APPLICATION OF NO-BAKE SODIUM SILICATE BINDER SYSTEMS

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Abstract

The application of self-setting sodium silicate binder systems will support the metalcasting industry's long term goals in pollution prevention while producing high-quality castings with reduced environmental concerns. This paper includes a thorough review of the 1982 work as it compares to current systems and environmental standards, resulting in more up-to-date information with regard to emission characteristics, especially, CO and CO_2.

Keywords: sodium silicate, carbon monoxide, carbon dioxide, binder

Introduction

Self-setting sodium silicate binder systems have been utilized for many years. In 1982, I co-authored a paper that was chosen as the AFS Division 4 Best Paper entitled, "The Mechanism, Control and Application of Self-Setting Sodium Silicate Binder Systems" and was published in AFS Transactions. The summary of the 1982 paper made a prediction of what the future would hold for the self-setting metalcasting industry as follows:

The purpose of this paper is to explain the characteristics of the ester setting sodium silicate binder system. An understanding of this system should provide a valuable tool with which quality castings may be produced. As the need increases to improve the foundry environment, the use of sodium silicate binders will be increased. No other binder system available today is as ecologically acceptable. Developing technology will continue to improve the self-setting silicate binder system for practical foundry application.[1]

Since 1982, there have been many developments in inorganic binders systems, but not limited to sodium silicate as a binder. These systems were developed primarily to meet the environmental regulations that have changed since 1982. These inorganic binders systems today support the goals of a metalcaster to meet or exceed environmental regulations and produce high-quality castings. The AFS Pollution Prevention Committee 4-N compiles and develops technical data and other information on low emission technology, products and other pollution prevention methods for the metalcasting industry. The committee identifies data gaps and guides research on pollution prevention technology, products and practices for the metalcasting industry. Sodium silicate binder systems can be useful to metalcasters that are focused on pollution prevention methods.

Recap of the Original Paper

In the 1982 paper, the selection of the raw materials in the self-setting sodium silicate process was critical and was thoroughly investigated. Various ratios of sodium silicate were evaluated, and 2.4:1 to 2.6:1 ratios of silica to soda products were the preferred selection. The organic catalyst selected was a blend of triacetin and diacetin (the blend was dependent upon the curing time). Also, an organic additive (carbohydrate polymer) was used to improve the collapsibility (shakeout) of the cured sand after the metalcasting process was complete. To date, one of the limitations that still remains is the collapsibility characteristic of the inorganic binder systems when compared to the current organic binder systems commonly used in the metalcasting industry.

The factors that influenced the physical characteristics of the self-setting sodium silicate binder systems were:

- Temperature—as the temperature of the aggregate decreased, the curing rate of the binder system was slower than designed and if the temperature of the aggregate increased, the curing rate of the binder system was faster than designed.
- Hot Properties—the self-setting sodium silicate binder system had a significantly different expansion characteristic than exhibited in the carbon dioxide (cold box) sodium silicate binder system.
- Knockout Properties (shakeout)—the addition of an organic additive into the binder system improved the knockout properties.
- Sag Test and Through Cure—the addition of an organic additive into the binder system improved (reduced) the sagging characteristic of the binder system.
- Aggregate Selection—the selection of the aggregate was important (additional investigations were required to verify this information).

Recommended practices for the self-setting sodium silicate process:

- The recommended sand temperature was 70 to 85F (21–29.4C).
- Adequet curing of a prepared mold is critical. Often the surface of the mold appeared cured even though the bulk of the sand in the flask was not properly cured.
- Support rods utilized in molds or cores must be at the proper temperature to prevent uneven curing of the prepared sand, 70 to 85F (21–29.4C).
- The binder and catalyst pumps used to add the raw materials into the sand for preparation must be calibrated. Also, the sand addition weighing system must also be calibrated.
- The order of raw material additions is critical. The additives (carbohydrate polymer) must be added first, catalyst second, followed by the sodium silicate binder (Note: Do not premix the ingredients in advance).
- Selection of the mold or core wash for the face of the cured sand is critical. Follow the manufacturer's recommendations for selection and application methods.

The 1982 paper reviewed the application of the self-setting silicate binder system after the prepared molding/core sand was cured, see Table 1.

Update to Original Paper

This update will focus on the two summary conclusions and the investigations that have been completed since 1982. The two conclusions were:

1. *"The purpose of this paper is to explain the characteristics of the ester setting sodium silicate binder system. An understanding of this system should provide a valuable tool with which quality castings may be produced.*[2]

2. *As the need increases to improve the foundry environment, the use of sodium silicate binders will be increased. No other binder system available today is as ecologically acceptable. Developing technology will continue to improve the self setting silicate binder system for practical application.*[2]"

The first updated section of this paper will focus upon the improvement in the "binding" characteristics of the self-setting sodium silicate binder process which will contribute to the production of a "quality casting."

Improvements in Strength Characteristics of Self-Setting Sodium Silicate Binder Process

Historically, sodium silicate binder processes (cold box or self-setting) have had lower tensile strengths than traditional organic binder systems used in metalcasting. The first part of this paper will focus on the various aggregates and aggregate types that are used in North American metalcasting facilities. Then, the paper will focus on the differences between sodium silicate binders and traditional organic binders for environmental considerations. Since no-bake sodium silicate binders are utilized for molding operation in metalcasting, some metalcasters have discovered that the high tensile strength properties that are observed in the organic binder

Table 1. Summary of the Application of Self-Setting Sodium Silicate Binder System

Observation	Cause	Cure
Friable surface	Catalyst has partially cured the sand mixture prior to ramming	Select a slower catalyst
	Sodium silicate has partially cured the sand mixture prior to ramming	Selection of silicate (ratio)
	Rough pattern	Improve equipment
Sand sticks to pattern	Sand mixture has not cured completely	Allow mixture to stand in box longer, or select a faster catalyst
	Poor ramming	Improve ramming techniques
	Rough pattern	Improve pattern equipment
Sagging & through cure	Under cured sand mixture	Allow sand mixture to stand longer or select a faster catalyst
	Insufficiently mixed sand mixture	Improve mixing technique
	Insufficient binder level	Increase or decrease the binder level. Check metering equipment.
	Insufficient catalyst level	Increase or decrease the catalyst level. Check measuring equipment

systems are not necessary. For this reason, many environmentally conscious metalcasters accommodated the lower tensile strength properties with improved mold handling techniques to take advantage of the environmental benefits of the sodium silicate process. The improvement in physical properties as measured in compression and tensile strengths can be accomplished with a number of methods, one of which is a reformulation of the binders and additives. Additives are not included in this paper.

Figure 1 is an excerpt from the 1982 publication which demonstrated the effect that sand type has upon the tensile strength of the self-setting sodium silicate binder system.[3] The impact of the aggregate (silica sand) selection on the tensile strength properties was investigated in this update.

This update will cover the effect of silica sands on the binding characteristics of a self-setting sodium silicate binder system. Testing was completed on a 2.58:1 sodium silicate binder at a 3% addition into the selected silica sand and the catalyst was a 1.5:1 ratio triacetin to diacetin mixture at a 0.3 % addition. In this investigation, the analysis of the variation in silica sand types was completed without additives to enhance the physical properties (tensile and compression strength). The mixing techniques were completed along with the guidelines found in the 1982 paper.

Since North America is fortunate to have a large variety of high-quality silica sands available to the metalcasting industry, this investigation studied sands that possess an AFS gfn (grain fineness number) between 55 and 60 and are available to the metalcasting industry. Table 2 is a comparison of the selected silica sands use during the investigation.

The sand mixtures were prepared with the selected silica sands, binders, and activators. The compression strength specimens were prepared using 2" x 2" 3 ram specimens and

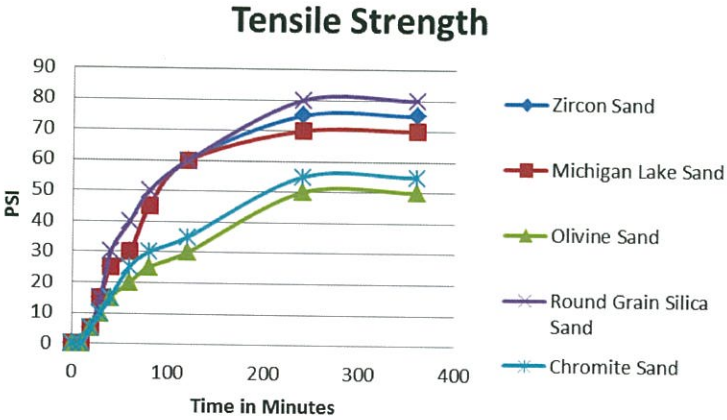

Figure 1. Tensile strength graphs for five different sands types from the 1982 work are shown.

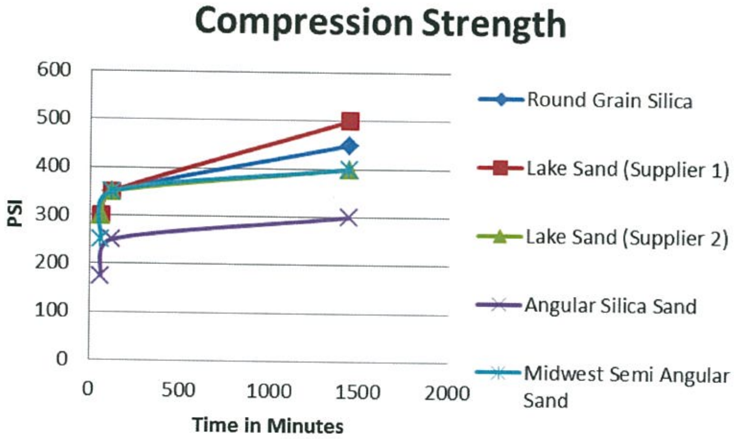

Figure 2. A comparison of the compression strength for the five sand types.

Table 2. Comparison of Selected Silica Sands

Properties	Round Grain Silica Sand	Lake Sand	Lake Sand	Angular Silica Sand	Midwest Semi Angular Sand
Screen Distribution	(percent) %				
#12	0	0	0	0	0
#20	1.4	0.1	0	0	0
#30	3.5	0.4	0.3	1	0.2
#40	17.6	2.2	1.9	5.6	5.3
#50	23.7	13.4	17.8	19.6	27.6
#70	23.8	50.8	42.7	34.9	34.5
#100	15.3	31.1	24.1	29.2	20.9
#140	9.9	1.8	11.9	8.9	8.8
#200	4.1	0.2	1.3	0.8	2.4
#270	0.7	0	0	0	0.2
Pan	0.1	0	0	0	0.1
AFS gfn	56	55	60	58	57
Surface Area (cm^2/gm)	128	137	150	225	120

the tensile strength specimens were prepared using a hand rammed standard "dog bone" shape. The density of the prepared specimens was monitored, the compression strength specimens were evaluated at 60 minutes, 120 minutes and 24 hours after the sand mixtures were prepared. The tensile strength specimens were evaluated every 5 minutes up to 120 minutes and then at 4 hours and 6 hours after the sand mixtures were prepared. A graphical representation of the compression strength and tensile strength properties can be found in Figs. 2 and 3.

From the data it can be observed that the self-setting silicate binder system investigated has shown that regardless of the sand shape the selected silica sand reacted with the catalyst and binder system in the same manner. The only observed differences are in the strength measurements. From this observation it can be concluded that the sand shape will have an impact on the ultimate binding properties. This can be measured through an evaluation of the density of the prepared specimens (Fig. 4). It can be concluded that (in general), as the prepared specimens weight decreased the compression and tensile strength properties decreased.

It can be concluded from this information that self-setting sodium silicate binders can be utilized to bond a variety of silica sand types. In actual metalcasting applications (and the 1982 paper), varying the quantity of binder and catalyst will result in increased compression and tensile strength properties. This update had the opportunity to compare specific silica sands as a comparison while the quantity of sodium silicate binder and catalyst were held constant. Since the addition of additives to the self-setting sodium silicate binders and catalyst have been known to increase strength properties (demonstrated in the 1982 paper), an understanding of this application can result in improved properties.

One of the best methods to understand the improvement in tensile or compressive strength properties of sodium silicate binder systems is to take a microscopic view of the "binder bridge" of the cured sodium silicate. Figure 5 is an example of a "binder bridge" of a weak (lower tensile strength) sodium silicate cured system with round grain silica sand.

It can be observed that at the contact points of the individual sand grains, the binder has formed a "cup" shaped impression where the adjacent sand grain was removed. From the tensile test performed on the cured sand mixture, the resulting tensile strength resulted in one-half of the desired property. In contrast, when the cured sand mixture was formulated with an additive into a sodium silicate bonder system, the tensile strength of the "binder bridge" increased. This improved sodium silicate binder system can be observed in Fig. 6. When microscopic analysis was completed, the fracture point of the cured sand with the increased tensile strength was as the cen-

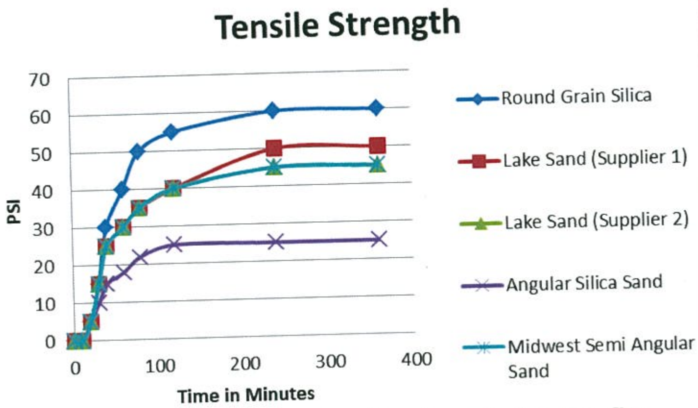

Figure 3. Comparison of tensile strength for the five sand types.

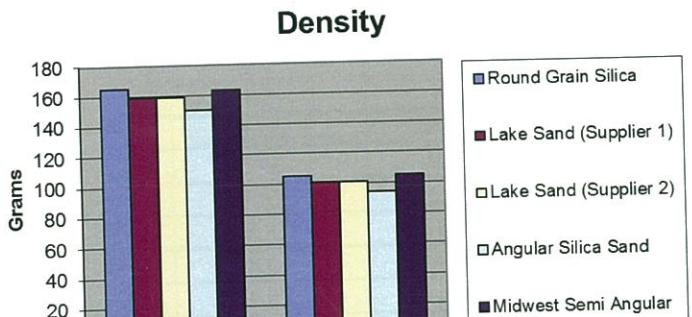

Figure 4. Density of the prepared specimens for the five sand types.

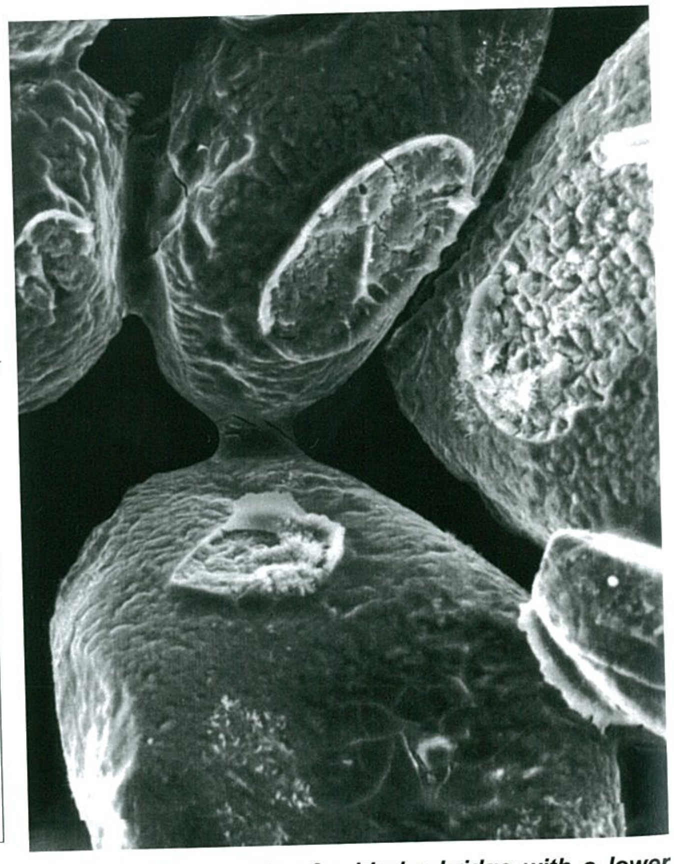

Figure 5. An example of a binder bridge with a lower tensile strength sodium silicate binder system on round grain silica.

ter of the bridge and not at the contact point of the sand grains (visually seen as the "cupping" characteristic in Fig. 7).

The dynamics in the improvement of the tensile strength of the cured sodium silicate binders (carbon dioxide or self-setting) has been improved through the addition of additives. The additives which are formulated into the sodium silicate binder systems vary with application and proprietary developments. These include both organic and inorganic materials at varying levels depending upon application and selection of the aggregate. The understanding and application of this technology has been one of the greatest leaps forward to the utilization of sodium silicate binder systems.

The second (updated) section will focus on the measurement and application of the self-setting sodium silicate binder process in the metalcasting application as an improvement in emission reductions at pouring, cooling, and shakeout when compared to organic binders systems.

Emission Reductions of the Self-Setting Sodium Silicate Binder Process

In the 1982 publication, one of the conclusions was:

As the need increases to improve the foundry environment, the use of sodium silicate binders will be increased. No other binder system available today is as ecologically acceptable. Developing technology will continue to improve the self setting silicate binder system for practical application.[4]

Since 1997, a number of environmental studies have been completed to understand the impact that core binding processes have on the metalcasting process at pouring, cooling, and shakeout. Environmental regulations have been driven to the forefront of the future demands of the metalcasting industry. Therefore, the future performance and expectations for any materials used in the metalcasting industry must meet current and future regulatory requirements. The Casting Emission Reduction Program (CERP) has been working on product and process developments to reduce emissions in green sand molding during pouring, cooling and shakeout.

Technikon operates CERP, a cooperative initiative between the Department of Defense (U.S. Army) and the United States Council for Automotive Research (USCAR). The members of the CERP Cooperative Research and Development Agreement (CRADA) include: The Environmental Leadership Council of USCAR (a Michigan partnership of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation); the U.S. Army Research, Development, and Engineering Command (RDECOM-ARDEC); the American Foundry Society (AFS); and the Casting Industry Suppliers Association (CISA). The U.S. Environmental Protection Agency (US EPA) and the California Air Resources Board (CARB) also have been participants in the CERP program and rely on CERP published reports for regulatory compliance data.

The primary objective of CERP is to evaluate materials, equipment, and processes used in the production of castings. Technikon's facility was designed to evaluate alternate materials and production processes that could achieve significant Hazardous Air Pollutants (HAP's) emission reductions. The facility's principal testing arena has been specially designed to facilitate the repeatable collection and evaluation of airborne emissions and associated process data. CERP has been evaluating sources of metalcasting air emissions since 1997. The program started with the approach of measuring the most common products utilized by the industry. This resulted in a database of "baseline" emission factors that could be utilized to measure lower emission products and processes as they have been introduced by casting suppliers. The supplier base has developed products and processes that fall into two categories; evolutionary and revolutionary.

The 1982 publication simply suggested that: *No other binder system available today is as ecologically acceptable.*[5] Since 1997, the CERP facility evaluated the emission characteristics of binder systems which included: CO, CO_2, HAP, POM (polycyclic organic matter), target analytes, and others. With this information available, a comparison of the ester-cured (self-setting) sodium silicate process can be completed. The first area to be reviewed was the emission characteristics of the self setting sodium silicate process for emitting carbon monoxide (CO).

Carbon Monoxide is classified as a criteria pollutant and therefore can trigger major source permitting, Part 70 – Title V, as well as major source requirements under the rules applying to "major modifications" (Attainment or Non-Attainment New Source Review). Emissions of CO_2 are not currently regulated, however state and federal initiatives are currently being considered that will likely result in future regulations requiring reporting and potentially regulating of these emissions. Metalcasting facilities installing new equipment, or making modifications to existing equipment that emit CO are subject

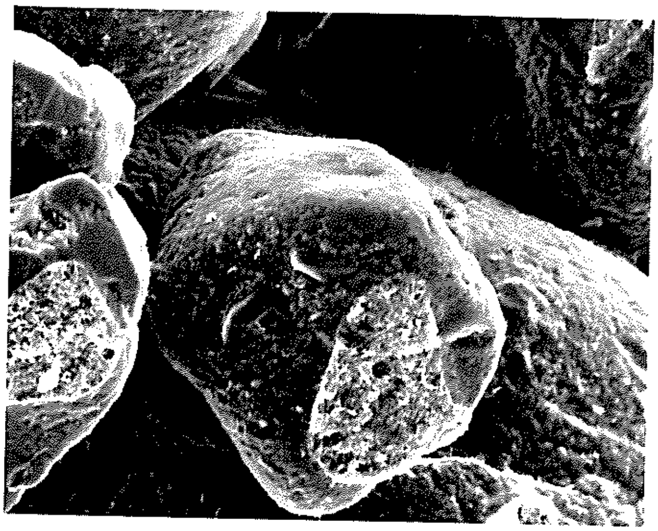

Figure 6. Higher tensile strength sodium silicate binder system on round grain silica.

to state and federal air permitting requirements.[6] A facility is "major" and subject to Title V air permitting requirements if it has the Potential to Emit (PTE) 100 tons of CO emissions or more per year. In addition, a facility in a CO attainment area with a CO PTE of greater than 100 tons per year is major for a New Source Review (NSR) permitting program. The NSR is a title applied to programs regulating the new construction of, and/or modifications to industrial sources which emit or will emit, air pollutants. Major source status under the Prevention of Serious Deterioration (PSD) is triggered at either 100 tons or 250 tons of CO emissions per year, depending on the facility's use of different types of metallic charge materials. The regulations requiring review under PSD went into effect in 1977 and the Title V permitting program was initiated in most states during the 1990's. EPA databases and reference documents do not quantify CO emissions from the pouring, cooling, and shakeout operations from metalcasting facilities. Historical research inquires in metalcasting emissions have focused on hazardous air pollutants and their variability in response to federal and state regulatory initiatives.[7]

At the CERP test facility a number of processes were evaluated for CO and CO_2 a comparison of the test results can be found in Table 4. A graphical representation of the comparison of the CO of the various no-bake binder systems evaluated can be observed in Fig. 7.

It can be observed from this data that the self-setting sodium silicate binder system (also referred to as no-bake) had the lowest amount of CO in pounds per ton of iron. As a comparison to the self-setting sodium silicate binder system, the cold box version of the sodium silicate binder system also had a low CO emission (Table 3) when compared to organic binder systems. Figure 8 is a comparison of this information.

In addition to the comparison of the binder systems, the researchers in the 2008 AFS publication investigated the source and contribution of materials that emit CO & CO_2 at pouring, cooling, and shakeout in the metalcasting process. The ester cured self-setting sodium silicate process was utilized to determine the impact that the carbon content of metals used in the process (and temperature) had on the emission of CO and CO_2. The specific comment from the 2008 publication was; "The major variables that will be needed to be investigated were the contributions of the carbon in cast iron to the emission levels of CO and CO_2, as well as the effects of metal temperature."[9] The resulting information can be found in Table 4 and in Fig. 9.

The AFS Transactions paper (08-031)[7] stated that the CO and CO_2 emissions testing at CERP included information that verified that the carbon in the molten cast iron contributes to the formation of CO and CO_2 in the plant. In order to tie this information (that utilized the self-setting sodium silicate binder process) into the final conclusion of the 2008 paper, additional work was reported. The conclusion (related to the sodium silicate as no-bake binders in this paper)

Table 3. CERP Iron CO and CO_2 Pouring, Cooling and Shakeout Stack Tests[8]

Published and Draft Tests CERP Test No.	Process Description	lbs/ton metal Test or Average CO	lbs/ton metal Test or Average CO2
GZ	Sodium Silicate (SS) Cores	1.40	4.06
FR	Phenolic Urethane (PU) Cores	1.82	NS
FQ	PU Coated Cores	1.99	NS
GG,FT,FR	PU Cores, Anti-veining	2.05	NS
GE	Coated ECOLOTEC CO_2 Cores	1.63	4.85
FU	Shell Cores	2.51	4.52
GH	Phenolic Hot Box Cores	1.94	5.23
GJ	Furan Warm Box Cores	2.04	4.32
GW	Iso-Set Cores	2.11	NS
GM	Oil Sand Cores	2.40	6.67
GX	Acrylic/Epoxy Cores	1.89	3.79
HD	Beach Box Cores	1.27	2.13
DG, DL, FP, DP	PU No-Bake Molds	4.77	NS
DW,DX,GI,EB	Furan No-Bake Molds	5.35	NS
DZ	Ester No-Bake Molds	4.32	NS
HT	SS, Ester Part 2 NoBake Molds	3.20	4.08
GN (Two Tests)	Shell Molds	10.80	70.13
GB	Greensand (GS) with Coated PU Cores	4.23	10.00
EA	GS with Seacoal Replacement and PU Cores	5.28	NS
GU,DR,DS,DT,DU	GS with SS Cores	4.71	NS
GQ, GU	GS Stars (High surface area)	5.51	13.33
GL	GS Stars, Graphite Parting	2.75	NS
FV	GS Stars, Graphite Parting	1.35	3.11

NS = Not Sampled

was that a major source of CO and CO_2 originates from the high metal temperature (Fig. 3 p.8),[7] not totally from the core binding process. The various no-bake processes contribute differently with the self-setting sodium silicate binder system having the lowest determined values of CO and CO_2. The emission level is dependent upon binder type, level and quantity of additives.

In addition to the previously reviewed information concerning the emission of CO and CO_2 during pouring, cooling and shakeout, the CERP testing facility also evaluated HAP, POM (Polycyclic Organic Materials), target analytes, and others. At the CERP testing facility "stack testing" was collected and analyzed for 68 target compounds using procedures based on the US EPA Method 18. Continuous monitoring of the total gaseous organic concentrations (TGOC) of the emission was conducted according to US EPA Method 25A. The HC (Hydrocarbons as Hexane) results represent the sum of all organic compounds detected and expressed as Hexane. The "Sum of Target Analytes" is based on the sum of the individual target analytes measured and includes selected HAP's (Hazardous Air Pollutants) and selected POMs listed in the Clean Air Act Amendments of 1990. The Sum of the HAPs is the sum of the individual target HAP's measured and included the selected POMs. (For addition information concerning information on CERP investigations visit the CERP website at: http://www.cerp-us.org/).

Since the 1982 publication suggested: *No other binder system available today is as ecologically acceptable*[11] the following information compares sodium silicates binders to other organic binder systems verifying the ecological advantages. Figure 10 compares two metal types (iron and aluminum) for HAP's from CERP test data on various core binding processes (organic and inorganic).

From the test data, the sodium silicate binder (labeled as "SS" in Fig. 10) in both iron and aluminum is lower than the "baseline" phenolic urethane binder system. In addition to the HAP's data collected at CERP another comparison that was completed during the same investigation compared the emission characteristics of benzene during pouring, cooling, and shakeout (also labeled as "SS" in the graph). Figure 11 is a graphical representation of the data.

A suggestion from the AFS paper that supplied the information for Figs. 10 and 11 stated: The progressive metalcasters of the future are going to have to do careful analysis as they

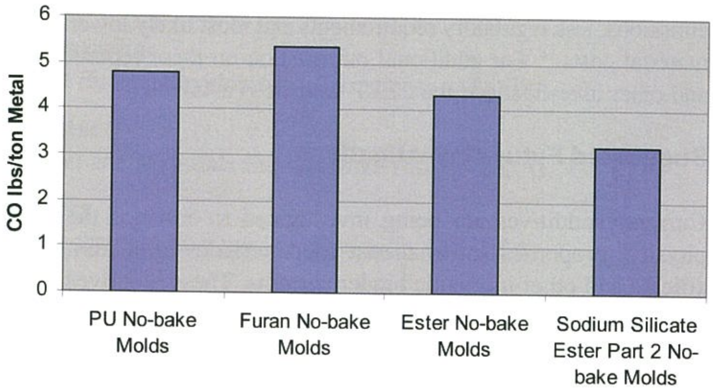

Figure 7. A comparison of CO levels in various molding processes.

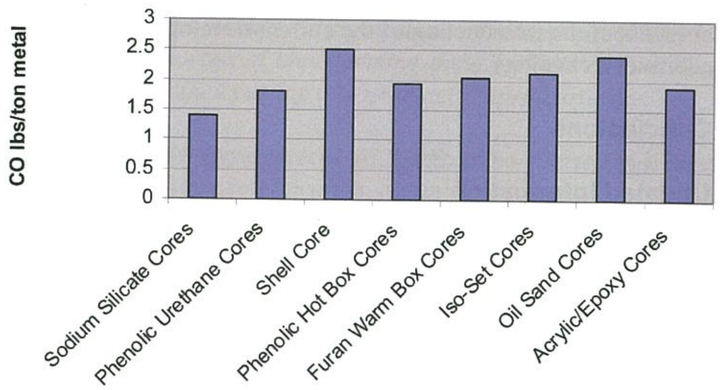

Figure 8. A comparison of CO in various core processes.

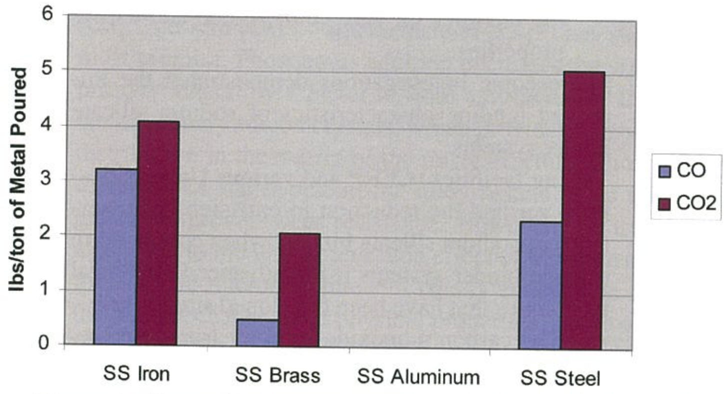

Figure 9. A graphical representation of CO and CO_2 results.

Table 4. CO and CO_2 Test Results (background corrected)[10]

CERP Test	Process	lbs/ton metal	
		CO	CO_2
GZ	Greensand No Seacoal, SS Core Iron	1.40	4.06
HT	Greensand No Seacoal, SS, Steel	0.51	1.93
HT	No-Bake SS with Ester Part 2, Iron	3.20	4.08
HT	No-Bake SS with Ester Part 2, Brass	0.49	2.07
HT	No-Bake SS with Ester Part 2, Aluminum	ND	ND
HT	No-Bake SS with Ester Part 2, Steel	2.31	5.07

ND = not detected

test and adapt environmentally friendly products and processes. Casting quality requirements and productivity issues will arise that will need to be solved. Once these issues are solved the metalcaster will reap the advantages of lower air emissions, less regulatory requirements and most likely lower material costs.[14] For additional information on these reports and other investigations the CERP website is available.

Suggested Future Investigations

Currently additives are being investigated to enhance the physical properties and shakeout characteristics of sodium silicate and other inorganic binder systems. These additives are currently focused on aluminum casting technology because sodium silicate and inorganic binders lend themselves very well to this technology. It will be important to investigate the emission characteristics at pouring, cooling and shakeout as their development continues. This paper was designed to review the applications of sodium silicate binders without the introduction of the current developments in additives technology.

Conclusions

Updated Information

- Higher tensile and compression strength properties can be accomplished through an understanding of aggregates.
  - Figure 1 showed a comparison of the tensile strength properties of varying sand types used in the North American metalcasting industry.
  - Figures 2 and 3 compared commonly used silica sands found in North American metalcasting facilities for both compression and tensile properties.
- Microscopic investigations demonstrated the improved binding characteristics of sodium silicate binder systems.
- Testing facilities (CERP and various Universities) have verified the reduction in emission characteristics of sodium silicate binders when compared to organic binder systems using advanced analytical techniques that have been developed since 1997.
  - The carbon monoxide level measured and reported in Table 3 (Fig. 7) showed that no-bake sodium silicate binders had the lowest level at 3.2 lbs/ton of test metal (average).
  - The lower carbon monoxide level was also observed in cold box sodium silicate binders as shown in Figure 8.
  - The comparison of both iron and aluminum has shown a reduction in HAP's when sodium silicate binders are used (Fig. 10).
- "The Foundry of the Future" will benefit from the development and application of inorganic binder systems (sodium silicate is one of the recognized processes).[15]

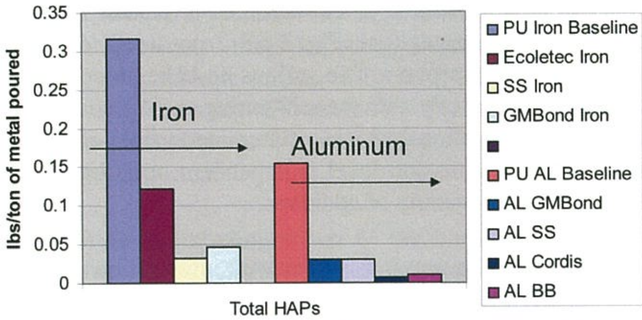

Figure 10. HAP Emissions from various core binding processes.[12]

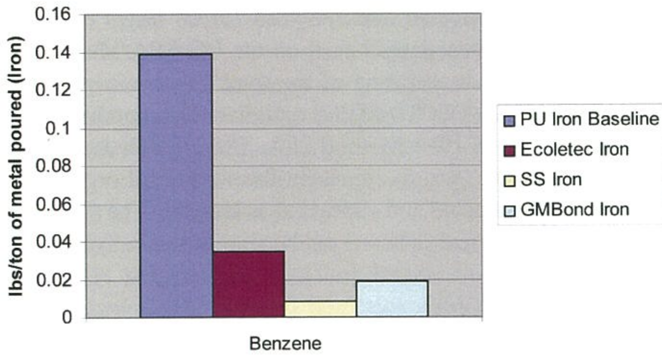

Figure 11. Benzene emissions from various cores binding processes.[13]

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