Abstract

Due to increasing environmental awareness, more and more foundries started to replace the organic binders with an environment-friendly binder system based on inorganics. However, inorganic binder systems can only replace the conventional organic binders if all requirements, set by the foundry industry are being fulfilled. One of these is the production of high-quality cores, indicative of good compaction, no surface defects, and high surface smoothness. Such types of cores can only be manufactured when the sand mixture shows sufficient flowability. This chapter presents a study on the flowability of various types of sand mixtures all including inorganic binder systems finally to be used for the production of sand cores for the foundry industry. Results have shown that the flowability of sand mixtures can be modified and improved by (1) the addition of small amounts of surface-active agents and/or (2) well-chosen additives characterized by micro-sized spherical particles. The addition of only a few amounts of surface-active agents resulted in a significant improvement of flowability and thus of core quality. Similar results were achieved with the use of small concentrations of spherical micro-sized particles.

Keywords: flowability, sand mixture, inorganic binder, alkali silicate, surfactant, surface tension, additive, spherical particles, powder flow tester, cores

1. Introduction

Environment-friendly binder systems for molds and cores are generally based on the use of a 2-component inorganic binder system consisting of a liquid alkali silicate and a powder-like solid consisting of various minerals. Since environmental awareness receives today more and more attention, the replacement of organic by inorganic binders result can be considered in this, resulting in a significant reduction of dirty smell and toxic emissions. This means that the introduction of the so-called inorganic binder system needs many research and development activities before it can replace the old-fashion organic binder systems. In this context, with the existing technology to heat cure the cores, high strength can be achieved, comparable with that obtained with the existing organic binders.
The new environment-friendly binder system SOLOSIL TX developed by Foseco, Vesuvius, is an inorganic thermosetting core binder, which combines the advantages of the organic binder regarding strength and productivity with environmental friendliness [1].

Achieving high-quality castings with the use of cores including the above-mentioned inorganic binder systems depend not only on the casting process itself and their processing parameters, but also on the quality of these cores. Use of cores with insufficient strength or with locally low compaction results in lower surface smoothness and often in defects of the casting surface. The main requirements to achieve high-quality cores and received from the foundry industry are:

- Use of relatively cost-effective and environment-friendly materials
- Easy to handle and to mix with various types of sand
- Sufficient bench life of the sand mixture
- Good flowability of the sand mixture
- No blocking of the inlet shooting nozzles
- High-quality cores with sufficient compaction and surface smoothness
- Short cycle times = short core production time
- Sufficient handling and casting strength of cores
- Sufficient breakdown/de-coring properties
- No gas formation during the casting process resulting in bad castings
- To achieve sufficient storage stability of the produced cores.

It is not the aim of this chapter to highlight and/or to discuss all parameters affecting the manufactured castings; this contribution is dealing with only one aspect: how to produce good quality cores (read: high compaction, no surface defects and high surface smoothness) with quartz sand as the filling material and well-chosen inorganic binder systems, the latter to achieve an environment-friendly working area.

High-quality cores can only be produced when the flowability of the sand mixture is such that the core box is filled completely. This means that the surface friction between individual sand grains and the wall friction, meaning the friction between the sand mixture and the surface of the core box, should be sufficiently low. Figure 1 shows a small part of two types of cores, one (left picture) with insufficient compaction due to low flowability, and the other (right picture) with high compaction—high flowability of the sand mixture.

Flowability of sand mixtures depends on various parameters: the nature and amount of the liquid binder, the nature and amount of the optional additive(s), and the type of the filling material. Regarding the additive and filling material, the flow properties of these components depend on several parameters, such as particle size distribution, particle shape, chemical composition, moisture and temperature [2].
Generally, the filling material is a given since foundries obtained their sand from local sand quarries. This means that only the nature and properties of the liquid binder and/or additive are (is) accessible for modification.

The objective of this chapter is to highlight some methods to determine, to influence and to optimize the physical and chemical properties of inorganic binder systems aiming at high flowability of the sand mixture.

2. Experimental

2.1 Equipment

2.1.1 Attension optical tensiometer

With the Attension optical tensiometer surface tension of liquids can be analyzed following the pendant drop method. Since the drop shape is partly related to the surface tension of the liquid, the captured image will be analyzed with a drop profile fitting method calculating the surface tension. This instrument has already shown its high accuracy and fast sampling rate, so results can be obtained within a few seconds. Figure 2 shows some pictures of this tensiometer.

2.1.2 PFT powder flow tester

The powder flow tester was initially developed to characterize the flow behavior of solid powder material with particle sizes up to a maximum of about 1 mm. Since there was also a need to determine and to define the flowability of sand mixtures with a relatively small amount of a liquid, it was considered to use the PFT also for these applications. To compare different types of sand mixtures, results will be published by a so-called “flow function” plot. This flow function plot shows the flowability of various types of samples over so-called different “consolidation stresses”, the latter being considered as compressive stress. This plot shows various regions starting from free-flowing, to easy flowing, cohesive, very cohesive to non-flowing. The lower the curve the higher the measured flowability. Figure 3 shows the PFT Brookfield powder...
flow tester. About this equipment, the weight of the sand mixture placed in the
can also be an indirect indication of the flowability. In this case, the
Hausner ratio (Eq. (1)) [3] can be used to obtain a more quantitative value of the
flowability:

\[
H = \frac{\rho_T}{\rho_B}
\]  

where \(\rho_T\) can be considered as the bulk density under pressure and \(\rho_B\) the freely
settled bulk density of the mix. The Hausner ratio is not an absolute value for
flowability but gives only a quantitative approach. The higher the Hausner ratio, the
lower the flowability. In the industry, also the Carr index \(C\) (Eq. (2)) [4] is sometimes
used, which is another value of flowability but related to the Hausner ratio:

\[
C = 100 - \frac{100}{H}
\]

where \(H\) is the Hausner ratio. The lower the \(C\) value, the higher the flowability.
2.1.3 Special types of core boxes

Besides the use of the PFT, also various types of test core boxes were developed to obtain more information on the flowability of sand mixtures based on inorganic binder systems (see Figure 4). These core boxes were manufactured aiming to measure/visualize the amount of sand mixture blown into the open space of the core box.

2.1.4 Core weight

Another approach to obtain indirect data related to the flowability of sand mixtures is to measure the core weight. From a general point of view, it is suggested that the higher the core weight, the higher the compaction. Compaction, which can be given as weight per core or by density, is related to flowability. In case the flowability of a sand mixture is low, core box filling is a severe issue finally resulting in a non-complete filling of the core box resulting in low(er) density of the produced cores.

2.1.5 Core shooter

The core shooter being used during this project is a Laempe L1. This core shooter is often used to produce transverse bars but also other types of cores can be manufactured with the Laempe laboratory machine type L1 being developed for manufacturing testing cores in heated and non-heated tooling, using gas hardening processes like CO₂, cold box and hot box. The sand mixture is automatically injected into the core box, which is clamped between the side presses, and heated at various temperatures. The release of high-pressure air blows the sand from the sand storage bunker into the core box at high speed. The total elapsed shooting time for transverse bars was set at 1 s and with a shooting pressure of 4 bar. In case of producing cores, these were purged with heated air for 60 (bars) or 120 (cylinders) s and at 120°C. The

![Figure 4. Various types of core boxes with different complexities to measure flowability of different sand mixture compositions.](image)
core box temperature was set at 140°C. However, deviations from these processing parameters are always possible since other types of cores need lower or higher shooting times and shooting pressures, shorter or longer purging times, lower or higher core box temperature, etc. In the case special types of core boxes are used to measure flowability, no curing step is considered. Pictures of this type of core blower are shown in Figure 5.

2.2 Various types of sand mixtures

The various types of sand mixtures can be characterized by the nature of the filling material, the type of the liquid inorganic binder and the type of additive.

2.2.1 Type of sand

In the case of sand, the most important structural parameters influencing the flowability of the sand mixtures, are the average grain size, the grain size distribution and shape. Generally, foundries will use that type of sand that is available from a local quarry near the production site, so to reduce transport costs. This means that the type of sand is a given parameter that can hardly be replaced by another type of sand. Tests presented in this contribution are mainly based on the use of H32 or H33 (Quarzwerke, Germany). These types of sand showed medium sphericity of the individual sand grains including a sub-rounded to a rounded shape. Figure 6 shows various types of sand grains with various shapes from very angular to well-rounded and from low sphericity to high sphericity. Macrographs of quartz sand type H32 and H33 are depicted in Figure 7.

2.2.2 Inorganic liquid binder

Not only the type of sand, but also the type of liquid binder affects the flowability of the sand mixture. In case the viscosity of the liquid binder is relatively high, it will have a detrimental impact on flowability. Viscosity can be modified by adding solvents with specific rheological properties, or by diluting the binder easily by adding a
small amount of water. Adding a small amount of water of 5 wt% already lowered the kinematic viscosity by 50%.

Next to modifying or adapting viscosity, also the surface tension of the liquid can play a significant role of importance. In case the surface tension (mN/m) is rather high, it will be difficult to produce new surfaces because this is energetically unfavorable. This is the case during core manufacturing when sand is blowing into the core box. Many times, individual sand grains will be separated from each other creating new surfaces (higher state of energy). This means that it is more difficult to separate two individual sand grains from each other when surrounded by a thin liquid film of the binder with high surface energy. So, it is expected that the lower the surface energy of the binder, the better the flowability. One of the means to modify surface tension is the use of a small amount of a so-called surfactant or surface-active agent. The lowest surface tension is achieved when the CMC (critical micelle concentration)
is reached, generally the addition of a few tens of percent based on the liquid binder. Once the surface area is fully occupied, the addition of more surfactant will not further reduce the surface tension of the liquid.

2.2.3 Additives to improve flowability

Special types of additives can be considered to further improve specific properties of the sand mixture as well as of the produced cores. Irregular shapes resulted generally in low flowability whereas on the other hand, spherical particles improved flowability. Often discussed in papers and patents, the use of a small amount of fly ash indeed improved flowability, which can be considered as a suitable fully inorganic mineral. Improved flowability will directly affect the bending strength due to improved compaction. Some results with various types of additives can be found in Ref. [1]. Figure 8 shows a macro- and micrograph of a certain type of fly ash. Also appointed is the use of graphite flakes which can modify flowability, see also Figure 9. The presence of platelets can improve tribological properties, so these particles can also be considered as an additive of sand mixtures with inorganic binder systems. In the following, only spherical particles being used as inorganic additives will be discussed in more detail.

![Figure 8](image1.png)
*Figure 8.*
Macrograph (left) and micrograph (right) of fly ash. Interesting to note is the spherical shape of the individual fly ash particles.

![Figure 9](image2.png)
*Figure 9.*
Macrograph (left) and micrograph (right) of graphite. Interesting to note is the platelet/flaky structure of the individual graphite particles.
3. Results and discussion

3.1 On the influence of the surfactant concentration

First series of tests were done with one type of the inorganic binder and with various concentrations of three types of surfactants, A, B and C. Figure 10 shows the surface tension as a function of the concentrations of the surfactants. Measurements with the Theta Attension optical tensiometer showed that the surface tension of the liquid inorganic binder was about 53 mN/m. The addition of 0.25 wt% bob (based on binder) surfactant type C to the liquid binder resulted already in a significant decrease of the surface tension to values of 20 mN/m. A further increase in the concentration did not result anymore in a further obvious decrease of the surface tension, since the CMC (critical micelle concentration) was already achieved. In case of surfactant type A or B, the decrease in surface tension was less pronounced.

With the use of the PFT powder flow tester, more information was obtained on the flowability properties of sand mixtures including various concentrations of the surfactant type C. Here, quartz sand type H33 was used. No additives were taken into consideration, only one type of liquid inorganic binder type. Figure 11 shows the unconfined failure strength as a function of the applied compressive stress. This failure strength is related to the cohesive behavior of the sand mixture, and as such, it can be used to evaluate quantitative flowability. This figure shows clearly that up to about 0.2 wt% bob surfactant type C, the increase in flowability was significant. Higher concentrations showed only a further small improvement of flowability. Another approach is to calculate the Hausner ratio and the Carr index. Table 1 shows the indices as a function of the concentration of the surfactant type C.

From Table 1 it is clear that the Hausner, as well as the Carr index, decreased with higher concentrations of the surfactant. This relationship indicates that the flowability of the sand mixture improved with the presence of the surfactant type C, whereas with a further increase in surfactant concentration (>0.2 wt% bob) the change in these values was much less.
3.2 On the influence of the type of surfactant

Not only the amount of added surfactant does influence the flowability of the sand mixture, but also the chemical composition can have an impact on this. Another series of tests were dealing with various types of surfactants. Results obtained with the PFT powder flow tester are depicted in Figure 12. This figure shows that the lowest flowability was achieved with the surfactant type F, and the highest with type D. In addition to these tests, flowability was also determined using a special type of core box for flowability measurements, as shown in Figure 13.

Based on these results, it can be concluded that the higher filling of the core box is thus related to a higher flowability as measured by the PFT (Figure 14).

In addition to the special type of core box, depicted in Figure 13, where only the weight of the sand could be measured, the one shown in Figure 15 will also visualize the filling rate. Also here, it is clear that the presence of a surfactant resulted in higher flowability.

As already shown, the addition of a small amount of a well-chosen surfactant indeed improved the flowability of the sand mixture. This was approved and confirmed by various testing methods including powder flow tester PFT, various types of core boxes, and by calculating the Hauser ratio and Carr index. Based on these results, a series of transverse bars were manufactured with the Laempe core shooter L1.
The outcome of these tests was that the bending strength, as shown in Figure 16, significantly improved with even a very low addition level of 0.05 wt% bob of the surfactant. The strength stabilized at concentration levels of 0.10 wt% bob or higher. Furthermore, also the sample weight (see also Figure 16) increased with the presence of a small amount of surfactant. Due to the higher compaction of the cores, the strength values were also higher, since higher compaction is directly related to a higher number of contact points (bonding bridges) between individual sand grains.

In addition to the use of surfactants, which lower the surface tension of the liquid binder and as such improve flowability, also the viscosity and the type of the liquid inorganic binder can play a significant role in the production of high-quality cores. The viscosity can be lowered by adding a small amount of water, thus reducing the solid content of the binder. Due to a lower viscosity, a more homogeneous sand mixture can be achieved. This means a more homogeneous distribution of the binder.
Figure 14.
Filling (weight of the sand blown into the core box) of a special type of core box as a function of the various sand mixtures.

Figure 15.
An example of the filling with a sand mixture without surfactant (left) and with surfactant (right).

Figure 16.
Bending strength values (sample weight on top of the individual bars (in g)) as a function of the amount of surfactant added to the inorganic liquid binder (wt% bob). In this case, 1.0 wt% bos additive type A01 was also present in the sand mixture.
around the individual sand grains, which probably can result in a net lower amount of binder to achieve similar strength and surface quality. Another approach is the use of lithium—or potassium silicate, next to sodium silicate. It is well-known that the viscosity of potassium silicate is lower than that of sodium silicate, however, care must be taken since differences in strength can occur.

This means that aiming high-quality cores can be rather complex, since the various chemical and physical parameters can play a role into this. The chemical structure and the concentration of the surfactant, the viscosity and chemical composition of the liquid binder (solid content and type and modulus of the silicate) and the amount or concentration of liquid binder based on the filling material will have an impact on the flowability of the sand mixture and thus directly on core quality (compaction, surface defects, surface friability and surface smoothness).

3.3 Use of additives to improve core quality

The addition of powder-like inorganic compounds, also called core additives, to sand mixtures is at present indispensable. Since the requirements from the foundry industry are continuously growing and more demanding, sand with only a liquid inorganic binder cannot fulfill anymore all requirements. Research and development on a new generation of inorganic additives are continuing, aiming to further improve the casting process. First of all, it needs to improve the surface quality of the core, indicative of high surface smoothness. Another advantage can be improved flowability which makes cores denser. In addition to this, it will support to fill complex core boxes, such as those being used to produce complex-shaped water jackets. A well-chosen core additive can also induce higher strength values, which helps to reduce the amount of binder to be added to the sand mixture. Thus, less water is present in the sand mixture and as such, the total cycling time (read: purging time with hot air) can be further reduced. On the other hand, the casting quality is also related to the amount and type of the core additive. A non-well-chosen additive can result in amongst others, metal penetration, gas defects, low de-coring properties and sand adhesion. As already mentioned, core additives are also added to improve flowability and thus compaction and strength of the cores.

A small addition of 0.6 wt% bos of the additive type A01 resulted in an obvious improvement of flowability of the sand mixture (see Figure 17). However, a further increase of the concentration level resulted in over-saturation inducing lower flowability. The addition of 1.8 wt% bos type A01 (spherical particles) resulted in an even lower flowability than adding 1.2 wt% bos. A similar approach was obtained by measuring the bending strength of transverse bars including the various concentrations of the additive. These results are shown in Figure 18. Here, it is clear that up to about 0.3 wt% bos additive type A01 strength values increased from about 350 to 480 N/cm², thus an increase in strength of about 30%. Starting from 0.3 up to about 1.2 wt% bos, strength values stabilized around values between 450 and 480 N/cm². Higher concentrations of the additive resulted in the decrease of the bending strength.

3.4 On the influence of micro- and nano-sized spherical particles

It is well-known that the grain size (distribution) of sand being used for cores and molds can strongly influence the surface morphology of castings. Relatively large grains result in large pores allowing penetration of the liquid metal, finally resulting in
the undesired surface finish of the product. To improve the surface finish, finer grains can be chosen to suppress or inhibit metal penetration during the casting process.

However, not only the grain size distribution but also properties like the geometry and shape of the chosen sand are important. The grain shape is defined in terms of angularity and sphericity. More information concerning this can be found in the Foseco Non-Ferrous Foundryman’s Handbook [6]. It is mentioned that grains with medium to high sphericity give good flowability, whereas more angular and lower sphericity of sand grains will result in low flowability, finally resulting in relatively low compactness (packing density of the sand grains).

To move individual sand grains independently of each other, relatively high friction forces $F_w$ have to overcome. A schematic view of individual sand grains with medium to low sphericity is depicted in Figure 19.
To enhance the flowability of such a type of quartz sand, one possibility is to add micro-sized spherical particles covering the outer surface of the sand grains in such a way that contact between the sand grains is obviously suppressed or even prevented. These particles will act as so-called “spacers” lowering the overall friction forces between the individual grains. In the case of inorganic additives, spherical micro-silica particles are often chosen to improve the flowability of the sand mixture. More information on flowability can be found in various references [7–12]. A micrograph of such a type of micro-silica is shown in Figure 20. Under the most ideal conditions, it can be expected that the relatively small particles of micro-silica cover the large sand grains by a uniform distribution.

A minimum number of these small spherical particles will be needed to achieve non-contact between the individual sand grains.

A schematic view of sand grains with the addition of micro-silica is shown in Figure 21. A common average diameter of quartz sand lies between 200 and 400 μm.
The specific diameter of spherical particles of micro-silica is between 0.1 and 2.0 \( \mu m \), significantly smaller than the sand grains. If the amount of added micro-silica is insufficient, the flowability of the sand mixture is far from the optimum, and sufficient compactness of the core and/or mold is difficult to guarantee. With the addition of a sufficient amount of micro-silica, flowability was significantly improved resulting in cores with good quality: sufficient packing density and smooth surface finish.

Based on these results, it was considered to improve further the flowability of such systems. Focusing on the guest particles, it was obvious that these were significantly smaller than the host (sand) particles. A similar model can be considered to design the mechanistic aspects of two spherical micro-silica particles. If a critical number of very small spherical particles (nano range) can be added in such a way that this cover
(uniformly distributed) the outer surface, a similar configuration can be expected as that with the sand grains (see Figure 22). Probably due to this modified configuration, the flowability of the sand mixture systems can be improved further. However, this theory can still be discussed. A micrograph of micro-silica particles covered with nano-particles is shown in Figure 23. First results have indeed shown that a small increase in flowability and bending strength was achieved with the addition of a small amount of nano-particles, in this case 0.05 wt% bos.

Based on these experimental data, the following model, as depicted in Figure 24, can be proposed, related to an improved flowability resulting in higher compactness of the core material, and as a consequence, higher bending strength.

Besides the use of micro- and nano-spheres to improve flowability, also other compounds/components are needed to meet all requirements related to high-quality casting surfaces. It is beyond the scope of this contribution to discuss all requirements,
but it shows that a well-balanced inorganic binder system is highly complex. In addition to high-quality cores, cold and hot strength, resistance against hot distortion, no interaction with the liquid metal, no metal penetration, good de-coring properties, etc. and finally re-use of core residue should be considered too.

4. Conclusions

Before inorganic binder systems can be considered to replace the existing organic binder systems, the combination of a liquid inorganic binder and an inorganic additive has to meet the requirements set by the foundry industry. Such a system can be extremely complex and one of the main requirements is to produce high-quality cores with sufficient compaction and with high surface smoothness. This can only be achieved when the flowability of the sand mixture is sufficient. In the case of optimizing only the flowability of the sand mixture, the liquid inorganic binder, as well as the inorganic additive, can play a significant role in this.

Results have shown that in the case of the liquid binder, various parameters can affect flowability, in particular, the presence of a small amount of a surfactant. The lower the surface tension, the higher the flowability. Also, the chemical composition of the surfactant (an-ionic, cat-ionic, or non-ionic) influences flowability.

Besides a modification of the liquid binder, also the additive can play a significant role. The size and shape of the individual particles of the additive, and also its addition rate to the sand, play also a significant role of importance. Flowability tests with the powder flow tester have clearly shown that spherical particles with specific (average) grain size with well-chosen addition rates can improve flowability finally resulting in sufficient compaction of cores and completely filling of core boxes being used for complex-shaped cores such as water jackets for cylinder heads.

The newly developed inorganic binder SOLOSIL TX by Foseco, the Netherlands, can be adapted in such a way that all requirements set by each individual foundry are met. For more complex applications, such as the production of water jackets, high flowability is needed, whereas high-quality less-complex cores can already be achieved with sand mixtures including lower flowability. In addition to flowability, also other properties of the sand mixtures and cores can be adjusted by a small modification of the environment-friendly inorganic binder system SOLOSIL TX.

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Conflict of interest

The authors declare no conflict of interest.
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