the residual binder. Subsequently, it was washed with water 2–3 times and dried, as shown in Fig. 21. The

Fig. 18: Multi-barrel strong scrubbing wet reclamation machine [1]

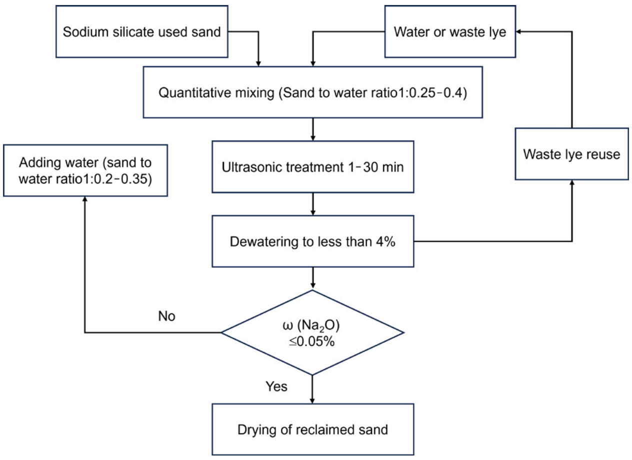


Fig. 19: Flow chart of ultrasonic wet reclamation of sodium silicate used sand [52]

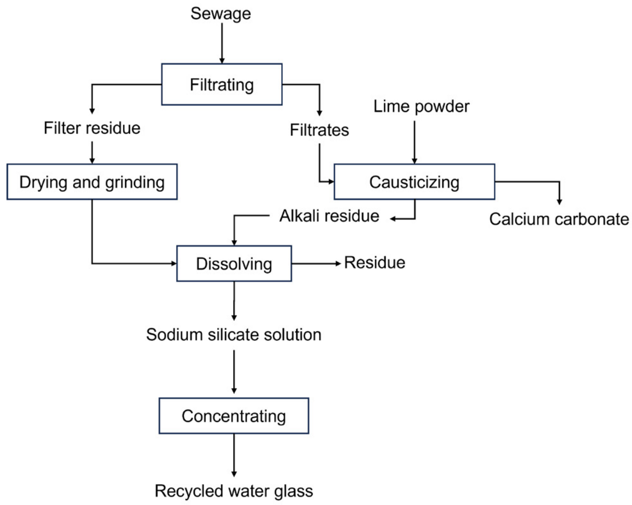


Fig. 20: Flow chart of recycling sodium silicate from used sand reclamation sewage [54]

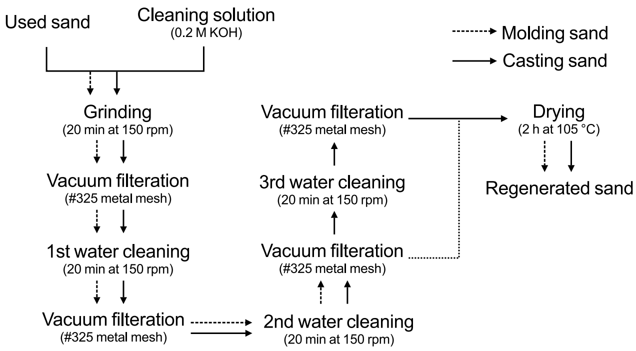


Fig. 21: Experimental procedure for wet reclamation [58]

results revealed that residual powder remained on the surface of the regenerated sand, with approximately 78% of its original properties retained. However, by simply adding the new silicate inorganic binder, the reclaimed sand achieved satisfactory bonding strength performance.

Lu et al. proposed a steam reclamation method for sodium silicate used sand, as shown in Fig. 22. The crushed and sieved used sand was placed in a closed or semi-closed container. Then, high-temperature steam at 100 °C or above was introduced into the container for steam soaking for about 30 min. The treatment solution generated by the steam process was filtered out from the bottom of the container. The sand inside the container was removed, dried, and then obtained as reclaimed sand. The water consumption for steam reclamation was approximately 60% of the mass of the used sand [59, 60]. In addition, the treatment of sewage from CO_2 sodium silicate sand with $CaCl_2$ was studied. The results showed that adding a 20% mass fraction of $CaCl_2$ solution as a treatment agent and mixing it with the sewage for 4 min effectively reduced the turbidity of the sewage to below 20 and adjusted the pH from alkaline to neutral [61]. The engineering value of this research remains to be verified.

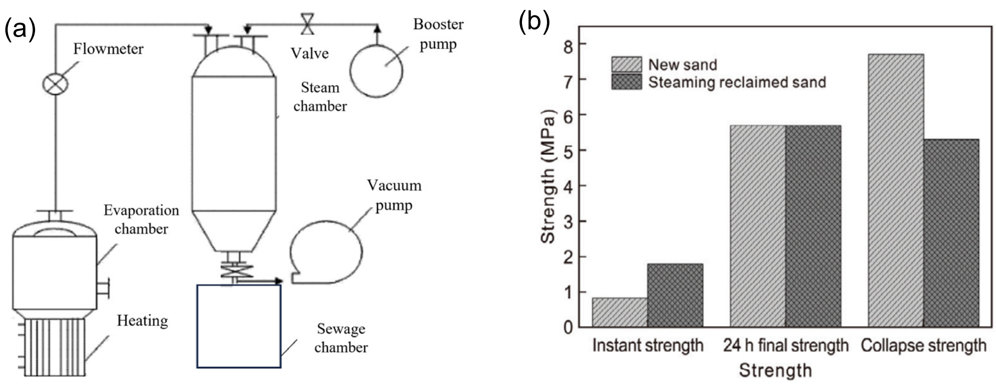


Fig. 22: Schematic diagram of steam reclamation and compressive strength results of reclaimed sand: (a) steam reclamation process; (b) compressive strength of reclaimed sand [60]

6 Summary and prospect

The inorganic binder used in casting, as a non-toxic, odorless, and environmentally friendly binder, has garnered widespread attention from foundry enterprise due to its promising applications in improving the casting environment, reducing production costs, and enhancing product competitiveness. However, whether it is the more maturely applied silicate inorganic binders or the under-development phosphate inorganic binders and those for 3D printing, there is still a long way to go before they can completely replacing organic binders. Continuous research, innovation, and refinement are necessary for foundry workers to achieve this goal.

(1) CO_2 cured sodium silicate sand and ester cured sodium silicate sand remain the most widely used inorganic binder sand in the production of steel castings, while new silicate inorganic binder sand has seen rapid development and application in the production of aluminum alloy castings. For silicate inorganic binders, whether applied to steel castings or aluminum alloy castings, improving the ambient temperature strength of molding (core) sand, enhancing the collapsibility of used sand, and promoting the reusability of reclaimed sand are the goals pursued in the development of this type of inorganic binder. Furthermore, deeper research is needed into the bonding mechanism and hardening characteristics of silicate inorganic binders, improving the quality of binder and hardener materials, refining traditional curing methods, processes, and equipment, and focusing on solving the recycling and reclamation problem of used sand.

(2) Compared to silicate inorganic binder sand, phosphate inorganic binder sand exhibits superior high-temperature strength and collapsibility, making it suitable for the production of steel and iron castings. However, phosphate inorganic binders have drawbacks such as high hygroscopicity, poor stability, and high cost, leading to limited application in molding (core) sand. Therefore, it is necessary to conduct in-depth research on the bonding and hardening mechanisms of phosphate binders, optimize the synthesis process, materials, and properties of the binders, improve traditional curing methods, and develop suitable reclamation processes, methods, and equipment for used sand to enhance the industrial applicability of phosphate inorganic binder.

(3) Inorganic binders for 3D printing have been a recent research focus. Currently, most 3D printing technologies use organic binders such as furan resin and phenolic resin, while the application of inorganic binders (mainly modified sodium silicate binder) in the binder jetting process is still in its early stages but shows a trend to replace organic binders. For inorganic binders used in 3D printing, the main tasks and development directions include researching suitable inorganic binder materials, curing methods (microwave curing, heat curing, self-curing, etc.), developing nozzle devices suitable for inorganic binder environments, and addressing issues such as low bonding strength and accuracy of the sand mold (core).

(4) The reclamation of used sand is a crucial step in achieving green and pollution-free casting processes, and the complete reclamation and recycling of used sand (zero emissions) is the goal pursued by foundry enterprises. The reclamation methods of inorganic binder sand primarily involve dry reclamation, medium-temperature heating combined with dry reclamation, wet reclamation, and composite process reclamation, each with its advantages and disadvantages. For different types of binder used sand, appropriate (low-cost) reclamation process equipment should be selected based on their performance characteristics and combined with the actual production of the enterprises to maximize the recycling of used sand.

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Conflict of interest

Prof. Zi-tian Fan is an EBM of *CHINA FOUNDRY*. He was not involved in the peer-review or handling of the manuscript. The authors have no other competing interests to disclose.

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