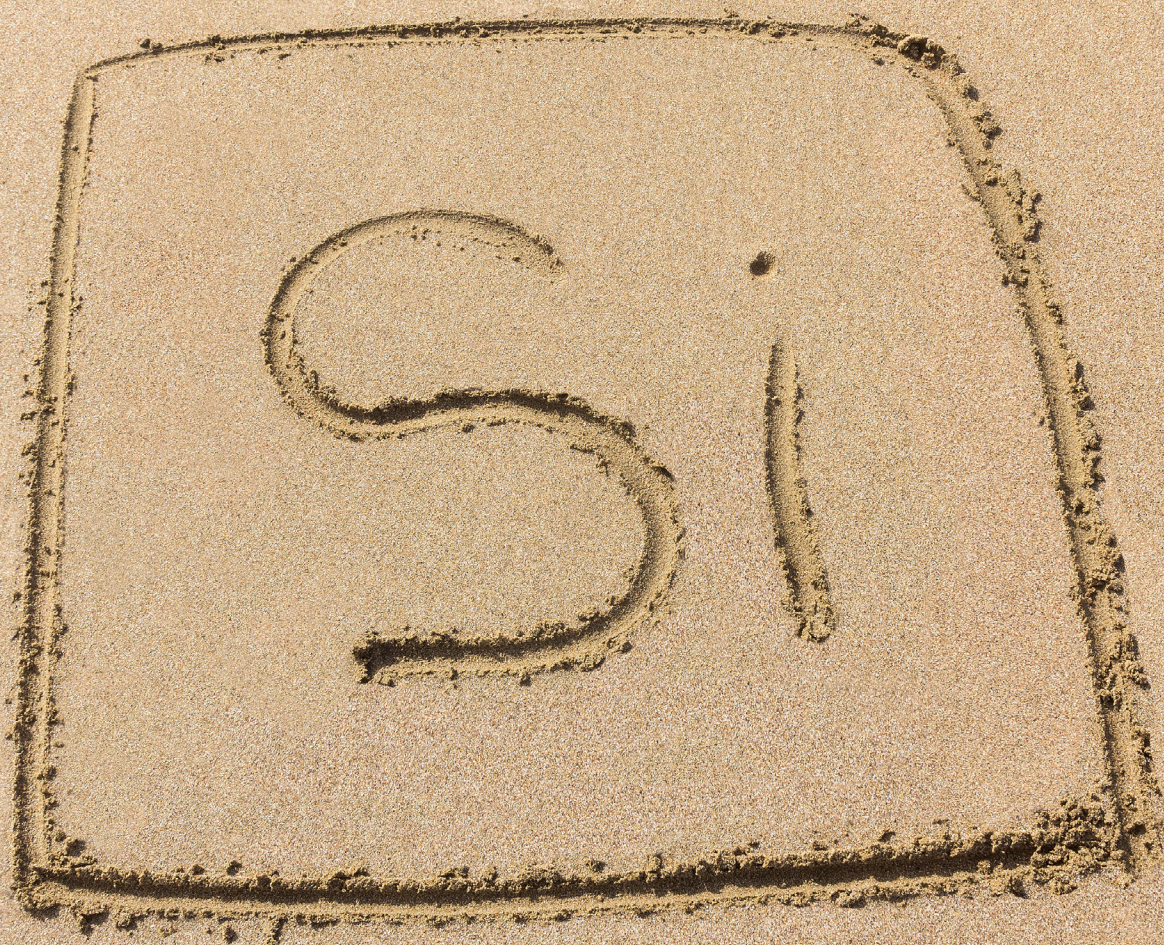


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Sand Binder Systems



Technical Paper

Part XIII: Silicate CO₂, Silicate No-Bake, CO₂ Cured Alkaline Phenolic

Thirteenth of a 13-part series filled with useful and up-to-date information about sand binder systems.

The Silicate CO₂ Processes

The silicate CO₂ binder system is recognized as the original cold box process, although it didn't start out that way. The use of sodium silicate as a binder was first described as a heat cured system in 1898 by British chemists Hargreaves and Poulson. It was first used in a Czechoslovakian foundry in 1947. It was introduced into US foundries as a heat cured system. It was not until 1968, when it was discovered that CO₂ gas could effectively produce cores and small molds, that the ester catalyzed silicate no-bake version was introduced.

Two very positive aspects of the silicate/CO₂ system make it stand apart from other cold box processes. First, it's based on inorganic chemicals. Second, because the CO₂ gas is non-irritating, it does not have to be captured and neutralized.

Binders – Sodium silicate binder is an aqueous solution of silicate (SiO₂) and soda (Na₂O) blended in a silicate/soda ratio between 1.90–3.22 to 1. Ratios from 2.0–2.8/1 are the average used in foundries. The higher the ratio the more reactive the system. This ratio is one of the principal determinants of binder performance as it effects final strength and gassing time.

The Curing Process – The silicate/CO₂ process is unique and complicated, but understanding the curing process is the key to process control that can ensure satisfactory results.

The curing process involves two distinct curing mechanisms.

First is "gelation" in which sodium silicate and water react with CO₂ gas to form a mixture of sodium carbonate and silica gel along with water. The CO₂ and the water in the binder form carbonic acid. Sodium silicate is alkaline. When the carbonic acid is formed, the pH of the silicate falls, reducing the amount of soda and increasing the silica. At this point the binder has formed about 20 to 40% of its ultimate strength. The second part of the curing process is dehydration of the binder, which occurs as the silica hydrogel dries to form a glass-like bond. It is during this phase that final strength is achieved.

One of the major problems with the silicate/CO₂ process is the tendency to over-gas some parts of the core to ensure that all parts of the core are cured. Over-gassing leads to sodium hydrogen carbonate, observed as white crystals on the sand. Over-gassing leads to short shelf life and friable cores.

Proprietary silicate binders have application-specific ratios and are blended with special additives to improve performance:

- Lower (2.0–2.2/1) and higher (about 2.7/1) silicate / soda ratios are formulated for special applications to give, respectively, better storage or handling properties.
- Shakeout additives can be blended in at the sand coater or with the resin. These include: Sugars, calcium carbonate, phenol, zinc carbonate, carbohydrates, etc.

The silicate/CO₂ process is used by a relatively small number of North American nonferrous and steel foundries, but in Europe the process is more widespread. Ester cured silicate no-bake systems have better handling properties than gassed systems and have far greater acceptance in foundries.

Disadvantages – The "old" process deficiencies still plague this first cold box system:

1. Shakeout remains a problem although additives (kaolinite clay, sugar, etc.) help enormously.
2. Significant volumetric expansion of the coated sand occurs at ferrous casting temperatures, but might not be a problem in nonferrous casting applications.
3. Erratic core shelf life due to over or under-gassing.
4. Poor gas curability below 50°F.
5. A tendency toward gray iron penetration defects.
6. A silicate/soda imbalance that causes bench-life problems when a high proportion of reclaimed mechanically or thermally reclaimed sand is used. Water reclamation is very successful with silicate systems, but is rarely used because of water disposal issues.
7. Water-base washes are usable but must be applied with care to minimize water-related strength loss.
8. Relatively high resin level (1.5–2.5%) requirements result in poor flowability and blowability, and can yield casting blow-type defects unless the core is fully cured and vented properly.
9. Even at a relatively high binder level, silicate/CO₂ cores can be weak when stripped. Low strength, combined with their slow-to-cure nature (compared to the quick-to-cure organic systems), results in a long machine cycle.

In spite of what may sound like an overwhelming number of process problems, the silicate/CO₂ binder system has an even longer list of advantages including the following:

1. It is environmentally "clean."
2. It can be quick to gas, and the gas does not require scrubbing.
3. Raw materials are plentiful and relatively inexpensive.
4. Any type of mixer can be used.
5. It is fully compatible with wood, plastic, or metal patterns.
6. Stripping from the pattern is quite good.
7. It works well with green sand-backed molds.
8. Better water-based wash developments and application techniques have made them a viable option to VOC-troubled alcohol refractory coatings.
9. Resin from the system can be cleaned up with water.
10. It is able to eliminate hot tearing defects in some applications because of its unique softening in the 1,000°F range.
11. Waste sand disposal is relatively uncomplicated.
12. Binder systems modified for better coating characteristics and mixtures of borax, starches, and resin polymers have been introduced that improve shakeout, improve low temperature gassing capabilities and shorten gassing cycles.

Efforts toward further development of the silicate/CO₂ binder systems are ongoing. Those who currently use them are likely to continue doing so and in the future more people will examine it because of its outstanding environmental advantages.

Ester Catalyzed Silicate No-Bake

The silicate ester catalyzed no-bake system consists of a sodium silicate inorganic resin, a liquid organic ester catalyst, and usually, a multitude of additives to improve core/mold shelf life, aid in shakeout, minimize casting defects, and enhance casting surface finish.

The development of silicate no-bakes began in 1964. Various materials were known to gel sodium silicate, but most gelled the silicate too quickly to provide the work time needed for use as a foundry binder. A catalyst was needed with a predictable, latent delayed reaction.

Liquid Ester Catalysts – In 1968 organic liquid ester catalysts were introduced. Silicate ester catalyzed no-bake can be used for core making and/or molding. It is used for facing with a green sand backup. The system works well with virtually any silica sand, as well as with olivine, chromite and zircon sands.

It should be noted that some operation successfully utilize CO_2 to accelerate the no-bake cure.

Operational Aspects – No gasses or fumes are evolved during the reaction between sodium silicate resin and the ester catalyst. The principal gas evolved during metal pouring is steam, but additives incorporated into the silicate each generate specific products of thermal decomposition. In general, the amount of gas generated during this binder's decomposition is high, compared to that generated by other no-bakes.

Shelf Life – Storage life of the silicate ester molds and cores is longer than with the silicate- CO_2 system. As with any resin binder, humid conditions deteriorate strength, but up to three weeks of shelf life in normal conditions might be expected of cores and molds made properly with a silicate-ester no-bake system. Shelf life is shortened considerably when the system is under-catalyzed, if the sand moisture content is greater than 0.3%, when sand temperature is below 50°F when coated, or when sand beyond its usable bench life is used.

Resin – Several grades of unmodified silicate resin ("water glass") are available. These are based on different molecular ratios between the silicate (SiO_2) and the soda (Na_2O). Ratios that work best with the ester catalyst vary from 2.5–2.8/1. The higher the silicate/soda ratio, the more reactive the binder is with a given catalyst.

Because sodium silicate resin is caustic, hand and eye protection are recommended when handling the liquid resin. Although water products from the core and mold-making processes are nontoxic, their alkaline nature can often lead to waste-water and solid-waste disposal problems.

Although the cost of plain sodium silicate is relatively low, shakeout additives can be expensive. The ester catalysts, compared to the resins, are expensive. The moderate price of the resin system unfortunately becomes high in terms of coated sand cost because binder level normally is in the 1.5–2.5% range, based on sand weight.

Catalyst – Hardening of ester-catalyzed silicate takes place progressively as a result of hydrolysis and a saponification reaction of the ester curing agent.

After dispersion in the silicate binder film, the ester slowly hydrolyzes to form a weak acid and an alcohol. The weak acid reacts with the soda portion of the silicate binder to form a sodium salt. As that reaction progresses, the silicate-to-soda-ratio increases, resulting in gelation of the binder.

Many organic esters can be used to gel sodium silicate. The speed of the reaction depends on temperature, silicate/soda ratio, and the type of esters used. Three common esters provide a range of set times: fast-speed–glycerol diacetate (diacetin), medium-speed ethylene glycol diacetate (EGDA), and slow-speed–glycerol triacetate (triacetin).

Additives – Sodium silicate by itself has relatively poor shakeout characteristics that are influenced tremendously by the temperature increase that occurs during metal casting. It is generally necessary to add something to improve shakeout. Dry materials such as coal dust, ground coke, wood flour, ground pitch, and forms of sugar, alumina silicate, and blends of those materials have been used to improve binder breakdown.

These powders improve shakeout, but generally result in reduced strength, poorer core storage, and less coated sand flowability. When additives are used in any appreciable amount they usually necessitate additional binder. Alumina silicate clay (kaolinite) does not generate gas as the organic additives do, and it improves shakeout in aluminum and ferrous castings. Liquid carbohydrate polymers, a recent innovation, significantly improve shakeout and reclamation.

Metal penetration and poor surface finish may be more pronounced in silicate than in other no-bake processes or in green sand molds of the same sand grain fineness. This is because there is no smoke generated from binder decomposition to provide a carbon barrier between the sand and metal. Many foundries correct the problem by adding ground coal to the mix or by washing the core or mold surface. The use of 2% kaolinite clay has a filler effect that yields surface smoothness and possible elimination of refractory coating application.

Black strap molasses and proprietary additives have been used with greater success than powders. A 10% sugar addition to the resin is normal, but up to 30% may be used to insure maximum shakeout. The more sugar, however, the more gas and the higher the viscosity of the resin. A minimum binder level remains the best way to work toward acceptable shakeout.

High-Temperature Volume Changes – Silicate-bonded silica sands have unusually high expansion characteristics as they go from room temperature to molten metal temperatures. The expansion creates spalling that appears as penetration or roughness. It is explained as follows: Silica sand, as it is heated, undergoes the increase in volume expected of any solid material. However, the silica undergoes three distinct crystalline phase changes, each of which is accompanied by an abrupt increase in volume during the transition.

Conclusion – Because silicate no-bake is an environmentally clean, convenient and acceptable binder system for producing cores and molds, more foundries are considering its use. The liquid ester catalyzed silicate no-bake does not suffer from the strength, storage, and shakeout problems that may result from CO₂ over-gassing and under-gassing.

There is no doubt that the ester catalyzed silicate no-bake system works acceptably in many foundry operations. When a foundry has established a successful application for silicate no-bake, it is likely to remain a viable choice in that foundry. Unfortunately, not enough foundryman consider the ester-catalyzed silicate system when they evaluate binders.

CO₂ Cured Alkaline Phenolic Cold Box

The CO₂ alkaline phenolic cold box process was introduced in the 1980s. Its resin is similar to those used in the methyl formate-cured ester phenolic cold box process, but it has been modified to cure upon exposure to the CO₂ gas. It is a hybrid inorganic/organic binding system in which the organic phenol-formaldehyde resin is dissolved in an inorganic water solution of caustic potassium hydroxide.

The Core Making Process – Like other cold box processes, the sand is coated with the binder and compacted into a pattern. The coated sand can be blown in standard core machines using suitably vented high production tooling, or it can be hand rammed and gassed in relatively simple tooling. After compaction, the CO₂ is passed through the sand mix to cure the resin.

Correct core box rigging and the right gassing procedures can affect cycle speed and core quality. Since it is important for the CO₂ gas to completely disperse in the tooling and pass over the coated sand without dehydrating the resin, a technique known as "static pressure gassing" is employed. The tooling is rigged so that under optimum gassing conditions the CO₂ passes through the core box with a minimum of velocity and volume so that it cures the resin without drying out the coating.

Since the viscosity of the resin increases at low temperatures, sand temperatures above 60°F are recommended to facilitate efficient mixing. The bench life of the mixed sand is shortened by the evaporation of water from the coated sand mix. Sand temperatures above 90°F should be avoided because the sand mix will crust over and shorten bench life. The alkaline phenolic resin works with silica, lake, bank, and specialty sands such as chromite and zircon. High acid demand value sands can slow curing and negative acid demand sand can decrease bench life. The use of olivine sand, because of its alkalinity, is not recommended.

Table 1 lists typical performance properties and compares them to some other common cold box systems.

Process	Binder Level	5 Minute Tensile	Cure Time 20 lb.Core	Bench Life @ 90°F	Shelf Life of Resin	Moisture Resistance
CO ₂ Cured Alkaline Phenolic	3.00 %	65	75 sec	1-2 hrs	6 months	Good
Phenolic Urethane	1.30%	150	5-10 sec	1-2 hrs	> 1 year	Good
Methyl Formate Alkaline Phenolic	1.75%	94	10-15 sec	2-3 hrs	3 months	Good
Acrylic-Epoxy SO ₂	1.10%	140	5-10 sec	weeks	> 1 year	Good
Silicate CO ₂	3.50%	43	75 sec	1-2 hrs	> 1 year	Good

Table 1: Performance properties of common cold box systems.

Data is from testing done during the original publishing of this article. Lower binder levels in all resin systems are achievable today as a result of continued research and development.

Sand Mixing – Conventional mixing equipment is suitable for sand coating. However, some precautions must be taken to insure equipment compatibility with the high pH of the resin. Binder levels will vary with the type of sand and the handling strength required, but will typically be 1.0–2.5% based on a 50–60 AFS-GFN silica. Coated sand should be transferred with the least amount of aeration possible to avoid loss of the water carrier. The sand mix will remain useable for four hours or longer if the mix is kept covered.

Casting Properties – Alkaline phenolic resin hardens significantly during exposure to heat during the casting process. This secondary thermal cure results in excellent erosion and veining resistance. Despite the high typical binder level, gas evolution is comparable to other binder systems because of the partial inorganic portion of the resin system. The CO₂ cured alkaline phenolic binder system is low in carbon content so that lustrous carbon defects are rather unusual. Core collapsibility and shake out is better than the silicate CO₂ system, but not as good as phenolic urethane or acrylic-epoxy, cold box systems. The absence of sulfur and nitrogen make this CO₂ cured system compatible with a variety of alloys.

Reclamation – The CO₂ cured alkaline phenolic resin system is alkaline in nature, so care must be taken not to contaminate reclaimed sand coated with other binders with the alkaline reclaimed sand. Reclaiming the sand even for rebonding with the same CO₂ cured alkaline phenolics is difficult because of potassium salts present. These are not burned off in the casting process or by heat from thermal reclamation. The potassium coats the sand grains and even fuses with the silica sand at high temperatures, preventing efficient rebonding.

Summary – The advantages of the CO₂ cured alkaline phenolic system are environmental:

- Low odors during core making and during casting.
- Low in phenol and formaldehyde.
- Soluble in water.
- Gassed with CO₂, which has no irritating or objectionable odors so no scrubbing of core box exhaust is required.
- Low in Volatile Organic Compound (VOC) emissions.

Even with its environmental advantages the CO₂ cured alkaline phenolic system has not found widespread use because of its low handling strength and productivity.

Environmental Binder Improvements

In the past decade many improvements in sand binders have resulted in better quality, higher productivity, and have contributed to worker safety and environmental protection. The foundryman, in many cases, has profited from these improvements. These changes usually involve the elimination of wasteful practices and better control of system variables.

Lead-free Binders – The elimination of lead not only benefits workers, but has also made foundry waste sand safer and easier to reuse, reclaim and dispose. The most common use of lead in binders was in the alkyd-oil urethane no-bakes. As the dangers of exposure to even low levels of lead became evident it was obvious that its use could no longer be tolerated.

The paint industry found combinations of other metals to replace lead as a drying agent. Foundry resin manufacturers did the same, replacing lead with other dryers. Today all foundry binder systems are available in lead-free versions.

Solvent Replacement – Chlorinated solvents have come under regulatory scrutiny because of the inhalation exposure and ozone layer depletion. The most common use of chlorinated solvents is in the core and mold making area where it was used as a carrier for releases and as a fast drying solvent in adhesive pastes. Performance of the chlorinated solvents in these applications provided the advantages of fast drying without flammability considerations.

For release agents three alternate approaches have been successfully used for chlorinated solvent replacement:

1. Chlorinated hydrocarbons have been supplanted by fast evaporating flammable carriers. These products must be used with caution because of the common method of spray application coupled with the flammable nature of these products.
2. In addition to their familiar role as heated pattern water emulsion release agents, these agents have been more extensively applied to room temperature curing processes. Of course, drying the water, especially when ambient temperatures are low and the sand binder system is sensitive to moisture, are drawbacks.
3. Release agents without carriers, or those comprised of 100% active components are becoming more popular. When applied properly, active release agents eliminate the emission of VOCs and can be very cost effective. Only a very thin film of this type of release must be applied to the tooling in order for it to be effective.

The elimination of chlorinated hydrocarbons in fast drying core pastes has been accomplished by the use of fast drying flammable solvents.

The Formaldehyde Issue – Formaldehyde is present in many binder systems and exposure to it has been a concern. Binder suppliers have endeavored to reduce formaldehyde content and to reduce the emission of formaldehyde during binder curing.

No-bake binder systems often contain a phenol-formaldehyde resin, which contains residual free formaldehyde from the manufacturing process. This has been reduced to low levels through more efficient manufacturing processes and the use of formaldehyde scavengers in the formulations. These efforts have result in low formaldehyde or formaldehyde-free no-bake systems. Installation of ventilation near the mixing area or in the direction of the air flow away from workers is adequate to keep formaldehyde levels below permissible exposure limits.

Heat curing systems can generate formaldehyde levels above the permissible exposure limits during core making. Formaldehyde generated during heat curing polymerizes the resin system. As the hot cores are ejected from the tooling the volatile formaldehyde "boils" off from the core and can enter the work area. This can pose a problem unless captured or kept at a very low level.

Phenolic hot box binders present a formaldehyde problem because they require some formaldehyde in the system to cross-link and cure the binder.

Formaldehyde levels in the binder have been reduced down to about 2% with corresponding improvements in the catalyst technology. Originally phenolic hot box resins contained up to 10% free formaldehyde. This reduction has improved the working environment for core machine operators and has made possible the use of local ventilation. Hot box resin has since been replaced with warm box resin, where formaldehyde levels are below 1.0%.

Volatile Organic Compounds – VOCs are chemicals emitted into the atmosphere from evaporation during use or during the casting process. Reductions in VOC emissions can be achieved by formulating with solvent systems that are less volatile in the first place, and by raising the solids content of the binder to reduce the level of viscosity reducing solvents.

As these changes are made, pumping the resin solutions and mixing them together on the sand may require increased attention. However in addition to reducing the VOC emissions, in order to help meet regulatory demands, these low VOC systems can result in much lower odor at the mixer and less gas evolution during the casting process.

Photochemically Reactive Materials – A special classification of VOCs, designated as photochemically reactive materials, has become strictly regulated in some areas of the country. These materials contribute very strongly to the photochemical reactions that produce smog and ozone. A foundry should check with its resin supplier to determine if binders with reduced levels of photochemically reactive solvents are suitable for its operation.

Conclusion – Improvements in existing technologies will make a better working environment for foundry workers and lessen the environmental impact of using binders. New technologies and processes will be developed that will compete with established binders. These will require changes in core and mold making processes, but the result will be more efficient use of raw materials, a safer workplace, and less harmful emissions.

The Final Conclusion

This finally concludes what is undoubtedly the longest series ever written about foundry resin binder systems.

In retrospect there are a number of basic lessons to be learned from this compilation:

- **Binder Systems Are Really Part of a Process** – You don't make a core, mold, or casting with resin, machines or even people. You make them with the process.
- **Process Understanding Leads to Positive Change** – Only with a thorough understanding of the manufacturing process can positive change be accomplished.
- **Process Variation Can Be Controlled** – Any process can be controlled and operated efficiently if the operating parameters are identified, understood, and controlled.
- **Sand is a Very Significant Part of Any Resin Binder Process** – The foundryman needs to believe in sand segregation and appreciate the chemical and physical aspects that occur to the process due to changes in the sand system.
- **Ecological Process Considerations** – These have become, and will continue to be, the biggest driver in binder selection, application, and use.

The Ten Most Often Asked Questions About Resin Bonded Foundry Sands

The following questions were posed in the first article of this series. Although the answers given below respond to the questions, it must be understood that so many individual factors can affect the reply that each answer should begin with the phrase "in general." No two situations are precisely the same.

1. How much tensile do you need to make a good core or mold?

As little as you need to set the core without breaking it or having the mold surface erode during pouring. This is influenced by conditions external to the process, such as bench life, humidity degradation, core wash application, etc. Remember that green sand makes a lot of excellent quality castings with only one psi tensile strength, but 150 psi tensile value is the one most large operations use for phenolic urethane cold box. Large chunky cores can get away with as little as 50 psi, and some resin binders don't develop much more than that at reasonable binder levels. The minimum tensile value for the shell coated sand process is usually based on hot tensile values, and warm box systems often use the tensile value developed at a given period in the dwell part of the core making cycle. It should be emphasized that cold tensile values are indicators of handling strength and hot tensile values are a better indicator of performance during casting.

2. What causes the most defects?

Lack of process understanding and control, along with lack of attention to detail.

3. What are the most important control elements of a resin bonded sand process?

The control elements that deserve special control depend on the process:

- In no-bake bonded processes they are sand and pattern surface temperature and recognizing the usable work time.
- In cold box processes they are tooling design and rigging, as well as bench life.
- In heated pattern processes they are correct and uniform pattern temperature.
- With core oil they are excess oven temperature and humidity.
- With silicates they might be the proper silicate/soda ratio, along with sand and resin temperature control.
- With all the resin coated sand processes, proper coating, sand and resin calibration, sand segregation and bench life are primary and ongoing concerns.

4. Which binder system produces the best castings?

In simple terms, the perfect binder system is the one that will produce the casting for the least cost with the lowest scrap within the environmental limitations imposed upon the operation.

Since there is no perfect system, the eventual selection must be based on experience, existing equipment and rational judgement.

5. Which process is the easiest to use and the least expensive to run?

The process best understood by the foundryman is invariably the easiest for him to run. And obviously, the one that produces the casting for the lowest cost is the least expensive to run. So called "cheap binder systems" can produce "cheap cores and molds," but the finished casting cost might be relatively high because of productivity delays, excessive scrap, casting repair, environmental costs, product waste generation, and disposal costs.

In simple terms – the process that produces a casting at the lowest cost and with the lowest scrap rate (within dimensional tolerances and environmental limitations) is the one to use.

6. Which is the most environmentally friendly process?

Among sand binders, the term "inorganic" is synonymous with "environmentally friendly." It should also be understood that every resin bonded sand process in widespread use is environmentally acceptable when run correctly.

7. What kind of sand is best for a resin coated sand process and does reclamation change that?

"Best" is based on the particular, relative cost/quality and productivity expectations of the foundry. Specialty, non-silica sands fall into a unique classification.

A smooth round grain silica sand will develop the highest strength properties with the least amount of binder, but might produce so many expansion related defects that a coarse, angular sand could be best for that particular application.

Reclamation causes physical changes to occur to the sand since it smooths and rounds the surface of the grains. The surface chemistry of reclaimed sand is drastically altered by the resin, catalyst, and additives that coat both new and rebonded sand. Even if the coating is almost completely removed during every reclamation cycle, the chemistry of the reclaimed sand, along with various residuals in the sand, vary somewhat with each cycle.

8. Should a foundry use more than one binder system? If they use more than one, does that cause any special problems for the reclamation process or for the green sand system?

There's no question that running a single type of resin simplifies a lot of things, so that would be ideal. However, there are always specific instances in which a casting can be made more effectively with some other system. Also, the rigging of patterns owned by customers, availability of process equipment, and the experience of the individual foundryman may encourage a multi-binder operation.

9. What are the most significant resin related problems encountered in mechanical reclamation, thermal reclamation, and resin bonded sand reutilization? Which system is "best" from those standpoints?

In mechanical reclamation problems are based on an increase in the sand's Loss On Ignition (LOI), or the accumulation of some element that alters resin reactivity during curing.

In thermal reclamation it's probably the change in screen distribution or the accumulation of an inorganic material such as sulfur. The shift in acid demand value that occurs when sand is exposed to high temperatures during metal pouring is a concern in silica lake sands.

From the green sand reutilization standpoint, clay residuals might have a positive effect on water penetration into bricks, but might cause a need for more binder in other applications. Cured sands that have been exposed to casting temperatures are suitable for many reutilization applications. However, there is no doubt that the individual application and many other variables require that each application be evaluated individually.

10. Can green sand be processed so that it can be used to make resin coated sand cores and/or mold? Are there special adjustments that need to be made to the green sand to make this possible?

Clay bonded, durable silica molding sand can undergo a combination of mechanical and thermal processing so that it can be used to make resin bonded sand cores and molds with any binder system.

However, economic feasibility is still the barrier to widespread acceptance.

Reclaimed green sand should be thought of as "another type of incoming raw sand." In all green sand reclamation operations there might be adjustments made for new chemical and physical characteristics. However, there are no "special" adjustments typically made to the process.

References

All ASK owned figures

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