SUSTAINABLE CORE-MAKING IN FOUNDRIES: COLLAGEN BASED LOW-VOC EMISSION BINDER AND IMPROVED PROCESS TECHNOLOGY

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The work discussed herein covers the two essential materials that comprise foundry cores; sand and binder. As foundries seek to meet ever-more stringent environmental regulation, new production technologies must empower foundry operators to meet their environmental permit limits. Cores are an essential molding component for iron foundries, yet cores produce solid waste and air pollution. The sand used in cores contributes to the overall solid waste stream from a foundry, whereas core binder degradation during metalcasting is a significant contributor to air emissions. Thus, the focus of the work herein focuses on process technology to reduce solid waste and a material technology to prevent air pollution generated from iron foundry cores.

The wet reclamation of waste foundry green sand for use as core sand has been demonstrated with applied ultrasonics, cavitation, settling (UCS) and advanced oxidants (AO). This technique reclaims sand, clay and coal from waste green sand while operating at near ambient temperature. The research presented herein evaluated a pilot-scale system that reclaimed waste green sand. AO treatments have been established as an effective way to diminish VOC emissions during mold cooling and shakeout. The sand reclaimed by this pilot system was the aggregate in cores that were utilized in full-scale production at Neenah Foundry, Neenah, WI.

Foundry core binders are conventionally petroleum based. These petroleum based binders are major contributors to air emissions during the casting process. The research herein conceptualized a novel collagen/alkali silicate core binder. This core binder demonstrated favorable thermal characteristics, while also resisting core distortion at high temperatures better than conventional foundry binders. During pyrolysis emission
characterization using thermal gravimetric analysis with mass spectrometry (TGA-MS), this core binder did not form many of the compounds attributed to emissions from conventional core binders. Through FTIR and XPS analysis, there is carboxyl stretching that occurs between collagen and alkali silicates. The carboxyls present in collagen are converted to carboxylates in the presence of alkali silicates, as demonstrated by XPS with a sub-peak appearing at 289 eV (for carboxylate) and a subdued sup-peak appearing at 288 eV (for carboxyl).

Further, this novel core binder was appraised during full-scale tests at Hitachi Metals Automotive Components (HMAC), Lawrenceville, PA; and could make good castings. When using 0.98% solid binder content of collagen-with-alkali silicates, the cores obtained a tensile strength of nearly 300 psi, which is 80 psi greater than 1.1% phenolic urethane cores. Also, this novel collagen and alkali silicate binder can produce castings without veining, without the use of anti-veining additives. These cores also exhibited excellent shake-out properties as the cores were removed in one-half the shake-out time as the conventional shake-out process at HMAC.
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“Do not rebuke a mocker or he will hate you; 
rebuke a wise man and he will love you.

Instruct a wise man and he will be wiser still; 
teach a righteous man and he will add to his learning.”

- Proverbs 9:8 and 9:9
Chapter 1

General Introduction

In the United States, manufacturing is a critical economic sector. Manufacturing accounts for over 11% of the U.S. Gross Domestic Product by producing $1.58 Trillion worth of goods in 2009 (BEA, 2010). While all manufacturing sectors are essential, one critical sector is the U.S. metalcasting industry. In the United States, during 2008, there were 2,170 foundries that produced 10.8 million tons of castings, of which 7.1 million tons were ductile or gray iron castings (Modern Casting, 2009). It should also be noted that in 2007, the United States produced 11.8 million tons of castings and during both of these years ranked second in world casting production (Modern Casting, 2009). Castings are an integral aspect for manufacturing, as they are employed in 90% of manufactured durable goods and capital equipment (AFS, 1998).

Since adopting the Clean Air Act in 1990, U.S. industries have worked to quantify, identify and subsequently reduce hazardous air pollutants (HAP’s) and volatile organic compounds (VOC’s). In 2005, there were slightly less than 16 million tons of VOC’s emitted from various sources within the United States. Industrial processes were the fourth largest contributing source, emitting over 1.6 million tons of VOC’s (EPA, 2009). In foundries VOC’s are emitted from multiple processes, including; melting metal, mold and core making, pouring, cooling and shakeout (PCS), core and mold coating, shot blast and grinding operations, release agents and pattern sprays. For a typical foundry, emissions from pouring, cooling and shake-out (PCS) are responsible for at least 90% of organic HAP’s produced. PCS emissions are largely attributed to the petroleum based core binders.
Most foundries utilize green sand molds for forming castings. Green sand is a mixture of silica sand (85-95%), bentonite clay (4-10%), carbonaceous materials such as bituminous coal (2-10%), and water (2-5%) (EPA, 1998). Green sand is formed using patterns to form the exterior geometry for castings. However, when more complex castings are produced, cores are the objects within a green sand mold that provide the geometry for cavities within castings. For example, when casting an engine block, the cavities that house pistons would be formed by placing cores in the mold. These cores are typically comprised of 97-99% new silica sand and 1-3% binder. Cores are conventionally bound together with petroleum based binder systems, such as phenolic-urethane or furans. When exposed to molten iron the core binders will briefly withstand high temperatures so as to provide the essential geometry for the casting, yet will breakdown and thermally degrade as the casting cools. Since the petroleum based binder thermally degrades, the sand used in the core will be easily removed from the casting cavity during shake-out, yielding sand for the green sand system. This core sand will replace waste green sand that is conventionally discarded in landfills. It is important to note that since the petroleum based binder thermally degrades, the products formed during core binder degradation can account for as much as 30-70% of a foundry’s VOC emissions (Glowacki et al., 2003) as well as emit numerous Hazardous Air Pollutants. Further, when conventional phenolic urethanes are used as binders to make cores, the binders are cured with triethyl amine (or other amines) which also emit noxious fumes during production.

It is well documented that foundry VOC emissions increase proportionately with an increase in core-loading (Goudzwaard et al., 2003, Glowacki et al., 2003). For
example, the total VOC emissions without cores and with advanced oxidation (AO) from Neenah foundry were measured to be 0.22 lb/ton of metal poured, yet an average core loading increased the total VOC emissions to 0.45 lb/ton of metal poured and a ‘heavy’ core loading increased the total VOC emissions to 1.4 lb/ton of metal poured (Glowacki et al., 2003). Considering other foundries and non-AO production lines, VOC emissions attributed to cores can vary from 30-70%, dependent on core loading (Glowacki et al., 2003). Recent work has indicated that VOC emissions for a collagen core binder are 70-80% less than phenolic-urethane (Wang et al., 2007).

Manufacturing facilities have the potential to produce air pollution, water pollution, and solid waste. Manufacturers are strained by regulatory compliance, and they must invest capital to meet environmental permits. In 2005, all U.S. manufactures spent $20.7 Billion on pollution abatement operating costs and $5.9 Billion in pollution abatement capital costs. In 2005, the U.S. foundry industry as a whole spent $453.1 Million on pollution abatement operating costs and an estimated $100 Million on pollution abatement capital costs. Iron foundries (NAICS 331511) spent $317.1 Million on pollution abatement operating costs. The $317.1 Million in abatement operation costs can be divided by media, with $187.3 Million spent on air abatement, $39.1 Million spent on water abatement and $90.6 Million spent on solid waste abatement (U.S. Census Bureau, 2008). Thus, air emissions represent nearly 60% of an iron foundry’s pollution abatement operating costs, while solid waste represents nearly 29% of abatement operating costs. With this in mind, the work herein focuses on devising new core binder technologies that limits air pollution and reuses solid waste streams. Within foundries, these opportunities for pollution prevention and sustainability actually offer considerable
financial advantages to the foundries, while helping to meet ever-more-stringent environmental regulations.

1.1 Sand Reclamation – Waste Sand to Core Sand

When silica sand is processed through a green sand system, the individual grains accumulate a carbonaceous deposit that originates both from the core binder residue and also from pyrolysis products that redeposit on the sand grain surface. This hydrophobic coating weakens the sand-water bonding mechanism that is necessary for mold integrity (Granlund and Swenson, 2002, Hoyt, 2001, Wang et al., 2006). This hydrophobic coating must be removed for successful sand reclamation. In conventional operations, when a large foundry that melts between 200,000 and 300,000 tons of iron per year does not practice sand reclamation, the foundry will consume 50,000 tons per year of silica sand, 20,000 tons per year of clay and 6,000 tons per year of coal (Land et al., 2002, Neill et al., 2001).

Conventional sand reclamation processes include: mechanical, wet and thermal sand reclamation systems (Wright, 2001, Granlund and Swenson, 2002, Hoyt, 2001). Wet systems have conventionally only been used for green sand reuse, mechanical systems for core sand reuse and thermal systems can be used for both core or green sand. Mechanical systems use abrasion to physically force residual material from silica grains (Wright, 2001, Granlund and Swenson, 2002, Hoyt, 2001). The clay coating, dust and silica fractures from the mechanical or pneumatic system are removed by the dust collection system (Wright, 2001, Granlund and Swenson, 2002, Hoyt, 2001). Thermal reclamation systems heat sand to between 930°F and 1475°F (499-802°C) (Wright, 2001), where organic matter from core sand is removed via combustion and the resultant
calcined layer on the clay surface is removed mechanically. However, calcium bentonite and sodium bentonite are destroyed at 850°F and 1150°F (454-621°F). This means that thermal reclamation removes organic residue but destroys valuable active clay in the process. Also, thermal reclamation requires much energy. Further, as of March 21, 2011, the Environmental Protection Agency has classified thermal reclamation units (used for reclaiming spent foundry sands) as solid waste incinerators (EPA, 2011). Mere conventional wet reclamation has been used, but has been deemed unfavorable due to high water volumes that must be treated, inadequate quality of product – specifically high MB (methylene blue) clay residual, and excessive floor space requirements (Wright, 2001, Granlund and Swenson, 2002, Hoyt, 2001, Fox, 2009).

In previous Masters of Science work, by this author (Fox, 2009) waste green sand and baghouse dust were processed by the Pneu-Col™ system, produced by Furness-Newburge (Fox et al., 2007, Fox et al., 2008a). Waste green sand with 7.9% MB Clay and 3.8% LOI (loss on ignition) could be reclaimed from this ultrasonic-cavitation device with a product that contained 0.4-1.0% loss on ignition, 0.4-0.6% MB Clay, and a variable yet controllable grain fineness number (GFN). Also, advanced oxidants (ozone and hydrogen peroxide) significantly diminished the LOI that was contained in product sand. In previous collaborative Penn State work by Cannon, Voigt and others AO-DBW (Advanced oxidant-dust-blackwater) systems were a proven method to process baghouse dust while reducing clay demand 20-35% (Neill et al., 2001, Land et al., 2002, Cannon et al., 2000, Goudzwaard et al., 2003). AO addition is an effective method that reduced VOC emissions in an operating green sand system (Goudzwaard et al., 2003). Also, the effluent AO-blackwater from an ultrasonic-cavitation device has been found to diminish
clay demands and decrease VOC emissions in a green sand system (Neill et al., 2001, Land et al., 2002, Cannon et al., 2000, Goudzwaard et al., 2003). The conventional AO-BW technologies required large settling tanks, until the advent of the Pneu-Col® system. Thus, the heavily clay and coal-loaded blackwater effluent from the Pneu-Col® process would be reintroduced in the sand cooling and pre-blend processes. The results from this earlier work showed that this sand reclamation process could restore waste green sand to a quality that would be suitable for green sand make-up, while achieving simultaneous clay and coal recovery (Fox et al., 2007). The work herein, demonstrates that the Pneu-Col® process can be utilized to recover waste green sand for use as core sand.

1.2 Conventional Core Technologies

The internal molding materials for casting technologies are referred to as ‘cores’. Cores provide molding for internal geometries in castings. For example, when casting an engine block cores provide the cavities for engine pistons. These internal molds are conventionally comprised of sand (97-99%) and an adhesive (1-3%). A few different sand types are used including chromite, olivine, zircon and silica sand (AFS, 1987). Silica sand is the most predominately-used sand type and utilized for the work herein. Silica sand is a material that possesses favorable thermal stability for cores, which is also used as green sand in external molding processes. Conventionally, sand is mixed with an adhesive and then compacted into a mold, commonly referred to as a ‘core box’ or ‘core mold’. During high volume core production, the sand and adhesive mix is compacted or ‘blown’, with compressed air into the core box, cured and the cores are removed. During low volume core production, the sand and adhesive mix is compacted into the core mold
by hand, cured and the cores are subsequently removed. The adhesives that bind together sand for cores are referred to as ‘core binders’.

There are a wide variety of core binders that have been used both historically and currently. Historically-used core binders, that are not-often used currently include: rubber cement, chemical cements such as oxychloride, sodium silicate, vegetable oils, mineral oils, marine oils, resins, rosin oils, pitch, sulfite binders, protein binders, molasses, cereal binders, Portland cement and clays (Dietert, 1966). Currently, core binders mostly consist of engineered petroleum based adhesives. Among the petroleum based core binders, the most common binder systems are the shell process, the furan process and phenolic urethane/or phenolic variations. The shell process utilizes sand grains which have been pre-coated with a resin, so the sand is ‘dry’ when compacted into a mold, and then is heated in the mold to solidify the resin adhered core. The furan process consists of furfuryl alcohol, plus various chemicals including phenol, phenolic derivatives, urea, formaldehyde and other additives – which are cured by using an acid catalyst. Multiple phenolic binders are utilized for core binders, however the phenolic urethane cold box process will be used as an example herein as this is the most common process. The phenolic urethane cold box (PUCB) process was first implemented in foundries in 1968. Three chemical parts comprise the PUCB system. The first part is a modified liquid phenolic resin, the second part is a modified polymeric isocyanate and the third is a gas catalyst. The gas catalysts are generally tertiary amines, such as triethylamine (TEA) or dimethylethylamine (DMEA). In general, TEA has less odor but is still pungent, while DMEA cures cores faster than TEA (AFS, 1987).
These phenolic urethanes must withstand the high temperatures experienced during the metalcasting process. For example, molten iron is poured into molds at temperatures between 2500-2800°F (1371-1537°C). However, phenolic resins are considered ablative materials (Lampman, 2003). Ablative objects are materials that have been reinforced with high-temperature stable materials, which erode slowly in a process known as ablation. The charred layer which has a substantially greater thermal resistance than the unused material erodes very slowly and as it erodes a new char layer is formed maintaining the thermal resistance. Ablative materials are commonly used for applications such as rocket exhaust nozzles, heat shields for space re-entry or decking on offshore oil rigs (Strong, 2008, Bahramian et al., 2009, Acharya et al., 2007). Rocket propellants can impart temperatures exceeding 3600 K to rocket nozzles (Acharya et al., 2007). Ablation occurs when there is significant heat flux across a surface, such as a rocket nozzle, causing material regression which has been determined to be linearly related solely to heat flux for a particular rocket nozzle (Kuo et al., 2009).

Inorganic/Organic composites, specifically silicate/polymer composites have demonstrated exceptional ablative properties (Bahramian et al., 2009, Vaia et al., 1999). In fact, silicate/polymer composites have slowed mass loss by an order of magnitude (Vaia et al., 1999). An essential element for ablative materials is that they must exhibit strong adhesion between the organic matrix and the filler materials – forming a solid composite (Torre et al., 2000). Thus, phenolic urethanes and sand form a composite that is believed to ablate, due to the nature of the chemical structure. Additionally, thermally stable materials generally have the following chemical structure characteristics; high bond strength, high activation energy, stabilization by resonance or inductive effects,
high heat capacity, absence of easily degraded atomic structures, intermolecular interactions, backbone stiffness and steric hindrances (Strong, 2008). Among these characteristics, intermolecular bond strength between aromatic rings and double bonded carbon to oxygen bonds hold the highest bond energy for organic bonds. Thus, by being both ablative and aromatic in chemical structure, phenolic urethanes form a core binder that performs well during the metalcasting process.

1.3 Collagen Binder

Collagen material has been used as an adhesive for 4000 years. Collagen is most commonly extracted from either animal hides or bones, with different processes used for each source. Hide glues are generally soaked in lime, then the collagen is extracted through hydrolysis to form gelatin, adjusted with acid, filtered, vacuum-evaporated, dried and ground to the desired particle size. Whereas, bone glues take bones which are crushed, treated with dilute acid then the collagen is hydrolyzed and extracted under pressure. The extracted glue is concentrated through vacuum-evaporation, drying and grinding. The adhesive characteristics are dependent upon the collagen source and processing techniques (Pizzi and Mittal, 2003).

Collagen is the fibrous protein that strengthens skin, tendon and bones; and this triple-helical material has tensile strength greater than steel. The individual collagen strands are 200-500 nm long; and each polypeptide strand is comprised of a three amino acid repeating sequences. These typically include a repeating sequence similar to X-Y-Glycine; where Glycine comprises about 34% of collagen, while the “X” and “Y” include proline (12%), alanine (10%), hydroxyproline (10%), glutamic acid (7%), or other amino acids (Palfi et al., 2007; Eastoe and Leach, 1958, Stainsby and Courts, 1958). Gelatin
also contains these same amino acid sequences, but is generally a shorter polypeptide strand.

The strands in the helical structure, tropocollagen, are held together and aligned by hydrogen bonds (Kawahara et al., 2005). Any given hydrogen bond is relatively weak, but when the strands are helically coiled around one another, the cumulative bonding strength can be considerable. However, as water penetrates the fibers, the hydrogen bonds are broken and this is what causes collagen to soften in water. At temperatures exceeding 60°C, these hydrogen bonds are broken, forming denatured collagen (i.e. gelatin); and this is when the polypeptide chains are free in solution (Kawahara et al., 2005). The adhesive that forms is hydrolyzed collagen (or gelatin), through the reaction below (Hofmeister, 1878 and Eastoe and Leach, 1958):

$$\text{C}_{102}\text{H}_{149}\text{O}_{38}\text{N}_{31} + \text{H}_2\text{O} \rightarrow \text{C}_{102}\text{H}_{151}\text{O}_{39}\text{N}_{31}$$

As an adhesive, these polypeptide chains re-align as water evaporates, and this causes a network of random alignments through hydrogen bonds (Stainsby and Courts, 1958). Denaturing is an essential step to maximize and enable the use of collagen as an adhesive.

Collagen can be denatured thermally or chemically. Depending upon purity, collagen typically denatures at around 60°C in water (Kawahara et al., 2005). However, this can also be achieved at lower temperatures with urea or acetic acid (Stumpe and Grubmüller, 2007 and Tiller et al., 2001). Urea acts as a chaotrope and disrupts the hydrogen bonds between polypeptide strands. However, it must be noted that a relatively high concentration of urea is required to completely denature collagen (Muthuselvi et al., 2008). While collagen may be denatured by different methods, hydrogen bonds still randomly re-assemble to provide toughness. Yet these hydrogen bonds are reversible as
they can be broken by hydration, thus the stability and durability of collagen adhesives is
poor when exposed to moisture.

Collagen was commercially developed and patented by General Motors (GM) as a
low emission binder under the name GMBond®, which was then sold to Hormel Foods.
The original patent for a collagen derived, gelatin core binder expires on January 28,
2013 (Siak et al., 1994). Hormel Foods currently holds the license to market GMBond®
as a low emission core binder system; their marketing brochure claims that foundry
emissions can be reduced by up to 95% for monitored VOC’s and HAP’s. The Casting
Emission Reduction Program (CERP) established baseline values for phenolic-urethane
binder; and they observed that when exposed to molten iron, collagen binders release
82% less benzene, 95% less phenol and 95% less naphthalene emissions than
conventional phenolic urethane. Additionally, the ambient-temperature tensile strength
for collagen for the marketed process is 230 psi. Tests for linear thermal expansion
reached a maximum at 0.8% expansion for GMBond® at 1500°F (816°C), while
phenolic-urethane binder exceeds 1.7% expansion at 1500°F (816°C) (Hormel Foods,
2005). Furthermore, Hormel markets the superior shakeout properties of GMBond®
(Hormel Foods, 2005). Despite the favorable air pollution prevention and mechanical
properties innate to collagen binder, it is believed that collagen alone does not withstand
molten metal erosion. Work presented later in this dissertation examines collagen
erosion due to molten metal exposure, which confirms that collagen alone does not
withstand molten metal erosion. Thus, it is necessary to increase the thermal stability of
collagen so that it provides necessary serviceability in casting applications.
The formation of covalent intermolecular cross-links between collagen molecules is an effective way to increase the mechanical integrity and stability of collagen (Chen et al., 2005; Charulatha et al., 2003; Usha et al., 2000; Wollensak et al., 2003b, Kato et al., 1989). Cross-linking also increases resistance to water solubility (Gupta et al., 2002, Pizzi and Mittal, 2003). Cross-linking has been reported to occur with tannic acid, a citric acid derivative, glutaraldehyde, formaldehyde, paraformaldehyde, hexamethylene-tetramine, glyoxal and dialdehyde starch (Heijmen et al., 1997, Taguchi et al., 2006, Harriger et al., 1997, Pizzi and Mittal, 2003). Also, some degree of moisture resistance occurs with metallic salts, such as ferric chloride or alum (Pizzi and Mittal, 2003).

Cross-linking with glutaraldehyde, formaldehyde and other aldehyde containing compounds occurs between the amine group on the collagen and the carboxyl on the aldehyde (Kanth et al., 2009). The electrons shared with a nitrogen atom by two individual hydrogen bonds in collagen are replaced by a double bond to a carbon atom in the aldehyde group (Kanth et al., 2009). Tannic acid cross-links form between collagen with hydrogen bonds, from the hydrogen in the hydroxyl group in tannic acid with the nitrogen in the amine group in the collagen (Heijmen et al., 1997). Cross-linking between a citric acid derivative and collagen occurs between the active ester groups and the amine groups in collagen (Taguchi et al., 2006). The establishment of cross-links does improve thermal integrity for collagen glues (Kanth et al., 2009, Samouillan et al., 2003).

To date there has been minimal research into the extent that collagen glues are able to withstand excessive thermal stress. Dry protein denatures at temperatures between 180°C and 250°C (Samouillan et al., 2000). Samouillan et al. studied the
effects of various cross-linking agents through thermally stimulated currents (TSC).

These authors indicated the importance to differentiate denaturing and degradation. Their results indicate that collagen alone denatures at 215°C, whereas gluteraldehyde cross-linked samples “shifted to higher values”. Their conclusion is that the collagen is stabilized by the aldehyde cross-links. Wang and Cannon et al., (2007) have performed TGA-MS (Thermal gravimetric analysis with mass spectrometry) where significant mass loss appears to begin at around 250°C, indicating that when collagen begins to denature that soon thereafter it also begins to thermally degrade.

Silicate and collagen hybrids may offer a way to improve thermal integrity. Sodium silicate is a water based adhesive that is extremely stable at high temperatures. There has been recent work investigating how collagen and silicates interact by Eglin et al. 2006 and Coradin et al. 2004. Collagen and silicates interact and form cross-linked structures through nucleation and expand through self-assembly at ambient temperature (Eglin et al., 2006). Also, these authors and others have found that the interaction between collagen and silicates is pH dependent. The crosslinking formation between collagen and silicates at room temperature has been studied by Coradin and others for biological application (Allouche et al., 2006, Eglin et al., 2005, Eglin et al., 2006, Coradin et al, 2005a, Coradin et al., 2005b). Further work has been performed by Gelinsky et al. (Gelinsky et al., 2008) creating a mineralized collagen; which was made by precipitating amorphous calcium phosphate from a collagen solution as the collagen fibrils were reassembling. These cross-links have the potential to increase the binding strength at room temperature (Gonzalez et al., 1991, Coradin et al., 2002), and high
temperature. For the work herein, we aimed to discern whether these cross-links could be maintained at elevated temperatures that occur when binders are exposed to molten iron.

1.4 Hypotheses

There are two overarching hypotheses herein, which can improve foundry core-making by; reduced material consumption and a low-emission collagen based core-binder technology. A collagen binder alone does not withstand molten metal without significant erosion due to the low bond energy of the hydrogen bonds. More specifically, the overarching hypotheses for this work are:

(A) Reclaimed sand, processed by the Pnue-Col\textsuperscript{TM}, can significantly reduce new core sand consumption, while yielding necessary casting quality.

(B) Optimized inclusion of cross-linking compounds, such as alkali-silicates, will enhance a collagen based binder resistance to high temperatures and molten metal erosion, due to improved bonding energy.

1.5 Scope of Work

The motivation behind this research is to reduce both solid pollution and air pollution, without incurring additional pollution abatement costs, yet hopefully reducing overall operating costs. Specifically, this work will focus processing spent foundry sand for use as core sand and the development of a novel collagen based core binder. This dissertation will have seven chapters. Each chapter (other than chapter 7) will be able to be read without support from previous chapters, with the goal of improving information transfer to readers. Chapter 1, is the general introduction, and Chapter 7, is the conclusion. Chapter 2, focuses on green sand processing for re-use as core sand. Chapter 2, is a multi-author work published in the American Foundry Society...
Transactions, which has been approved for use herein. John Fox is the first author, while Fred Cannon, Robert Voigt, Jim Furness, Frank Headington, Dave Coan and Steve Lewallen all contributed as co-authors. Chapter 3, transitions to core binders by detailing binder development methods and initial results which guided subsequent work. Chapter 4, examines the thermal mechanical properties of a novel collagen/alkali-silicate binder. Chapter 4 is a multi-author work, John Fox is the lead author, while Fred Cannon, Nicole Brown, He Huang and Jim Furness all contributed as co-authors. Chapter 5, focuses on the emission characteristics of a novel collagen/alkali-silicate binder as compared to conventional binders, while gleaning information about the chemical interactions between collagen and silicates when utilized as a core binder. Chapter 6, provides a practical full-scale test using 250 cores produced with the collagen/alkali-silicate binder in a casting demonstration at Hitachi Metals Automotive Components (HMAC). Chapter 7 is the concluding chapter.
1.5 References


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Chapter 2

Waste Green Sand to Core Sand Reclamation, Demonstration via Casting Study, with Simultaneous Clay Recovery via a novel Ultrasonic-Cavitation System

Abstract

A novel waste green sand reclamation process employed cavitation, advanced oxidants, sonication and settling to remove carbonaceous pyrolysis products from silica grains, and segregated the silica sand from the clay, coal and carbonaceous products. The authors employed this reclaimed silica sand to prepare cores that were used in full-scale foundry operations. These cores employed 0-100% reclaimed sand that was made-up with 100-0% new sand; and the mixture was bonded with 1.3% phenolic urethane core binder. The waste green sand initially contained 7.5% MB (methylene blue) Clay, 3.4% loss on ignition, and 66 grain fineness number; and following reclamation, the silica sand hosted a mere 0.2% MB Clay, 0.3-0.6% LOI, 16% #140 mesh sand, and 60-68 GFN. Cores that contained 40-100% reclaimed sand and 1.3% binder, yielded dog bones that offered 140-210 psi tensile strength; whereas 100% new sand yielded 210-240 psi tensile strength. When the cores that contained 40-100% reclaimed sand were employed at full-scale to make a complex slip yoke, they yielded the same high quality castings without veining as did cores that contained 100% new silica sand; as discerned by inspectors visually inspecting castings while they did not know which was which.

1. Introduction

In previous work, the authors evaluated an ultrasonic-cavitation device for reclaiming waste green sand (Pneu-Col® system, produced by Furness-Newburge, Versailles, KY). From those tests, results indicated that the ultrasonic-cavitation device
could produce silica sand that contained 0.4-1.0% loss on ignition, 0.4-0.6% MB Clay, and a variable yet controllable grain fineness number (GFN). Also, advanced oxidants (ozone and hydrogen peroxide) significantly diminished the LOI that was contained in product sand. Results indicated that the LOI trended upward with increased GFN. The results from this earlier work showed that this sand reclamation process could restore waste green sand to a quality that would be suitable for green sand make-up; and this meant that a foundry could operate with considerably less sand purchasing and wasting (Fox et al., 2007). The objective of the work herein was to yet further test the hypothesis that the reclaimed sand could also be used for making cores.

When silica sand becomes processed through a green sand foundry system, the sand grains accumulate a carbonaceous deposit that originates both from the core binder residue and also from pyrolysis products that redeposit as a “raincoat” on the sand grain surface. This hydrophobic carbon ‘raincoat’ weakens the sand-water-clay bonding mechanism that is necessary for mold integrity (Wright, 2001, Wang et al., 2005, Wang et al., 2006). As presented earlier, AO-DBW (Advanced oxidant-dust-blackwater) systems are a proven method to process baghouse dust while reducing clay demand 20-35% (Neill et al., 2001, Land et al., 2002, Cannon et al., 2000, Goudzwaard et al., 2003). Furthermore, AO addition is an effective method that reduced VOC emissions in an operating green sand system (Goudzwaard et al., 2003). Also, the effluent AO-blackwater from an ultrasonic-cavitation device has been found to diminish clay demands and decrease VOC emissions in a green sand system (Neill et al., 2001, Land et al., 2002, Cannon et al., 2000, Goudzwaard et al., 2003).
As a yet further extension of this earlier work, the authors sought to discern whether the reclaimed sand from an ultrasonic-cavitation system could reclaim sand to core sand quality. New core sand requirements are generally more stringent than green sand specifications. Specifically, typical specifications indicate that new core sand should contain no more than 0.3% clay or oxides. The sand should exhibit neutral pH, while the acid demand value should range from 0-5 and acceptably ranges from 5-20. Round grains are most favorable for strength while sub-angular grains are best for veining control. The preferred grain fineness number (GFN) typically ranges from 50-60, while it is reported that the resin demand increases with an increased GFN. Particular consideration for a wet sand reclamation system pertains to the moisture content: the optimum should remain below 0.10% moisture, while the useable sand may contain up to 0.25% moisture. Sand grain temperatures of 70-80°F offer the most favorable coring properties, while 50-105°F grain temperatures are usable (Ashland, 1999).

The objectives herein have been to; (a) further evaluate ultrasonic processing techniques with regard to output quantity and quality, by determining the more favorable conditions for preparing core sand. (b) Test how rinsing, drying and de-dusting effects the sands’ MB Clay, LOI, and grain fineness number; and how they affect the tensile strength and casting quality of cores that are made with this reclaimed sand.

2. Materials and Methods

2.1 Waste Green Sand

Prior to pilot-scale operations, the authors filled twenty 55-gallon barrels with waste green sand from an operating line from Plant 2 at Neenah Foundry, Neenah, WI. We processed this sand throughout the summer; and it contained on average 7.5% MB
Clay, 1.57% Volatiles, 3.38% LOI, 3.34% Fines and an AFS washed grain fineness number of 66 (see Table 2.1). Additionally, the sand classified as a 4-sieve sand across the 50, 70, 100 and 140 US Mesh screens (see Figures 2.2 and 2.3).

### Table 2.1. Waste Green Sand Tested Parameters, Prior to Processing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB Clay</td>
<td>7.50 ± 0.39</td>
</tr>
<tr>
<td>Percent Volatiles</td>
<td>1.57 ± 0.12</td>
</tr>
<tr>
<td>LOI</td>
<td>3.38 ± 0.14</td>
</tr>
<tr>
<td>Percent #140</td>
<td>12.95 ± 1.92</td>
</tr>
<tr>
<td>Percent Fines</td>
<td>3.34 ± 0.86</td>
</tr>
<tr>
<td>GFN</td>
<td>66 ± 3</td>
</tr>
</tbody>
</table>

### 2.2 Sand Reclamation System

The demonstration-scale sand reclamation system included a 400 gallon tank, an 11.5 HP submersible pump, two sand settling tubes and connecting piping (see Figure 2.1). Each of the settling tubes hosts two pneumatically operated diaphragm valves, one at the top, which regulates sand conveyance into the tubes; and the second at the bottom, which regulates the discharge of processed sand. The two settling Tubes are referred throughout as Tube A, the first tube in flow direction; and Tube B, the second tube in flow direction. The system’s 400 gallon tank was filled with 360 gallons of water. This reclamation system has been described with greater detail in Fox et al., 2007. Tests were operated at 0.5 lbs/gal, 1.0 lbs/gal and 1.5 lbs/gal as further discussed herein. During continuous operation, the authors maintained solids content at the set points (0.5 lbs/gal to 1.5 lbs/gal) by adding waste green sand make-up while product reclaimed sand was discharged from the tubes. The degree of cavitation controlled slurry flow rate and system pressure (Table 2.2). Advanced oxidants were maintained with sparged Ozone ($O_3$) to saturation levels; and the Hydrogen Peroxide ($H_2O_2$) addition maintained a 500 ppm $H_2O_2$ dose. Other advanced oxidants became generated as products from the
continuous ultrasonic irradiation reacted with the O₃ and H₂O₂ (Suslick, 1989).

Moreover, the ultrasonic irradiation induced the carbon residues to become released from the sand grains surfaces.

Figure 2.1. Sand Reclamation System flow schematic, showing the pump, tank, induced cavitation, ozone, H₂O₂, ultrasonic irradiation and flow across Tube A and B.

Sand reclamation operations employed several distinct sequences; and water circulation via pumping occurred during all these sequences. The sequences included; (1) water filling, (2) waste sand addition, (3) the wash sequence, during which the top and bottom diaphragm valves were closed for 0 or 10 minutes, (4) the settling sequence, during which the top valves were opened and the bottom valves remained closed for 4 or 10 minutes, (5) the discharge sequence, during which the top valves were closed and the bottom valves were opened for 1 minute, and (6) the clean-out cycle, when all water and sand residue was rinsed out of the storage tank and piping so as to prepare for the next trial.

The first set of exploratory trials employed batch operations, for which the authors employed all six sequences for each batch (see Table 2.4 below). For the next set of trials, operations proceeded in pseudo-continuous mode. Specifically, for each round
of testing, the authors added 360 gallons of water into the system; and this water remained within the system for ten cycles of washing, settling and discharge (unless otherwise noted). Also, we added 360 pounds of waste green sand into this storage tank at the beginning of these rounds (when operating at 1 lb/gal), and then we made up with another 70-80 pounds of more waste green sand each time we discharged 70-80 pounds of product reclaimed sand. The settling Tube A, with it’s 6” diameter and 4’ length could hold up to 60-65 pounds of wet product sand per discharge event, while the 4” diameter Tube B could hold 10-15 pounds.

For all sand reclamation operations, the authors employed saturated ozone levels, 500 ppm hydrogen peroxide, ultrasonics, and continuous water recirculation via pumping at 27 or 61 gpm.

### Table 2.2. System Flow Rate and Pressure when Operating Under Intense and Moderate Cavitation Conditions

<table>
<thead>
<tr>
<th>Degree of cavitation</th>
<th>Flowrate</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intense Cavitation</td>
<td>27 gpm</td>
<td>30 psi</td>
</tr>
<tr>
<td>Moderate Cavitation</td>
<td>61 gpm</td>
<td>22 psi</td>
</tr>
</tbody>
</table>

#### 2.3 Sampling and Testing

The authors sampled settled sand from both Tubes A and Tube B during each test protocol, unless otherwise indicated. The sample collection containers were a five gallon bucket (for Tube A collection) and a 2.5 gallon bucket (for Tube B collection), and after filling these with discharged product sand, the authors completely mixed the bucket contents, then gathered a grab sample. Sand test parameters included MB Clay, percent volatiles, loss on ignition and AFS washed sieve distribution. These tests all were performed in accordance with AFS standards (AFS, 1988). This is with the exception that for MB Clay testing, the sonication time was 10 minutes, as opposed to the 7 minute
AFS standard. Additional information regarding testing procedures can be found in Fox et al., 2007.

2.4 Sand Rinsing

In order to rinse the discharged sand, we first weighed the desired amount into a 2.5 gallon bucket. Next, we added the specific water volume to the bucket in order to achieve the desired sand-to-water rinsing ratio. In order to rinse this reclaimed product sand, the authors mixed a prescribed weight of product sand with a prescribed volume of water in a 2.5 gallon bucket. We completely mixed the sand-water blend, so as to create a slurry for 30 seconds. This simulates the anticipated full-scale rinsing process that will be required for core sand reclamation. Next, we prepared the sand for drying by decanting the rinse water from the bucket. Also, the authors performed additional decanting by dropping the bucket 10 times from a height of 3-6 inches; and we anticipated that this would simulate the anticipated compression that would occur during full-scale filter press operations.

2.5 Drying and De-Dusting

Drying and de-dusting was performed in a proto-type fluidized bed drier, which was comprised of an 18”x18”x3’ box with a sloping bottom (by Furness-Newburge). Hot air at 300-320°F migrated upward through this bed at 25-35 cfm; and the bed was partially filled with one part wet sand plus one part previously dried sand. Within this chamber, the hot air plus previously dried sand caused the wet sand to fluidize and to dry, without clogging or channeling. Upon reaching less than the desired 0.1% moisture, the sand was sampled as necessary and stored in a sealed 55-gallon barrel for core sand use.
2.6 Core Production

The authors produced cores at the full-scale production level that facilitated a complex slip yoke casting that posed particular difficulty. Our rational was that if the reclaimed sand could be used in this difficult casting that exhibited a high propensity towards veining, then the reclaimed sand could be used for most any core situation. The core resembled a tapered cylinder; and this posed similar casting difficulties as for a step cone (Giese and Thiel, 2007). The processed sand and yet un-used sand were weighed and added to the full-scale 250 pound mixer. All cores were produced with 1.3% phenolic-urethane binder and treated in a cold-box process. Additionally, an anti-veining additive was added at 4% during the mixing process, unless otherwise listed. We then delivered the newly mixed sand to a core production station, where the sand was molded into the desired cores, treated in the cold box process, and labeled to identify the reclaimed sand content. Once prepared, the cores were stored for no more than 72 hours before we used them in the full-scale production.

2.7 Core Sand Tensile Strength

Dog bones provided tensile strength measurements; and these appraised a range of reclaimed sand percentages. Following sand and phenolic-urethane mixing, we removed a grab sample from which we formed dog bones. The dog bones were treated with a tertiary amine gas in the cold box process. Once produced, the dog bones were tested for tensile strength within 9-17 minutes after being produced. Dog bones were tested in triplicate, with the average and standard deviation reported herein.
2.8 Casting Study

The authors selected a product based on the difficulty in casting and propensity to vein. The product cast was a truck slip-yoke which has a core shaped as a tapered cylinder. Between 20-25 slip yokes were produced for each reclaimed sand percentage appraised. After the castings left shake-out, but before they entered the cleaning room, the castings were removed from the full-scale process for evaluation. A numeric ranking system was established similar to that reported by Giese et al., 2007. For this particular casting study, the yokes were isolated by their identification based on reclaimed sand content and anti-veining additive presence or absence. Then, 15 slip yokes were selected randomly. Next, three individuals who work within the quality assurance department at the supporting foundry ranked the castings. This evaluation was operated as a blind study; i.e. the three individuals did not know the percent reclaimed sand in the corresponding core when they ranked the casting quality. To prevent any bias from occurring during the evaluation, the authors herein did not participate in the evaluation. The three individuals participating in the study were not informed until after the study as to the specific variations in production methods.

The quality checkers ranked the castings relative to both veining and burn-in, on a 1-5 scale, with subjective ratings as associated with numeric values as shown in Table 2.3.
Table 2.3. Numerical Value Associated with the Subjective Rating for the Casting Quality Analysis

<table>
<thead>
<tr>
<th>Numeric Value</th>
<th>Subjective Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Very Poor</td>
</tr>
<tr>
<td>2</td>
<td>Poor</td>
</tr>
<tr>
<td>3</td>
<td>Average</td>
</tr>
<tr>
<td>4</td>
<td>Good</td>
</tr>
<tr>
<td>5</td>
<td>Excellent</td>
</tr>
</tbody>
</table>

Similar to the work done by Giese et al., 2007, the rankings were not quantified by a strict measurement of veining or burn-in, but the rankings were simply subjective, as the evaluator determined quality. This enabled rapid analysis across a wide range of reclaimed sand variations, with 15 castings from each sample group evaluated. Evaluation results were tabulated from all three evaluators, for each sample group; with the average and standard deviation calculated. Therefore the lowest rated castings would be less desirous, whereas a higher rated casting would be an excellent product that could be sold with typical cleaning room final preparation.

3. Results

3.1 Effect of Solid Content on Output and Sand Quality

The authors first set out to determine which operating conditions would be most favorable for continuous full-scale operation, relative to sand-to-water ratio and settling time. Thus, factorial batch tests compared results with 0.5, 1.0 or 1.5 pounds of sand per gallon of water, and with 4 or 10 minutes settling time. The solid slurry content was evaluated at 0.5, 1.0 and 1.5 pounds of sand per gallon of water. In these tests, the discharge material from Tube A and B was combined, manually mixed, and sampled. As shown by the Table 4 data, the percent LOI was lower at 1 lb/gal than at 0.5 lb/gal; and
the percent #140 with 1 lb/gal and 4 minute settling time was nearly as much as with 0.5 lb/gal. Also, the authors observed that the 1 lb/gal slurry exhibited less clogging and equipment wear than did the 1.5 lb/gal operation. For these reasons, the authors selected the 1 lb/gal conditions in subsequent trials.

Table 2.4. System Output and Sand Parameters when Operating in Batch Mode at 0.5, 1.0 and 1.5 pounds/gallon with Settle Times of 4 or 10 minutes (Mixture of Tube A and B Product Sand)

<table>
<thead>
<tr>
<th>Operation (lbs/gallon)</th>
<th>Settle Time (min.)</th>
<th>% MB Clay</th>
<th>% Volatiles</th>
<th>% LOI</th>
<th>Percent #140</th>
<th>% Fines</th>
<th>GFN</th>
<th>Average Tube A output (lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>10</td>
<td>0.51 ± 0.04</td>
<td>0.80 ± 0.03</td>
<td>1.2 ± 0.03</td>
<td>11.80 ± 0.24</td>
<td>1.35 ± 0.19</td>
<td>63 ± 0.3</td>
<td>48</td>
</tr>
<tr>
<td>0.5</td>
<td>4</td>
<td>0.53 ± 0.01</td>
<td>0.72 ± 0.03</td>
<td>0.87 ± 0.01</td>
<td>11.35 ± 0.35</td>
<td>1.18 ± 0.02</td>
<td>63 ± 0.2</td>
<td>39</td>
</tr>
<tr>
<td>1.0</td>
<td>10</td>
<td>0.43 ± 0.02</td>
<td>0.51 ± 0.01</td>
<td>0.55 ± 0.01</td>
<td>5.71 ± 0.05</td>
<td>0.54 ± 0.09</td>
<td>56 ± 0.03</td>
<td>59</td>
</tr>
<tr>
<td>1.0</td>
<td>4</td>
<td>0.49 ± 0.01</td>
<td>0.51 ± 0.04</td>
<td>0.57 ± 0.04</td>
<td>7.13 ± 0.07</td>
<td>0.47 ± 0.03</td>
<td>59 ± 0.01</td>
<td>60</td>
</tr>
<tr>
<td>1.5</td>
<td>10</td>
<td>0.44 ± 0.00</td>
<td>0.48 ± 0.03</td>
<td>0.52 ± 0.00</td>
<td>5.78 ± 0.02</td>
<td>0.40 ± 0.04</td>
<td>56 ± 0.02</td>
<td>65</td>
</tr>
<tr>
<td>1.5</td>
<td>4</td>
<td>0.61 ± 0.01</td>
<td>0.52 ± 0.00</td>
<td>0.61 ± 0.04</td>
<td>7.22 ± 0.02</td>
<td>0.53 ± 0.08</td>
<td>59 ± 0.02</td>
<td>63</td>
</tr>
</tbody>
</table>

3.2 Controlling Sand Output Through Cavitation

It had previously been determined that the degree of cavitation affected the GFN, the percent #140 retained and the percent loss on ignition (Fox et al., 2007). Specifically, as the GFN and #140 rose, the LOI trended upward. Furthermore, moderate cavitation produced coarser sand with lower LOI, whereas intense cavitation produced finer sand with slightly higher LOI. As portrayed in that previous work, an important balance was to retain as much #140 sand as possible, while segregating out the clays (MB Clay) and
carbon (LOI). This required balance, because the clays and carbon settled only slightly more slowly than did the #140 sand.

3.3 Pseudo Continuous Operation

For the work herein, the authors sought to discern how these parameters would trend when the reclamation system operated in pseudo continuous mode, while retaining the same 360 gallons of water, but while also frequently adding new waste sand as product reclaim sand was discharged. These trials employed a 7 minute wash sequence and 10 minute settling sequence; and Round I employed moderate cavitation, while Round II employed intense cavitation.

As shown by Round I and II results in Table 2.5, the percent MB clay and percent LOI essentially reached steady-state level within 4-7 discharge cycles; while the percent #140 sand and other sieve classification values reached steady state within 7 discharges. When intense cavitation was employed, the Tube A sand character trended toward 0.5% MB clay, 0.5% LOI, and 7-8% #140 sand, while the Tube B sand character trended toward 0.5% MB Clay, 0.65% LOI, and 9-10% #140 sand. When moderate cavitation was employed, these parameters trended similarly; and with slightly higher #140 sand (11-12%) in Tube B. With intense cavitation (Round II), many of the parameters trended similarly as for moderate cavitation, although the Tube B grain fineness numbers trended higher than for the other three conditions.
Table 2.5. Product Sand Properties for Pseudo-Continuous Operations: Same 360 Gallons of Water Used Through Each Round of 10 Discharges, 1 lb sand/gal Water; Make-Up Waste Sand Added After Discharge; Saturated Ozone; 500 ppm H₂O₂, 10 Minute Settle Time

<table>
<thead>
<tr>
<th>Round</th>
<th>Wash Time (Minutes)</th>
<th>Cavitation Intensity</th>
<th>Discharge</th>
<th>MB Clay</th>
<th>Percent Volatiles</th>
<th>Percent LOI</th>
<th>% Size #140</th>
<th>% Fines</th>
<th>Grain Fineness Number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>I</td>
<td>7</td>
<td>Intense</td>
<td>1st</td>
<td>0.41±0.02</td>
<td>0.50±0.02</td>
<td>0.61±0.07</td>
<td>0.74±0.04</td>
<td>0.62±0.06</td>
<td>1.13±0.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4th</td>
<td>0.42±0.01</td>
<td>0.40±0.01</td>
<td>0.49±0.07</td>
<td>0.62±0.03</td>
<td>0.53±0.07</td>
<td>0.78±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7th</td>
<td>0.48±0.01</td>
<td>0.46±0.01</td>
<td>0.36±0.00</td>
<td>0.56±0.01</td>
<td>0.46±0.00</td>
<td>0.69±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10th</td>
<td>0.54±0.01</td>
<td>0.50±0.01</td>
<td>0.46±0.03</td>
<td>0.51±0.03</td>
<td>0.57±0.04</td>
<td>0.64±0.03</td>
</tr>
<tr>
<td>II</td>
<td>7</td>
<td>Moderate</td>
<td>1st</td>
<td>0.34±0.02</td>
<td>0.37±0.01</td>
<td>0.41±0.01</td>
<td>0.38±0.03</td>
<td>0.48±0.03</td>
<td>0.44±0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4th</td>
<td>0.40±0.01</td>
<td>0.34±0.01</td>
<td>0.38±0.06</td>
<td>0.38±0.00</td>
<td>0.42±0.06</td>
<td>0.44±0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7th</td>
<td>0.42±0.01</td>
<td>0.44±0.03</td>
<td>0.30±0.03</td>
<td>0.44±0.06</td>
<td>0.41±0.01</td>
<td>0.47±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10th</td>
<td>0.58±0.01</td>
<td>0.41±0.02</td>
<td>0.45±0.01</td>
<td>0.57±0.01</td>
<td>0.48±0.03</td>
<td>0.67±0.04</td>
</tr>
<tr>
<td>III</td>
<td>10</td>
<td>Moderate</td>
<td>1st</td>
<td>0.47±0.01</td>
<td>0.39±0.01</td>
<td>0.35±0.10</td>
<td>0.49±0.01</td>
<td>0.45±0.07</td>
<td>0.52±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4th</td>
<td>0.41±0.01</td>
<td>0.36±0.01</td>
<td>0.37±0.01</td>
<td>0.42±0.06</td>
<td>0.49±0.01</td>
<td>0.52±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7th</td>
<td>0.40±0.01</td>
<td>0.45±0.01</td>
<td>0.43±0.04</td>
<td>0.35±0.01</td>
<td>0.47±0.01</td>
<td>0.44±0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10th</td>
<td>0.56±0.01</td>
<td>0.50±0.01</td>
<td>0.46±0.01</td>
<td>0.43±0.01</td>
<td>0.56±0.03</td>
<td>0.52±0.03</td>
</tr>
</tbody>
</table>
The authors employed the AFS sieve classifications of the Round I reclaimed sand from discharge cycles 1, 4, 7 and 10; and mathematically computed a composite of these. For the Round I trials, these composite sieve analyses appeared as in Figure 2.2, while those for the Round II trials appeared as in Figure 2.3. As show, when intense cavitation was employed, Tube A product had less #140 and #100 sand than did the waste green sand that it originated from, and more #70, #50 and #40. In contrast, the Tube B product had nearly as much #140, more #100, and the same #70, 50 and 40 as did the waste green sand. Thus, when employing intense cavitation, Tube A accumulated more of the coarser material, while Tube B more of the accumulated finer material; and this is what one might anticipate with Tube B following Tube A in flow sequence. When moderate cavitation was employed in Round II (Figure 2.3 data), the trends were similar but less pronounced.

The authors next sought to discern whether pseudo-continuous operations could achieve the same results even if the wash cycles were eliminated. If so, this could save processing time during ultimate full-scale operations. These trials appear as Round III in Table 2.5; and they engaged moderate cavitation. As shown, the same favorable MB Clay, LOI, and #140 sand was achieved in these trials as had been achieved with their counter parts that had employed the 7 minute wash sequence with moderate cavitation (Round II, Table 2.5). As similar to before, the MB Clay became 0.4-0.5%, the LOI became 0.5%, and the 3140 sand was 6-8% from Tube A and 10-11% from Tube B. The sieve classifications reached steady state within 7 cycles; while the LOI and MB clay reached steady state during even the first cycle.
Figure 2.2. Sieve Distribution for processed waste green sand compared to the average product sand using pseudo-continuous operation, intense cavitation, 7 minute wash cycle, 10 minute settle cycle, ozone sparge, 500 ppm H₂O₂ and 1 pound per gallon sand to water ratio; mathematically computed composite of cycles 1, 4, 7 and 10.
The authors also mathematically computed a composite average of the cycle 1, 4, 7 and 10 sieve classifications (as per above). These composite averages showed the same trends in sieve classification progression when the wash cycle was excluded (Figure 2.4) as when the wash cycle was included (Figure 2.3). However, without the wash cycle, the changes manifest in Tube A and Tube B were less pronounced.
3.4 Effect of Rinsing, Drying and De-Dusting to Processed Sand

As a part of this demonstration testing, the authors sought to determine whether better sand quality could be derived by water-rinsing the reclamation system’s product sand, and then drying/de-dusting it. For the latter, the authors tested a pilot-scale sand dryer/de-duster unit to appraise this.

The reclaimed sand used in these trials had been produced by practicing pseudo-continuous operations (round IV), while using moderate cavitation, 7 minute wash, 10 minute settling, 2 pounds sand/gallon water and 10 cycles of discharge. During these trials, there was a continuous bleed and make-up of water.

We appraised three levels of rinsing in these trials: 5.5 gallons water/100 pounds of sand, 22 gallons water/100 pounds sand, and no rinsing.
As seen in Table 2.6, when rinsing used either of the two water-to-sand ratios, the product sand after rinsing and drying/de-dusting exhibited a useful reduction in MB clay (decrease of 62-69%), LOI (decrease of 45%) while maintaining nearly the same #140 sand. In contrast, when the rinsing step was excluded, the de-dusting/drying achieved only a slight drop in MB Clay and no drop in LOI. Specifically, the favorable combination of ultrasonic-cavitation, rinsing, drying and de-dusting yielded reclaimed sand that contained 0.16% MB Clay and 0.33% LOI; and these are very near the specifications for new core sand previously discussed.
Table 2.6. Effect of Rinsing and Drying/De-Dusting on Sand Properties
(Reclamation Used Moderate Cavitation; During Pseudo-Continuous Operations, Round IV)

<table>
<thead>
<tr>
<th>Rinse Ratio (water: sand)</th>
<th>Parameter</th>
<th>Product Sand</th>
<th>Rinse Sand</th>
<th>% Change</th>
<th>Dried and De-dusted Sand</th>
<th>% Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5 gal: 100 lbs</td>
<td>% MB Clay</td>
<td>0.42 ± 0.01</td>
<td>0.21 ± 0.02</td>
<td>-50</td>
<td>0.16 ± 0.02</td>
<td>-62</td>
</tr>
<tr>
<td></td>
<td>% Volatiles</td>
<td>0.60 ± 0.08</td>
<td>0.43 ± 0.01</td>
<td>-28</td>
<td>0.29 ± 0.01</td>
<td>-52</td>
</tr>
<tr>
<td></td>
<td>% LOI</td>
<td>0.60 ± 0.08</td>
<td>0.48 ± 0.06</td>
<td>-20</td>
<td>0.33 ± 0.01</td>
<td>-45</td>
</tr>
<tr>
<td></td>
<td>Percent #140</td>
<td>7.03 ± 0.32</td>
<td>7.24 ± 0.70</td>
<td>+3</td>
<td>6.42 ± 0.60</td>
<td>-9</td>
</tr>
<tr>
<td></td>
<td>% Fines</td>
<td>0.61 ± 0.07</td>
<td>0.69 ± 0.18</td>
<td>+13</td>
<td>0.58 ± 0.09</td>
<td>-5</td>
</tr>
<tr>
<td></td>
<td>GFN</td>
<td>58 ± 0.5</td>
<td>58 ± 2</td>
<td>0</td>
<td>57 ± 1</td>
<td>-2</td>
</tr>
<tr>
<td>22 gal: 100 lbs</td>
<td>% MB Clay</td>
<td>0.42 ± 0.01</td>
<td>0.17 ± 0.02</td>
<td>-60</td>
<td>0.13 ± 0.01</td>
<td>-69</td>
</tr>
<tr>
<td></td>
<td>% Volatiles</td>
<td>0.60 ± 0.08</td>
<td>0.27 ± 0.01</td>
<td>-55</td>
<td>0.28 ± 0.00</td>
<td>-53</td>
</tr>
<tr>
<td></td>
<td>% LOI</td>
<td>0.60 ± 0.08</td>
<td>0.36 ± 0.03</td>
<td>-40</td>
<td>0.33 ± 0.01</td>
<td>-45</td>
</tr>
<tr>
<td></td>
<td>Percent #140</td>
<td>7.03 ± 0.32</td>
<td>7.55 ± 0.84</td>
<td>+7</td>
<td>6.46 ± 1.10</td>
<td>-8</td>
</tr>
<tr>
<td></td>
<td>% Fines</td>
<td>0.61 ± 0.07</td>
<td>0.58 ± 0.11</td>
<td>-5</td>
<td>0.36 ± 0.00</td>
<td>-41</td>
</tr>
<tr>
<td></td>
<td>GFN</td>
<td>58 ± 0.5</td>
<td>59 ± 1</td>
<td>+2</td>
<td>57 ± 1</td>
<td>-2</td>
</tr>
<tr>
<td>No Rinsing</td>
<td>% MB Clay</td>
<td>0.36 ± 0.02</td>
<td>-</td>
<td>-</td>
<td>0.29 ± 0.01</td>
<td>-19</td>
</tr>
<tr>
<td></td>
<td>% Volatiles</td>
<td>0.51 ± 0.07</td>
<td>-</td>
<td>-</td>
<td>0.40 ± 0.00</td>
<td>-22</td>
</tr>
<tr>
<td></td>
<td>% LOI</td>
<td>0.55 ± 0.04</td>
<td>-</td>
<td>-</td>
<td>0.54 ± 0.03</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>Percent #140</td>
<td>7.24 ± 1.06</td>
<td>-</td>
<td>-</td>
<td>9.20 ± 0.43</td>
<td>+21</td>
</tr>
<tr>
<td></td>
<td>% Fines</td>
<td>0.63 ± 0.10</td>
<td>-</td>
<td>-</td>
<td>0.72 ± 0.09</td>
<td>+14</td>
</tr>
<tr>
<td></td>
<td>GFN</td>
<td>58 ± 1</td>
<td>-</td>
<td>-</td>
<td>60 ± 0</td>
<td>+3</td>
</tr>
</tbody>
</table>

3.5 Microscopic Photos

Microscopic photos exhibited the visual changes that accompanied the progression through reclamation, rinsing and de-dusting (i.e. for the Table 2.6 sands).

The waste green sand photographed in Figure 5A illustrates the carbon ‘raincoat’ found
on sand grains. Whereas, the ultrasonic-cavitation processed sand in Figure 2.5B, depicts considerable carbonaceous coating removal, although loose coal fines still appear on the surface and intermingled between grains. Carbonaceous fines disappeared following rinsing (Figure 2.6A); and the drying/de-dusting yielded a yet cleaner product (Figure 2.6B). The improved visual clarity corresponded to the decline in MB clay and LOI that have been presented in Table 2.6.

Figure 2.5A. Original Waste green sand prior to processing.
Figure 2.5B. Ultrasonic-cavitation processed sand (Round IV composite)

Figure 2.6A. Ultrasonic-cavitation processed sand (Round IV) that has been rinsed.
Figure 2.6B. Ultrasonic-cavitation processed sand that has been dried and de-dusted.
3.6 Sand Used In Core Tests

Next, the authors prepared reclaimed sand for use in cores. By inspecting the sieve classifications of the above trials, we anticipated that we could attain a sieve size distribution that conformed to the supporting foundry’s specification for core sand if we employed intense cavitation, and then collected product from only Tube B, which yielded a higher fraction of the finer grains. With this as the goal, we conducted five more rounds of pseudo-continuous operations. Each of the Rounds V-IX employed intense cavitation, ozone, ultrasonics, 500 ppm H₂O₂, and 1 lb sand/gallon water. During each round the same 360 gallons of water re-circulated for the full 10 cycles of discharge; and make-up waste green sand was added when reclaimed, product was discharged. The first cycle employed a 10 minute wash and 10 minute settling sequence, while cycles 2-10 each used 0 minutes wash and 10 minutes settling.

The sand parameters for the cycle 1-10 composite of Tube B sand appears in Table 2.7. This table depicts the reclaimed product, and also this product after it was rinsed and dried/de-dusted. As shown, following drying/de-dusting this core-sand candidate contained 0.24% MB Clay, 0.58% LOI, and 15.9% #140 sand. The sieve classification for this reclaimed, rinsed, and dried/de-dusted sand appears in Figure 2.7. As shown, this sand that was subsequently used for cores fell between the low and high spec ranges for every grain size.
Table 2.7. Reclaimed Sand Parameters for the Sand Used to Produce Cores with an Anti-Veining Additive

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reclaimed Sand</th>
<th>Dried and De-Dusted Sand (used in cores)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB Clay</td>
<td>0.51 ± 0.01</td>
<td>0.24 ± 0.01</td>
</tr>
<tr>
<td>% Volatiles</td>
<td>0.69 ± 0.10</td>
<td>0.50 ± 0.06</td>
</tr>
<tr>
<td>LOI</td>
<td>0.88 ± 0.06</td>
<td>0.58 ± 0.04</td>
</tr>
<tr>
<td>Percent #140</td>
<td>14.35 ± 0.11</td>
<td>15.93 ± 0.01</td>
</tr>
<tr>
<td>% Fines</td>
<td>0.88 ± 0.02</td>
<td>0.88 ± 0.11</td>
</tr>
<tr>
<td>GFN</td>
<td>66 ± 0</td>
<td>68 ± 0</td>
</tr>
</tbody>
</table>

Figure 2.7. Sieve Distribution for sand used to make cores compared to the lowest core sand specification and highest specification for core sand.

3.7 Core Sand Tensile Strength

The authors then prepared dog bones with this core sand (i.e. that sand depicted in Table 2.7 and Figure 2.7), and monitored their tensile strength. All of these dog bones contained 1.3% phenolic urethane and 4% anti-veining agent for the array of dog bones.
The percent reclaimed/rinsed/dried sand ranged from 0 to 100% while the balance of new (virgin) core sand conversely ranged from 100 to 0%. The positive control with 100% new sand yielded an average tensile strength of 212 psi, while the samples with 100% reclaimed sand averaged 157 psi. In comparison, the 40% reclaimed sand dog bones yielded 192 psi, and the 70% reclaimed dog bones yielded 165 psi (Figure 2.8, Table 2.8). Photographs exhibited that the dog bones became darker as the percent reclaimed sand increased (Figure 2.9).

![Figure 2.8. Tensile Strength with respect to percent reclaimed sand, for cores made with anti-veining additive.](image-url)
Table 2.8. Tensile Strength Testing for Each Sample Averaged into Figure 2.8.

<table>
<thead>
<tr>
<th>% Reclaimed Sand</th>
<th>Replicate Number</th>
<th>Tensile Strength (psi)</th>
<th>Time elapsed from core making to tensile strength testing (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>215</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>187</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>208</td>
<td>11</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>202</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>203</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>169</td>
<td>11</td>
</tr>
<tr>
<td>70</td>
<td>1</td>
<td>173</td>
<td>9</td>
</tr>
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<td></td>
<td>2</td>
<td>165</td>
<td>10</td>
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<tr>
<td></td>
<td>3</td>
<td>157</td>
<td>11</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>164</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>170</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>134</td>
<td>13</td>
</tr>
</tbody>
</table>

Figure 2.9. Dog bones produced with anti-veining additive and 100% reclaimed sand (Top-left), 70% reclaimed sand (Bottom-left), 40% reclaimed sand (Top-right) and 0% reclaimed sand (bottom-right).

3.8 Casting Quality Analysis

Next, the authors prepared cores that were used in the full-scale production of slip yokes for trucks. These cores employed the same Tube B composite sand from the Round V-IX trials. All cores included 1.3% phenolic urethane binder and 4% anti-veining agent, while the proportion of all sand that was reclaimed ranged from 0-100%. After preparing the slip yokes in full-scale operations, their casting quality was appraised
by three Neenah employees who routinely monitor this parameter. These appraisals were conducted without the panelists knowing how much reclaimed sand had been included in the cores. The 5 was for highest quality, while 1 was for the lowest quality.

The castings manufactured with cores produced from 40%, 70% and 100% ultrasonic-cavitation processed sand had average ratings of 4.27 to 4.73 relative to veining, and 3.96 to 4.0 for burn-in (Table 2.9). Interestingly, these appraisals stood more favorable than those for the cores that had used 100% new sand: 4.0 relative to veining and 3.22 relative to burn-in. However, the statistical verification is not supported for these castings to be considered of ‘superior’ quality relative to the all-new sand control. Overall, this convincingly shows that ultrasonic-cavitation reclaimed sand can be used to produce quality castings. The presence of high quality surface finish and the absence of unfavorable veining are illustrated in Figures 2.10A and 2.10B.

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Veining</th>
<th>Std. Dev.</th>
<th>Burn-In</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Reclaimed, With Anti-Veining Additive</td>
<td>4.47</td>
<td>0.50</td>
<td>4.00</td>
<td>0.00</td>
</tr>
<tr>
<td>70% Reclaimed, With Anti-Veining Additive</td>
<td>4.29</td>
<td>0.46</td>
<td>4.00</td>
<td>0.00</td>
</tr>
<tr>
<td>40% Reclaimed, With Anti-Veining Additive</td>
<td>4.73</td>
<td>0.45</td>
<td>3.96</td>
<td>0.21</td>
</tr>
<tr>
<td>0% Reclaimed, With Anti-Veining Additive</td>
<td>4.00</td>
<td>0.58</td>
<td>3.22</td>
<td>0.47</td>
</tr>
</tbody>
</table>
3.9 Trials With No Anti-Veining Agent

The authors also appraised whether the use of reclaimed sand could eliminate the need of adding a veining agent. These trials, likewise, involved making dog bones and cores for full-scale castings; but in this case, the anti-veining agent was not included. These cores employed the Round II sand (with moderate cavitation) that was a composite from Tubes A and B, from all 10 discharge cycles (Table 2.5 data). Before using this for cores, this reclaimed sand first experienced rinsing and drying/de-dusting, and after which its sand parameters were as shown in Table 2.11.

The tensile strength achieved by these dog bones was high enough, with 162-201 psi for dog bones with reclaimed sand versus 244 psi for these with new sand (Table 2.10). However, the casting qualities were merely poor to average relative to both veining and burn-in, regardless of whether reclaimed sand was used or only new sand was used. Thus, this sand reclamation process did not eliminate the need for anti-veining additive. Figure 2.11 depicts the kind of veining that occurs when no anti-veining additive is used when making cores with new sand.
Figure 2.11. Casting Produced with 100% new sand and no core sand additive

Table 2.10. Numeric Rankings for Castings Produced with Cores that Contained 20-100% Reclaimed Sand Make-Up, with no Anti-Veining Additive

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Veining</th>
<th>Std. Dev.</th>
<th>Burn-In</th>
<th>Std. Dev.</th>
<th>Tensile Strength (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Reclaimed</td>
<td>2.64</td>
<td>1.07</td>
<td>2.73</td>
<td>1.25</td>
<td>162</td>
</tr>
<tr>
<td>60% Reclaimed</td>
<td>2.67</td>
<td>0.64</td>
<td>2.91</td>
<td>1.14</td>
<td>165</td>
</tr>
<tr>
<td>40% Reclaimed</td>
<td>2.64</td>
<td>0.57</td>
<td>3.09</td>
<td>0.60</td>
<td>201</td>
</tr>
<tr>
<td>20% Reclaimed</td>
<td>3.18</td>
<td>0.44</td>
<td>3.42</td>
<td>0.54</td>
<td>162</td>
</tr>
<tr>
<td>0% Reclaimed</td>
<td>2.24</td>
<td>0.48</td>
<td>2.33</td>
<td>0.56</td>
<td>244</td>
</tr>
</tbody>
</table>

Table 2.11. Sand Parameters for Sand Used to Produce Cores without an Anti-Veining Additive

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reclaimed sand</th>
<th>Dried and De-dusted Sand (used in cores)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB Clay</td>
<td>0.47 ± 0.07</td>
<td>0.18 ± 0.02</td>
</tr>
<tr>
<td>% Volatiles</td>
<td>0.44 ± 0.03</td>
<td>0.32 ± 0.03</td>
</tr>
<tr>
<td>LOI</td>
<td>0.45 ± 0.01</td>
<td>0.34 ± 0.03</td>
</tr>
<tr>
<td>Percent #140</td>
<td>5.84 ± 0.53</td>
<td>8.29 ± 0.43</td>
</tr>
<tr>
<td>% Fines</td>
<td>0.31 ± 0.13</td>
<td>0.40 ± 0.03</td>
</tr>
<tr>
<td>GFN</td>
<td>57 ± 1</td>
<td>60.0 ± 1</td>
</tr>
</tbody>
</table>

4. Summary

These tests proved that successful core sand reclamation could be achieved with the ultrasonic-cavitation device; and this reclaimed sand made cores that yielded high-
quality castings. Core strengths were reported between 157-201 psi when reclaimed sand make-up ranged between 40-100%. Sand drying and de-dusting was beneficial to sand quality as it reduced the LOI and MB Clay.

5. Acknowledgments

Funding and support for this research was provided by Neenah Foundry, Furness-Newburge Inc., Pennsylvania State University, and the National Science Foundation grant number DMI – 0524940. In all, the first author hefted 20 tons of sand during the trials herein.

6. References


Chapter 3
Binder Development; Methods and Initial Results

Abstract

The purpose of this chapter is to provide greater detail pertaining to the methods used to guide early phase binder development. The loosely catalogued evidence that collagen alone cannot withstand molten metal erosion was confirmed through the wedge erosion test. Since collagen alone could not withstand molten metal erosion, the next step was to determine – “Why?”. Decomposition kinetic calculations using the Flynn-Wall method determined that the chemical composition of collagen cannot withstand thermal degradation as well as the petroleum based binder, phenolic urethane. Starting from ground zero, we sought to use thermogravimetry to rapidly appraise core binder formulations. Thus, various chemical cross-linkers were coupled with collagen so as to improve the resistance to thermal decomposition. Thermogravimetry confirmed that cross-linkers used herein could improve the thermal stability of collagen. However, the collagen and sodium silicate composite proved to produce the most favorable thermogravimetric response, as this response most closely resembled the phenolic urethane response. Beyond thermogravimetry, hot distortion tests were utilized to further rapidly assess core behavior at high temperatures. Hot distortion tests further elucidate how a binder will perform at full-scale.

1. Introduction

This chapter should provide insight pertaining to the initial phase of binder develop and initial results which guided subsequent research. Initial work investigated using collagen as a core binder since previous studies determined collagen adhered cores
reduce VOC emissions by as much as 70-95% 70-95% less than phenolic-urethane (Wang et al., 2007, CERP, 2007). However, there were loosely catalogued evidence that collagen alone could not withstand the rigors of molten iron pouring. Perhaps the most important characteristic that cores must posses is described by Dietert [cores should be…] “…sufficiently strong to resist erosion and deformation by metal during the filling of the mold.” (Dietert, 1966). Thus, any core binder must be able to produce good castings before emissions reductions become a viable parameter to also consider.

Therefore, the priority in the initial phase of research was to confirm whether or not a collagen adhered core can withstand molten metal erosion, when compared to a control core adhered with conventional core binders.

The wedge erosion test, as described by Tordoff and Tenaglia 1980, and Henry et al. 2003, was utilized to appraise a collagen core compared to a conventional core. The results confirmed that collagen alone could not withstand the rigors of metal pouring, as per this specific test. To further elucidate the specific nature of failure, the innate chemical resistance to thermal decomposition was appraised through thermogravimetry.

Specifically, a thermograviteric technique called the Flynn-Wall method, now standardized as ASTM 1641-07, was utilized to calculate the activation energy for thermal decomposition (ASTM 1641-07, Flynn and Wall, 1966, Flynn 1983). The Flynn-Wall method is a non-isothermal approach to determining the activation energy, $E_a$, for thermal decomposition kinetics. By heating a sample at multiple heating rates, a plot is derived for the logarithm of the heating rate versus the reciprocal of the temperature at constant conversion. This plot is then utilized to determine the Arrhenius activation energy, $E_a$ for thermal decomposition. The thermal decomposition appraisal determined
that the innate composition of collagen does withstand thermal stress as well as the petroleum based conventional phenolic urethane core binder. Thus, further thermogravimetric analysis was pursued in conjunction with chemical modification to improve collagen’s resistance to thermal decomposition.

Specifically, it was hypothesized that chemical cross-linking could overcome collagen’s innate poor resistance to thermal decomposition, as chemical decomposition has been reported to improve collagen’s thermal resistance, as per Chen et al., 2005; Charulatha et al., 2003; Usha et al., 2000; Wollensak et al., 2003b, Kato et al., 1989. Cross-linking has been reported to occur with tannic acid, a citric acid derivative, glutaraldehyde, formaldehyde, paraformaldehyde, hexamethylene-tetramine, glyoxal and dialdehyde starch (Heijmen, 1997, Taguchi et al., 2006, Harriger et al., 1997, Pizzi and Mittal, 2003). These cross-linking mechanisms and others were investigated with thermal gravimetric analysis so as to discern whether they could provide improved resistance to thermal decomposition. Specifically, we aimed to match or nearly match the thermal decomposition profile of conventional phenolic urethane, with a collagen based binder system. During thermogravimetry, we appraised the novel collagen based binder systems to native collagen, as the negative control, and to conventional phenolic urethane, as the positive control. A collagen and sodium silicate binder system nearly matched the thermal decomposition profile of conventional phenolic urethane, indicating that this binder system offers favorable thermal characteristics for use as a binder system.

To further evaluate thermal resistance, hot distortion tests were utilized using a natural gas flame with an adiabatic flame temperature of 1960°C. Resistance to distortion is important as unwanted movement or distortion causes casting defects, and this
resistance to distortion is a key component described by Dietert (Dietert, 1966). The initial hot distortion tests indicate that conventional phenolic urethane and sodium silicate are capable to distort to the maximum measurable levels without failure or breaking. The goal is to create a binder that withstands high temperature distortion better than conventional binder technologies.

2. Materials and Methods

Silica sand was provided by Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67-73. Sodium silicate was a modified sodium silicate provided by J.B. DeVenne INC. (Berea, OH). This modified sodium silicate formulation contained 42.5% by weight of dry solids. Collagen was provided by Entelechy (Plymouth, MI), and came as a dry powder, which was hydrolyzed to form gelatin. The phenolic urethane binder that was heat-set was provided by Ashland Chemical Company (Columbus, OH); and it came as a two-part binder that cured when mixed and heated.

2.1 Wedge Erosion Test

Molten iron erosion tests were performed using the protocol described in Tordoff and Tenaglia 1980, and Henry et al. 2003. This test uses a four part core to create a complete mold. The four core parts consist of a constant head pouring cup, sprue, wedge mold and reservoir (as depicted in Figures 3.1, 3.2, 3.3, 3.4). This produces a finished casting as depicted below in Figure 3.5. The four cores were formed by mixing Wedron silica sand with binder in a lab-scale batch mixer. For the sodium silicate cores, silica sand was mixed with 1.28% sodium silicate (dry weight), by weight of sand. For the collagen cores, silica sand was mixed with 1% collagen, by weight of sand. The collagen
was thermally denatured at 70°C in water at a weight ratio of 3 parts water to 1 part dry collagen. The mixed sand and binder was then hand packed into wooden core boxes for each of the four molds. The cores were cured and then removed from the molds.

The iron was melted in an Inductotherm (Rancocas, NJ) Dura-Line electric induction furnace in the Penn State pilot foundry in an electric induction furnace. Approximately 70 pounds of molten iron between 2600 and 2700°F (1427-1482°F) was poured into the constant head pouring cup. From the constant head pouring cup, the iron flowed down the sprue and across the wedge surface and subsequently into the reservoir. The total vertical drop from the constant head pouring cup to the wedge surface was 20 inches. The iron cooled and solidified. The mold was removed and the resultant wedge castings were quantified and compared.

Figure 3.1. The reservoir mold in the wedge erosion set-up, an 8” by 8” by 8” core, with a 6” by 6” by 6” reservoir.
Figure 3.2. The wedge core mold, which allows molten iron to be poured onto the surface of the core as it passes into the reservoir (Figure 3.1).
Figure 3.3. The sprue mold, which is 16” long and sits atop the wedge mold, is held within flasks that have been packed with green sand.
Figure 3.4. Wedge erosion test set-up. The four part mold is packed within a flask and green sand.
2.2 Arrhenius Activation Energy Determination

Collagen and phenolic urethane were compared via decomposition kinetics determination through thermal gravimetric analysis (TGA) via the Flynn-Wall method (Flynn and Wall, 1966, Flynn, 1983, Hatakeyam, 1998). The method herein closely followed ASTM method 1641-07 (ASTM, 164107), with variations described herein. This method used approximately 10 grams of sample (prepared as described in section 2.3) which was heated from ambient temperature at 10°C, 20°C and 30°C per minute, in duplicate. The samples were heated while being purged with high-purity Argon. As per method 1641-07, it is noted that off-gassing may be the rate limiting reaction at heating rates exceeding 10°C per minute, however, during metalcasting heating rates experienced
by core binders may be as much as 500°C to 2500°C per minute and off-gassing may be the rate limiting decomposition reaction. Thus, the heating rates were the fastest available with this particular TGA. Following sample analysis, the activation energies were calculated using 60% decomposition, which is above the maximum decomposition value (20%) recommended by ASTM-1641-07.

2.3 Thermal Gravimetric Analysis

Previous tensile strength tests revealed that collagen produces the strongest cores when denatured in water around 70°C. Thus, collagen was denatured with water at a 3:1 ratio (water: dry collagen). Once denatured, the compound or compound mixtures were added to the collagen at a 1:5 ratio (compound: collagen), unless noted otherwise in Table 3.1. The binder samples were mixed by hand with a spatula for approximately one minute and then poured into an aluminum weighing pan. These samples were then dried for 12 hours in a 110°C oven. Phenolic Urethane samples were prepared at a 55:45 ratio, 55 parts A to 45 parts B as is common industry practice. The phenolic urethane was then cured with heat, instead of the typical triethylamine (TEA) or dimethylethylamine (DMEA) gas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic Urethane</td>
<td>0.55 parts A, 0.45 parts B</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>Modified Sodium Silicate</td>
</tr>
<tr>
<td>Collagen</td>
<td>5 g Collagen</td>
</tr>
<tr>
<td>C + Glutaraldehyde</td>
<td>5 g Collagen, 1 g Glutaraldehyde</td>
</tr>
<tr>
<td>C + Alum</td>
<td>5 g Collagen, 1 g Alum</td>
</tr>
<tr>
<td>C + Fructose</td>
<td>5 g Collagen, 1 g Fructose</td>
</tr>
<tr>
<td>C + Glyoxal</td>
<td>5 g Collagen, 2 g Glyoxal</td>
</tr>
<tr>
<td>C + Silicate + Modifier</td>
<td>10 g Collagen, 28 g Na-Silicate + 5g Modifier</td>
</tr>
</tbody>
</table>
A small portion of binder was removed with a scalpel from the sample pans to fit into the thimble sized alumina pan used for TGA. The samples were 15.0 mg ± 5.0 mg. The samples were placed in a TGA-DSC, which performs simultaneous thermal gravimetric analysis and differential scanning calorimetry. The test commenced at room temperature in a 100% Argon atmosphere, then the sample was heated at 10°C per minute from ambient temperature to 500°C or 1000°C. The trials were repeated and each prepared sample was tested in duplicate.

2.3 Hot Distortion Tests

For hot distortion testing (HDT), the samples were formed into hand packed cores, in a 16- sample wooden core box, which created candy bar-sized cores that were 6 inches long, 1 inch wide and 0.5 inches cm thick. In this core box, the bindered cores were cured at 110°C for 1 hour, with the exception of heat cured phenolic urethane which was cured for 24 hours.

Hot distortion tests were performed with a custom hot distortion test device (Figure 3.6). The samples were clamped in place such that a Bunsen burner flame was centered on the exposed 6 inch of sample. The micrometer monitored the deformation at a location that was 0.5 inches from the end opposite the clamp. This deformation was monitored up to a maximum of 13.53 mm. The samples were heated in the center of the test bar with a natural gas flame that emanated from a 1 inch diameter perforated Bunsen burner. The flame had an adiabatic flame temperature of 1960°C at its source; and the perforated burner plate remained 1 inch from the bottom of the cantilevered sample. The micrometer transmitted deformation readings every second; and these readings were logged by the computer. For each binder condition, 10-15 samples were analyzed via hot
distortion testing. The results exhibited inherent variability in both time to given
deflection, and deflection at failure (See discussion below).

Figure 3.6. The custom hot distortion test device, with flame (left), sample during
test (middle), and failed sample (right).

3. Results and Discussion

3.1. Wedge Erosion Tests

Collagen alone was used as a control with the wedge erosion tests utilized by Tordoff and
Tenaglia 1980, and Henry et al. 2003. As illustrated in Figure 3.1, a 6” by 6” by 6”
reservoir allows approximately 70 pounds of iron to flow across a 60° wedge surface,
refer Figure 3.2. The sodium silicate control illustrated that a core can withstand the
rigors of this experiment (Figure 3.7). The sodium silicate control core illustrated no
signs of erosion and produced a smooth casting surface. However, the collagen adhered
core could not withstand the rigors of the casting process. The collagen core not only
eroded, but burned completely through the core allowing complete metal penetration
(Figure 3.8). Molten metal erosion of this type indicates that when collagen alone is used
as a core binder the castings would possess deformations requiring the casting to be either
scrapped or machined. Increasing scrap or increasing machining is very costly for
foundries. The inability of collagen alone to withstand molten metal erosion via the
wedge erosion test confirms that collagen alone does not work as a core binder.
Figure 3.7. Wedge erosion surface for 1.28% sodium silicate (dry weight) core.

Figure 3.8. Wedge erosion surface for 1% collagen core. NOTICE: complete erosion.
3.2 Arrhenius Activation Energy Determination

The activation energy for decomposition kinetics was evaluated. The purpose of this was to determine if the chemical structure that comprises collagen prohibits high temperature use, as the activation energy for decomposition would suggest. To calculate these values, the Flynn-Wall method was used, which is now standardized as ASTM method 1641-07. In this experiment collagen was compared to phenolic urethane, a petroleum based binder. An initial comparison between collagen (Figure 3.9) and phenolic urethane (Figure 3.10) indicates that phenolic urethane resists thermal degradation superiorly to collagen, as phenolic urethane retains a greater amount of mass at higher temperatures than collagen. To quantify this apparent relative difference in thermal degradation kinetics, the maximum recommended value of decomposition of 20% was used to calculate the activation energy. However, since core binders are exposed to such extreme conditions during metalcasting, it was assumed that 60% decomposition would be more appropriate. Therefore, for each binder system, the temperature at which 60% decomposition (which corresponds to approximately 60% mass retained) occurs was determined for each heating rate and replicate. These values were converted to Kelvin and used as the denominator in 1000/Temperature (K) and plotted versus the log of the heating rate. Linear regression determined the slope of this line (Figures 3.11 and Figures 3.12) for the initial calculation of the activation energy. The activation energy was calculated using:
E = -(R/b) * Δ(log β’)/Δ (1/T)  

(ASTM 1641-07 eq. 1)

Where;

E = Arrhenius activation energy, J/mol
R = gas constant, 8.314 J/(mol · K)
Δ(log β)/Δ (1/T) = slope derived from Figures 3.2.3 and Figures 3.2.4.
b = approximation derivative from ASTM 1641-07 Table 1 (0.457/K)
Tc = temperature for point of constant conversion for β’
β’ = heating rate nearest the midpoint of the experimental heating rates, K/min

Following three calculation iterations, the Arrhenius activation energies were determined to be 130.0 kJ/mol for collagen and 145.7 kJ/mol for phenolic urethane, Table 3.2. This confirmed that indeed the innate chemical composition of collagen inhibits high temperature applications, such as use as a core binder for iron castings. Additionally, this indicates that increasing collagen’s thermal stability would improve binder resistance to molten metal erosion.

![Figure 3.9. Thermal Gravimetric Analysis for collagen heated at 10°C, 20°C and 30°C per minute, 100% argon atmosphere with replicate analysis (R)](image-url)
Figure 3.10. Thermal Gravimetric Analysis for phenolic urethane heated at 10°C, 20°C and 30°C per minute, 100% argon atmosphere, with replicate analysis (R).

\[ y = -7.3343x + 13.062 \]

Figure 3.11. Arrhenius Plot of heating rate and constant conversion data for collagen at 60% decomposition.
Figure 3.12. Arrhenius Plot of heating rate and constant conversion for phenolic urethane at 60% decomposition.

Table 3.2. Flynn-Wall /ASTM Method 1641-07, Arrhenius Activation Energy for thermal decomposition for collagen and phenolic urethane binder systems.

<table>
<thead>
<tr>
<th>Binder System</th>
<th>Activation Energy (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collagen</td>
<td>130.0</td>
</tr>
<tr>
<td>Phenolic Urethane</td>
<td>145.7</td>
</tr>
</tbody>
</table>

3.3 Thermal Gravimetric Analysis (TGA)

Collagen innately does not possess the chemical composition necessary to withstand the rigors of metal casting as indicated by the wedge erosion test and thermogravimetric based thermal decomposition activation energy calculations. It was hypothesized that collagen could be utilized in metalcasting if the resistance to thermal decomposition was increased through cross-linking. To accelerate the testing process, instead of creating wedge samples and pouring iron (several day process at lab-scale) or calculating the activation energy for each sample (multiple day process at lab-scale), duplicate
thermogravimetric analyses were processed. The intention was to perform duplicate thermogravimetric analyses, with cross-linked collagen, which would produce a thermogravimetric response similar to that of conventional phenolic urethane. When sample size and heating rate are constant, this is a rapid method to assess the relative thermal resistance between samples. In the instance of this thermogravimetric research, collagen served as the negative control, phenolic urethane as the positive control and collagen plus various compounds/suspected cross-linkers served as the test samples. In Figure 3.13, collagen and phenolic urethane are compared to sodium silicate. Collagen decomposes more rapidly than phenolic urethane when heated at 10°C per minute. It should also be noted that sodium silicate does not decompose below 80%; this is indicative to the poor shake-out qualities inherent to unmodified sodium silicates.

When collagen is cross-linked with glutaraldehyde the resulting binder system has improved thermal resistance, compared to collagen alone. However, collagen + glutaraldehyde does not possess thermal resistance equal to phenolic urethane (Figure 3.14). The collagen + alum (potassium aluminum sulfate) binder system appears to have improved thermal resistance when compared to collagen alone, however it appears to lack thermal resistance in the 300-500°C range (Figure 3.15). When collagen + fructose were cross-linked there was no improvement to thermal resistance (Figure 3.16). The collagen + glyoxal binder system loses mass faster than collagen alone to 300°C, however above 300°C glyoxal performs better than collagen alone (Figure 3.17). When collagen was cross-linked with tannic acid as per Heijmen et al., there was slightly more resistance to thermal decomposition below 250°C; however above 250°C the sample seemed to retain similar thermal decomposition characteristics as collagen alone (Figure 3.18).
When collagen was cross-linked with ellagic acid there were significant improvements to thermal stability. Further, when redwook bark was analyzed without any collagen, the sample possessed greater resistance to thermal decomposition than phenolic urethane above 425°C (Figure 3.18).

Figures 3.13 through 3.18 generally indicate that when collagen is coupled with cross-linkers the resistance to thermal decomposition can improve. However, there was not a collagen and organic cross-linker sample that proved to be as effective at withstanding thermal decomposition as phenolic urethane. To improve thermal resistance, collagen was coupled with sodium silicate and a modifier. The collagen + silicate sample had improved thermal resistance. In fact, the collagen + silicate sample possesses a near identical thermogravimetric response as phenolic urethane (Figure 3.19). This favorable thermogravimetric response is the behavior/thermal resistance that was sought. The results for thermogravimetry are detailed in Table 3.3.
Figure 3.13. Thermal Gravimetric Analysis for Controls Tested, including; Phenolic Urethane, Sodium Silicate and Collagen.
Figure 3.14. Thermal Gravimetric Analysis for collagen and phenolic urethane, compared to collagen cross-linked with glutaraldehyde.

Figure 3.15. Thermal Gravimetric Analysis for collagen and phenolic urethane compared to collagen coupled with alum.
Figure 3.16. Thermal Gravimetric Analysis for collagen and phenolic urethane compared to collagen with fructose.

Figure 3.17. Thermal Gravimetric Analysis of collagen and phenolic urethane compared to collagen with glyoxal.
Figure 3.18. Thermal Gravimetric Analysis of collagen and phenolic urethane compared to collagen with tannic acid, collagen with ellagic acid and redwood bark powder (Sequoia Sempervirens).
Figure 3.19. Thermal Gravimetric Analysis of collagen and phenolic urethane compared to collagen with sodium silicate and a modifier.

Table 3.3. Summary Table for Thermal Gravimetric Analysis for all Binder Systems.

<table>
<thead>
<tr>
<th>Binder System</th>
<th>TGA (°C) at 10% Mass Loss</th>
<th>TGA (°C) at 50% Mass Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic Urethane</td>
<td>244.7</td>
<td>438.7</td>
</tr>
<tr>
<td>Collagen + Silicate + Modifier</td>
<td>260.4</td>
<td>420.3</td>
</tr>
<tr>
<td>Collagen</td>
<td>202.2</td>
<td>328.3</td>
</tr>
<tr>
<td>Collagen + Alum</td>
<td>201.8</td>
<td>390.8</td>
</tr>
<tr>
<td>Collagen + Glutaraldehyde</td>
<td>250</td>
<td>368.6</td>
</tr>
<tr>
<td>Collagen + Glyoxal</td>
<td>175.6</td>
<td>340.3</td>
</tr>
<tr>
<td>Collagen + Fructose</td>
<td>170.2</td>
<td>325.3</td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>183</td>
<td>n/a</td>
</tr>
<tr>
<td>Collagen + Tannic Acid</td>
<td>236</td>
<td>329</td>
</tr>
<tr>
<td>Collagen + Ellagic Acid</td>
<td>267.5</td>
<td>391</td>
</tr>
<tr>
<td>Sequoia Sempervirens (redwood) bark</td>
<td>281</td>
<td>534</td>
</tr>
</tbody>
</table>
3.4 Hot Distortion Tests

Thermogravimetry yields insight as to core binder stability at high temperatures, yet does not provide insight as to whether the core remained stable at higher temperatures. In a foundry setting, rapid distortion at high temperatures can unfavorably lead to casting defects and subsequently increased scrap rates. To quickly ascertain whether core binder systems would possess structural integrity at higher temperatures, hot distortion tests were performed. These hot distortion tests indicated that phenolic urethane (Figure 3.20) and sodium silicate (Figure 3.23) could both produce cores that withstood the natural gas flame without breakage. However, sodium silicate distorted after a much shorter exposure time than phenolic urethane. Since both of these binder systems generally work well for metalcasting, it is reasonable to conclude that a core should be able to distort to the maximum measurable limit, for this custom machine.

Both 1% collagen (Figure 3.21) and 2% collagen (Figure 3.22) (both as dry weight percentages), were unable to withstand the natural gas flame to the maximum measurable limit. Using a higher level of binder, 2% collagen, was able to resist distortion longer than 1% collagen, yet was still unable to reach the maximum measurable limit. It is interesting to note that collagen is able to withstand the natural gas flame longer without distortion than both phenolic urethane and collagen. Due to the favorably thermogravimetric response offered by collagen and glyoxal, we tested this combination for hot distortion resistance. When collagen was coupled with glyoxal (Figure 3.24), there was no significant increase in time to distortion; however there was an increase in time from distortion to breakage (Table 3.4). Despite having a promising thermogravimetric response, the collagen and sodium silicate cores performed poorly.
The collagen and sodium silicate cores distorted more rapidly than collagen and broke sooner than collagen cores (Figure 3.25).

Figure 3.20. Hot Distortion Test Results for sand cores that were adhered with 1% phenolic urethane and heated over a natural gas flame.
Figure 3.21. Hot Distortion Test Results for sand cores that were adhered with 1% collagen and heated over a natural gas flame.

Figure 3.22. Hot Distortion Test Results for sand cores that were adhered with 2% collagen and heated over a natural gas flame.
Figure 3.23. Hot Distortion Test Results for sand cores that were adhered with 1.28% (dry weight) Sodium Silicate and heated over a natural gas flame.

Figure 3.24. Hot Distortion Test Results for sand cores that were adhered with 0.71% collagen and 0.29% glyoxal and heated over a natural gas flame.
Figure 3.25. Hot Distortion Test Results for sand cores that were adhered with 1% collagen (dry weight) and 0.43% (dry weight) Sodium Silicate heated over a natural gas flame.

Table 3.4. Hot Distortion Test summary table, detailing the average time to 1mm distortion, average distortion at breaking and the average final distortion time at breaking.

<table>
<thead>
<tr>
<th>Binder System</th>
<th>Average Time (sec) to 1 mm distortion</th>
<th>Average Distortion (mm) at breaking</th>
<th>Average Final Distortion time (sec) at breaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 % Phenolic Urethane (Heat Cured)</td>
<td>50.1</td>
<td>13.5+ mm (3 broke @ less)</td>
<td>84.5</td>
</tr>
<tr>
<td>1 % Collagen</td>
<td>65.4</td>
<td>4.2 mm</td>
<td>71.3</td>
</tr>
<tr>
<td>2 % Collagen</td>
<td>69.8</td>
<td>9.6</td>
<td>84.7</td>
</tr>
<tr>
<td>1.28 % Sodium Silicate</td>
<td>21.7</td>
<td>13.5+ mm (no break)</td>
<td>30.3</td>
</tr>
<tr>
<td>0.71% Collagen and 0.29% glyoxal</td>
<td>67.5</td>
<td>3.82</td>
<td>94.9</td>
</tr>
<tr>
<td>1 % collagen coated sand + 0.43 % sodium silicate</td>
<td>44.4</td>
<td>2.5 mm</td>
<td>54</td>
</tr>
</tbody>
</table>
4. Conclusions

Initial molten iron tests confirmed the widely held industry belief that collagen alone does not bind cores together that can withstand the rigors of iron casting. The innate chemical composition of collagen does not withstand thermal stress as well as phenolic urethane. The Arrhenius activation energy for decomposition kinetics confirmed that phenolic urethane resists thermal decomposition superiorly to collagen. The thermogravimetric response confirmed the hypothesis that cross-linking can improve the thermal stability of collagen, demonstrated by the collagen and glutaraldehyde sample as well as the collagen and glyoxal sample. However, the improvement to collagen with most cross-linkers did not match the thermal stability of phenolic urethane. Interestingly, when collagen is coupled with sodium silicate a thermal gravimetric response can be produced that is nearly identical to phenolic urethane. Hot distortion tests for both sodium silicate and phenolic urethane indicate that these two binders withstood the natural gas flame until maximum measurable limits were reached. Since both of these binders yield good casting products, it seems probable that withstanding the flame without breaking is a necessary characteristic. Further, the hot distortion tests for collagen + glyoxal and collagen + sodium silicate did not perform well. However, the thermogravimetric response for collagen + sodium silicate is very favorable and should not be discounted due to poor initial hot distortion tests.
5. References


Chapter 4

Physical and Mechanical Property Characterization of a Novel Collagen-Alkali Silicate Hybrid Foundry Core Binder as Compared to Conventional Foundry Binders

Abstract

Metalcasting within the United States aims to meet ever-more stringent environmental standards as new process technologies are developed. Conventional foundry core binders are responsible for up to 70% of a foundry’s volatile organic compound (VOC) emissions. New core binder technologies are essential for environmental sustainability within foundries. Herein, conventional and novel foundry core binders were appraised using thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), hot distortion testing (HDT) and (Pilot-scale) molten iron erosion tests. Inherently, these tests cannot replace full-scale casting trials to evaluate binder effectiveness, however, these tests were performed to more fully elucidate binder properties that might cause casting defects or other unwanted behaviors at high temperatures. During each of these lab protocols, the combination of collagen plus alkali silicate as binders exhibited properties that matched or exceeded those of conventional phenolic urethane. Also, in iron erosion testing, the collagen/alkali silicate binder exhibited the same low erosion as conventional phenolic urethane. In hot distortion testing, the collagen-alkali silicate binder exhibited longer resistance to thermal bending, and comparable thermal flexibility to conventional phenolic urethane.
1. Introduction

Metalcasting is integral to American industry as castings are employed in nearly 90% of manufactured goods and capital equipment. Within the metal casting industry, the process technologies are required to meet ever-more stringent environmental standards. However, conventional core binders emit up to 70% of a foundry’s volatile organic compound (VOC) emissions (Glowacki et al., 2003, Wang et al., 2007). A number of foundry managers have expressed an interest in replacing the conventional binders with novel low-emission core binders -- if they can offer the same physical and mechanical properties at high temperatures. This paper describes the thermal and thermomechanical stability of novel, low VOC binders for sand cores as compared to traditional binders. Inherently, these tests cannot supersede casting trials to evaluate binder effectiveness, but they can certainly elucidate nuances useful for understanding full-scale behavior.

Sand cores are important components of metalcasting operations. When cast objects require one or more hollow cavities, such as in engine blocks, sand cores are used to create these cavities. Sand cores typically contain 97-99% sand and 1-3% binder, and are conventionally held together with petroleum-based adhesives, specifically phenolic-urethane or furans. The cores must have adequate strength at room temperature and also maintain structural integrity when exposed to molten metal. During metal pouring, the maximum temperatures experienced by cores range from 1510°C at the molten iron interface, down to 50-300°C several inches away from this interface; temperature exponentially declines from the metal interface through the core (Wang et al., 2006). Paradoxically, after withstanding molten metal exposure and subsequent cooling the
binder must then disintegrate during shake-out, so that the sand can be easily removed from the cast product cavities.

Several conventional petroleum-based binder systems, such as phenolic urethanes and furans provide structural integrity, shake-out propensity, and casting quality. However, these phenolic urethanes and furan binders will thermally decompose after metal exposure, emitting as much as 30-70% of a foundry’s VOCs and hazardous air pollutants (HAPs) (Glowacki et al., 2003, Wang et al., 2006). As expected, VOC and HAP emissions increase proportionately with an increase in core-loading (Goudzwaard et al., 2003, Glowacki et al., 2003). Recent work has determined that VOC emissions for a collagen core binder are 70-95% less than phenolic-urethane (Wang et al., 2007, CERP, 2000), prompting further investigation.

Despite the significant and necessary emission reductions enabled by collagen, it is only marginally employed in foundries. The inability of collagen (alone) to withstand significant temperatures imparted by molten iron (1290°C – 1510°C) at the molten metal and sand interface is the key reason that collagen is not implemented ubiquitously through the industry. Specifically, this inability incurs erosion when molten iron pours onto the collagen (alone)-bindered sand; and this produces costly casting defects. Collagen, which is available in large quantities as a by-product of the meat-packing industry, is the fibrous protein that strengthens skin, tendon and bones; and at ambient temperature, this triple-helical material has a tensile strength equivalent to steel (Buehler, 2006). The individual collagen strands are 200-500 nm long; and each polypeptide strand is comprised of a three amino acid repeating sequences. These typically include a repeating sequence similar to X-Y-Glycine; where Glycine comprises about 34% of
collagen, while the “X” and “Y” include proline (12%), alanine (10%), hydroxyproline (10%), glutamic acid (7%), or other amino acids (Palfi and Perczel, 2007, Eastoe and Leach, 1958).

When collagen is used as an adhesive, the triple helical structure is denatured in water. Then as the adhesive dries, the polypeptide strands randomly re-align and bond through Hydrogen Bonds (Stainsby, 1958). Hydrogen Bonds between the polypeptide strands are numerous, yet each bond is ‘weak’, with bond energy less than 25 kJ/mole and are at least an order of magnitude less than covalent bonds (Emsley, 1980, Buehler and Ackbarow, 2007, IUPAC, 2006). The authors sought to increase the adhesive integrity at high temperatures by increasing the bond energy (Strong, 2008) in a collagen binder system by utilizing well-documented covalent intermolecular organic cross-linking to increase the mechanical integrity and stability of collagen (Chen et al., 2005, Charulatha and Rajaram, 2003, Usha and Ramasami, 2000, Wollensack and Spoerl, 2004, Verzigl et al., 2002, Kato and Silver, 1989, Harriger et al., Heijmen et al., 1997, Taguchi et al., 2004, Kanth et al., 2009). Cross-linking also increases resistance to water solubility (Gupta et al., 2002, Pizza and Mittal, 2003) which would improve core storage when exposed to humidity. Of the types of cross-linking that could be employed, it has been the inorganic silicate cross-linking that we found achieved the more favorable results than organic cross-linking under the thermal duress imposed.

Specifically, the authors sought herein to include alkali-silicates in conjunction with collagen to produce a ‘hybrid’ organic/inorganic binder. Silicate cross-links with the amino group on the peptide chain of collagen (Coradin et al., 2002); and this phenomenon can be used advantageously in binders. The crosslinking formation between
collagen and silicates has been studied by Coradin and others for biological application (Allouche et al., 2006, Elgin et al., 2005, Eglin et al., 2006, Coradin and Livage, 2005, Coradin et al., 2005). This cross-link has the potential to increase the binding strength at both room temperature (Gonzalez et al., 1991, Allouche et al., 2006), and high temperature. Further work has been performed by Gelinsky et al. (2008) creating a mineralized collagen; which was made by precipitating amorphous calcium phosphate from a collagen solution as the collagen fibrils were reassembling. Over time, the amorphous mineral phase transformed to nanocrystalline hydroxyapatite which then precipitated onto collagen fibrils. Yet, the utilization of collagen and silicates for use in foundry applications is novel. The authors hypothesized that the alkali-silicates will provide strength when exposed to molten metal, while the low-VOC emitting collagen will gradually decompose after thermal exposure, as is conventionally desirable in the foundry industry, so as to provide easy sand removal after metal solidification.

Alkali-silicates, specifically sodium silicates are widely used as adhesives and are also commonly used as core binders in the metalcasting industry (Rabbii, 2001, Lambourne and Strivens, 1999, Veinot et al., 1990, Srinagesh, 1979). Despite their many favorable characteristics, unmodified sodium silicate binders have one key problem – difficulty in shakeout or the inability to breakdown after metal solidification (Srinagesh, 1979). Other forms of alkali silicates are potassium and lithium silicates; most importantly lithium silicates are the most insoluble following curing (Lambourne and Strivens, 1999, Veinot et al., 1990), which is attributed to the smaller ionic radius of lithium than that of sodium or potassium (Venoit et al., 1990). Additionally, a blend of potassium and lithium silicates provides a similar level of moisture resistance as lithium
silicate (Veinot et al., 1990). The increased moisture resistance provided by lithium silicates is favorable for foundry core storage.

The objectives of the work herein were; (1) develop a novel low-emission foundry core binder (2) benchmark the relevant physical as well as mechanical properties for both conventional binders and novel binders that could influence casting quality, and (3) provide a practical lab-scale test framework that can be utilized as a pre-cursor to full-scale molten metal tests that predicts foundry binders ability to withstand molten metal erosion. The driving hypothesis for this work is that collagen is a low-emission adhesive that when used alone cannot provide the physical and mechanical properties necessary to withstand the high temperatures imparted at the molten metal interface experienced by cores, however when collagen is coupled and cross-linked with alkali-silicates the ‘hybrid’ binder can provide the necessary physical and mechanical properties for use in metal casting.

2. Materials and Methods

2.1 Materials

Sodium silicate was a modified sodium silicate provided by J.B. DeVenne INC. (Berea, OH). This modified sodium silicate formulation contained 42.5% by weight of dry solids. Collagen was provided by Entelechy (Plymouth, MI), and came as a dry powder. The phenolic urethane binder that was heat-set and cured by triethylamine (TEA) was provided by Ashland Chemical Company (Columbus, OH); and came as a two-part binder that cured when mixed and heated. The blended potassium/lithium silicate was provided by PQ Corporation (Malvern, PA), and came as a liquid with 29%
solids content. Silica sand was provided by Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67-73.

2.2 Sample Preparation Overview

Samples for thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and hot distortion testing (HDT) were prepared as described in respective test sections. In general, DMA and HDT samples were prepared by bindering sand with binders, and the mix was molded into gum-stick sized core samples (12.0 ± 0.3 mm x 5.0 ± 0.15 mm x 35.0 ± 0.0 mm) for DMA; or candy bar sized samples (15.24 cm x 2.54 cm x 1.27 cm) for HDT. The samples for DMA and HDT experiments contained the typical percentages of sand (98-99%) and binder (1-2%) that would be used in a foundry setting. For DMA and HDT experiments, bindered cores were made to include 1 to 3% of the binder plus 99 to 97% silica sand as per Table 1. Bindered core samples were prepared by mixing (1000 g) of washed foundry silica sand with the core binder system for 90 seconds at Level ‘2’ Solid State Speed Control, in a Commercial Kitchen Aid Mixer, Model Number KSMC50S (St. Joseph, MI).

TGA and DSC samples contained no sand, since this allowed us to track mass and heat changes more comprehensively; and these samples were prepared with only the binder components as indicated in Table 4.1.

2.2.1 Sample Preparation for Dynamic Mechanical Analysis (DMA) and (DSC)

For DMA analyses, the samples were hand packed into an 8-part wooden core mold. For the DMA test, the gum-stick sample size was 12.00 ± 0.30 mm x 5.00 ± 0.15 mm x 35.00 ± 0.00 mm (clamp determined the length). Samples were then cured at
110°C for one hour, with the exception of phenolic-urethane (that was heat cured), which was cured for 24 hours. The samples were then removed from the core mold and placed in a desiccator for overnight storage. The phenolic urethane samples that were TEA-cured were provided to the Penn State team by Hitachi Metals Automotive Components (HMAC) USA, LLC foundry, Lawrenceville, PA. These samples were produced in core making machines using 1.1% phenolic urethane, and were TEA cured in full-scale operation. These production foundry cores had a 3” by 1” diameter rod protruding from the main core. The Penn State team removed these rods, and manually filed them down to the standard size used for DMA testing.

For DMA analyses, samples were analyzed using a TA Instruments DMA Q800 unit, (New Castle, DE) with a dual cantilever clamp. The samples were heated at 10°C per minute to 500°C, while the drive shaft oscillated with 5 μm amplitude at a frequency of 20 Hz. During testing, the samples were maintained in a nitrogen atmosphere, to mimic the atmospheric conditions experienced in the foundry core processing zone; the nitrogen was purged at 2 L/min.

### 2.2.2 Hot Distortion Test (HDT)

For hot distortion testing (HDT), the samples were formed into hand packed cores, in a 16- sample wooden core box, which created candy bar-sized cores that were 15.24 cm long, 2.54 cm wide and 1.27 cm thick. In this core box, the bindered cores were cured at 110°C for 1 hour, with the exception of heat cured phenolic urethane which was cured for 24 hours.

Hot distortion tests were performed with a custom hot distortion test device. The samples were clamped in place with 2.54 cm of sample clamped on an iron ledge, the
Bunsen burner flame was centered on the exposed 12.7 cm of sample and the micrometer monitored the deformation at a location that was 1.27 cm from the end opposite the clamp. This deformation was monitored up to a maximum of 13.53 mm. The samples were heated in the center of the test bar with a natural gas flame through 2.54 cm diameter perforated Bunsen burner, which had an adiabatic flame temperature of 1960°C at its source; and the perforated burner plate remained 2 cm from the bottom of the cantilevered sample. The micrometer transmitted deformation readings every second; and these readings were logged by the computer. For each binder condition, 10-15 samples were analyzed via HDT. The results exhibited inherent variability in both time to given deflection, and deflection at failure (See discussion below).

### 2.2.3 Sample Preparation for Thermal Gravimetric Analysis (TGA)

For TGA and DSC analyses, neat binder (no sand) samples were prepared, so that the thermal gravimetric profile for the binder would not be masked by excessive sand mass that was thermally inert. For collagen samples, 5 grams of collagen was mixed with water at a 1:3 mass ratio (collagen: water) at 70°C. Once denatured, the collagen-water mixture was poured into an aluminum weighing pan to be dried at 110°C for 12 hours. For the modified sodium silicate, 10 g (4.3 g dry mass) was poured into an aluminum weighing pan to be dried at 110°C for 12 hours. A hybrid binder system with 10 g collagen and 8.7 grams of K/Li silicate (dry mass basis) was prepared and dried at 110°C for 12 hours. For the other hybrid binder system, 10 g of collagen was added into a solution (8.5 g dry mass) of a modified sodium silicate, the entire mixture was heated at 70°C and stirred vigorously for 5 minutes. The hybrid binder mixture was then poured into an aluminum pan and dried at 110°C for 12 hours. For the conventional phenolic
urethane, samples were prepared with, 55 parts A to 45 parts B (by mass), as is common industry practice; then dried at 110°C for 24 hours.

Table 4.1. Sample composition prepared for Testing.

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition for TGA and DSC*</th>
<th>Composition for DMA and HDT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium silicate</td>
<td>4.3 g Modified Sodium Silicate</td>
<td>12.8 g Na-Silicate (dry mass), 1000 g Sand</td>
</tr>
<tr>
<td>Collagen</td>
<td>10 g Collagen, 30 mL Water</td>
<td>10 g Collagen, 1000 g Sand</td>
</tr>
<tr>
<td>C + K/Li silicate</td>
<td>10 g Collagen, 8.7 g K/Li Silicate (solids content)</td>
<td>10 g Collagen, 8.7 g K/Li silicate (dry mass), 1000 g Sand</td>
</tr>
<tr>
<td>C + Na silicate</td>
<td>10 g Collagen, 8.5 g Na-Silicate (solids content)</td>
<td>10 g Collagen, 8.5 g Na-Silicate (dry mass), 1000 g Sand</td>
</tr>
<tr>
<td>Phenolic urethane</td>
<td>0.55 parts A, 0.45 parts B</td>
<td>10 g Phenolic Urethane, 1000 g Sand</td>
</tr>
</tbody>
</table>

*All compositions on dry-mass basis.

For TGA tests, a small portion of dried binder (10 to 20 mg) was removed with a scalpel to fit into the thimble sized alumina pan used for TGA. The samples were placed in a TA instruments SDT 2960 – Simultaneous DSC-TGA. The test commenced at room temperature in a 100% Argon atmosphere, with heating at 10°C per minute to 600°C. Trials were tested in duplicate with the average between these duplicates representing the TGA curves included herein. Duplicaed results averaged a variation of slightly more than 5.8%.

For DSC tests, the binder samples were shaved and finely powderized with a razor blade. DSC analyses used a 2.0 mg sample, and employed a TA Instruments TA-Q100 DSC (New Castle, DE). A hermetic pan was used to hold samples; and the pan lid was punctured with an 8-penny finish nail so as to prevent the pan from ‘jumping’ from the heating element during analysis, due to build-up of volatiles. Samples were purged
with nitrogen gas at 50 mL/min. Samples were analyzed in duplicate with a temperature ramp of 10°C/min to 510°C.

2.2.4 Sample Preparation for Pilot-Scale Molten Iron Erosion Test

Cores were produced with (a) collagen, (b) sodium silicate, (c) sodium silicate plus collagen, (d, e) potassium /lithium silicate plus collagen (higher and lower silicate levels), (f) heat-cured phenolic urethane (prepared at Penn State), and (g) tri-ethylamine (TEA)-cured phenolic urethane (prepared at HMAC foundry). Except for “g”, all cores were prepared at Penn State; where they were hand packed to be 12.7 cm by 12.7 cm wide and 5.1 cm thick. These dimensions are with the exception of the TEA cured phenolic urethane cores, which possessed a 7.6 cm by 7.0 cm flat surface. This flat surface was extracted from a flat portion of a production core, which originated from our supporting foundry, HMAC. Cores were placed on a stand at a 45° angle. Molten iron, which was at 2620-2720°F (1438 - 1493°C) was poured onto the surface of the core from a height of 20.3 cm by passing the molten iron through a constant-head spout that was made of core sand. The iron was melted in an Inductotherm (Rancocas, NJ) Dura-Line electric induction furnace in the Penn State pilot foundry; and 6.5-24.2. kilograms (14.3-53.3 pounds) were poured onto the core. After running off the angled core, the molten iron was captured in a ladle, then weighed and poured back into the induction furnace. The cores were then removed and evaluated for erosion and surface characterization. Molten iron erosion tests for conditions c, d, e, f, and g were tested in triplicate, while a, b, and e were tested in duplicate. Results listed are the averages of these analyses.

The cores were evaluated for core scratch hardness before and after the pour. In accordance with American Foundry Society (AFS) 3318-00-S, scratch hardness test
which measures resistance to impression, by pressing the core surface with a Dietert
(Detroit, MI) Scratch Hardness Tester. The core scratch hardness was measured 2.5 cm
from where the metal flowed off the core. The erosion depth was measured using
Mitutoyo calipers. Also, as a second measure of the erosion cavity that had been created
during iron pouring, displacement sand was poured into the erosion cavity and scraped
level using a metal bar. Then this displacement sand was poured into a pan and weighed
to quantify the cavity of sand mass that had been eroded during metal pouring.

3. Results and Discussion

3.1 Thermal Gravimetric Analysis (TGA)

Core binder thermal gravimetric analyses have exhibited the mass retained by dry
resins after exposure to high temperatures (up to 800°C). In Figure 4.1, it can be seen
that the inorganic sodium silicate retained the most mass up to the highest temperatures
(80% at 500°C). Collagen retained the least mass (50% at 328°C), while phenolic
urethane (heat cured) retained 50% mass at 438°C (Table 3). Our tentative objective has
been to achieve a TGA mass loss profile that roughly mimicked phenolic urethane, as
such behavior might offer the more favorable simulated balance of structural integrity
during molten iron exposure and binder decomposition during shakeout. This balance of
mass loss was best mimicked by collagen + sodium silicate (50% mass loss at 646°C),
and collagen + K/Li silicate (50% mass loss at 600 °C).
Figure 4.1. Thermal Gravimetric Analysis for Binders Tested while heating at 10°C per minute to 500°C while purged with Argon, including; Collagen, Phenolic Urethane (Heat-Cured), Sodium Silicate, 1 Part Collagen and 0.85 Parts Sodium Silicate, and 1 Part Collagen and 0.87 Parts Li/K Silicate.
3.2 Differential Scanning Calorimetry

DSC is another means of exploring the thermal stability within systems. Recall that samples were oven-cured for 24 hours at 110°C, then evaluated. Broad endothermic peaks dominate the thermograms (Fig 4.2, from first heating cycle). These peaks may suggest initial glass transitions. Although glass transitions classically appear as endothermic step transitions, we suspect that those have been obscured by the oven annealing, resulting in the relatively large, broad peaks. Alternatively, the endothermic peaks may be occurring due to evolution of volatiles; note the temperature region corresponds to significant mass loss in the TGA. Due to the broad nature of these peaks, it is impossible to assign Tg values. Thermograms from the second heating cycle were very flat (data not shown), suggesting that DSC may lack the sensitivity to detect Tgs within the cured networks. Since we suspected DSC lacked the sensitivity to evaluate Tg within the cured samples, we conducted DMA testing, which adds a mechanical perturbation, hence increasing sensitivity.
Figure 4.2. DSC thermogram showing Heat Flow (W/g) (exo up) for Collagen, Phenolic Urethane, Sodium Silicate, 1 part Collagen plus 0.85 parts Sodium Silicate and 1 part Collagen plus 0.87 parts Li/K Silicate.

3.3 Dynamic Mechanical Analysis

DMA was performed to analyze the core’s physical properties at high temperatures as well as to determine the glass transition temperature. The storage modulus and tan delta (tan δ) figures are depicted herein. The storage modulus relates to the elastic component of material response; high modulus values indicate stiff materials,
whereas lower values indicate compliant materials (Sepe, 1998, PerkinElmer, 2008, Menard, 2008). In Figure 4.3, we observe significant modulus drops, which typically indicate the glass transition (Tg) data from Figure 4.4 support this assignment. Also, differences among the collagen-based and non-collagen systems are apparent in the 275-300°C region; collagen and the collagen-hybrids reach minimum modulus in this region, whereas phenolic urethane and sodium silicate show modulus plateaus. The plateaus suggest crosslinked networks, and of the two, the sodium silicate is notably more stable than phenolic urethane. In fact, at approximately 350°C, the modulus of the phenolic urethane samples became indistinguishable from those of either the neat collagen or the collagen-hybrid systems. Note that all of the samples show slightly increased modulus values from 350°C to 500°C, indicating the presence of a crosslinked network that has some thermal stability.

Table 4.3 contains the percent storage modulus retained at 300°C and 450°C with respect to original storage modulus. Sodium silicate retained 37.2% of the original storage modulus at 450°C, while collagen retained only 4.8%. The collagen and alkali-silicate hybrids retained 9.4 and 20.5%, for Li/K silicate and sodium silicate, respectively. The phenolic urethane samples retained 4.4 and 6.5% at 450°C. The relative storage modulus retention indicates which cores are most strong at higher temperatures.

The DMA tan δ is a unitless parameter that corresponds with the tangent of the phase lag of material response. This phase lag as defined as ratio of the loss modulus (E’’; the component of the modulus that has a time-dependent or viscous response) to the storage modulus (E’; which represents the elastic or instantaneous response). Peaks in
the tan δ represent damping events. For polymers, this is typically interpreted as a relaxation, commonly a glass transition (Tg) (Sepe, 1998, PerkinElmer, 2008, Menard, 2008).

Figure 4.4 contains DMA tan δ plots. Note that most samples exhibit two peaks. The first peak generally correlates with drops in storage modulus (Fig 4.3); hence, we interpret this as the initial Tg. The secondary peak, occurring at higher temperatures, is typically broader, suggesting heterogeneity within the network and possibly an increased crosslink density. It is possible the samples were incompletely cured, and that the Tg evolved during the analysis. This would result in a second Tg peak at higher temperature which is more broad. DSC data (Fig 4.2) did not indicate any residual cure; however, it may not be sensitive enough to monitor changes within thermoset networks. An alternative possibility is the presence of distinct phases within the system, suggesting inhomogeneity. Perhaps the material associated with the sand grains has unique intermolecular associations, which is reflected in a second relaxation event. The sodium silicate sample only shows one tan δ, but it is unique in its breadth, suggesting a highly heterogeneous network structure.
Figure 4.3. Dynamic Mechanical Analysis for bindered sand samples heated at 10°C per minute to 500°C while purged with 2 L/min of Nitrogen, showing the Storage Modulus for sand bindered with: (a) 1% Collagen; (b) 1% Phenolic Urethane (Heat-Cured); (c) 1.3% Sodium Silicate; (d) 0.85% Sodium Silicate plus 1% Collagen; and (d) 0.87% Li/K Silicate plus 1% Collagen. Insert: Shows temperature regime from 250°C to 375°C (rubbery plateau), with Storage Modulus range from 0 to 125 MPa.
Temperature (°C)

Tan Delta

Sodium Silicate
Phenolic Urethane
Collagen
Collagen + Sodium Silicate
Collagen + Li/K Silicate

Figure 4.4. Dynamic Mechanical Analysis for core samples heated at 10°C per minute to 500°C while purged with 2 L/min of Nitrogen, showing Tan Delta for sand that was bindered with: (a) 1% Collagen; (b) 1% Phenolic Urethane (Heat-Cured), (c) 1.3 % Sodium Silicate; (d) 0.85% Sodium Silicate plus 1% Collagen; and (d) 0.87% Li/K Silicate plus 1% Collagen.

3.4 Hot Distortion Test

Core samples distorted as they were exposed to a natural gas flame. Interestingly, we observed full distortion to the maximum degree measureable with the instrument (13.5 mm) when we appraised cores that were bindered with either phenolic urethane,
sodium silicate, collagen plus sodium silicate, or collagen plus Li/K silicate. In contrast, collagen alone was the only core binder that was unable to reach the maximum distortion (Refer Fig. 4.5). It is interesting to note that both sodium silicate and collagen with lithium/potassium silicate blend were the cores that remained undistorted for the longest time (more than 100 seconds before >4 mm distortion). In a foundry setting, rapid distortion at high temperatures provides unwanted core behavior; possibly yielding casting defects. Yet further, the ability for the lithium/potassium silicate core to withstand thermal stress the longest until even distorting 1 mm is very favorable for many core scenarios in castings. The ability to withstand breakage until the maximum measurable degree also corresponds with a cores ability to withstand molten iron as demonstrated in section 3.5.
Figure 4.5. Hot Distortion Test Results for sand cores that were bindered with (a) 1% Collagen; (b) 1% Phenolic Urethane (Heat-Cured); (c) 1.3% Sodium Silicate; (d) 0.85% Sodium Silicate plus 1% Collagen; and (e) 0.87% Li/K Silicate plus 1% Collagen. -Cores were heated over a natural gas flame.

3.5 Molten Iron Erosion Test

When the molten iron was poured onto cores, we observed that the sodium silicate, and collagen plus silicate hybrid cores did not erode, whereas both phenolic urethane cores exhibited slight erosion, and the collagen (alone) cores exhibited significant erosion. The sodium silicate core decreased slightly in hardness after having
17 kilograms of molten iron poured over the surface. The collagen plus silicate hybrid cores exhibited more decrease in hardness than did sodium silicate (alone) when experiencing a similar amount of molten iron. The phenolic urethane cores eroded slightly, losing only 0.02 cm of core depth and 0.42 to 0.72 grams of sand per kilogram of iron poured. Also, the hardness of the phenolic urethane core decreased significantly when experiencing molten iron, to less than half the sodium silicate core hardness. The collagen (alone) core exhibited the greatest erosion, even with the least amount of molten iron poured onto it. The collagen core erosion depth was approximately 20 times greater per kilogram of molten iron poured than for phenolic urethane. However, it has been demonstrated in these tests that when collagen is composited with either sodium silicate or Li/K silicate, the molten metal erosion was prevented; and the core performed as desired.

**Table 4.2. Molten iron erosion tests summary table for sand cores that were bindered as shown. (The balance of the core material was 98-99% silica sand)**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
<th>1% Collagen (Heat cured)</th>
<th>1% PU (Heat cured)</th>
<th>1.1% PU (TEA-cured)</th>
<th>1.3% NaSil</th>
<th>0.85% NaSil, 1% Col</th>
<th>0.87% Li/K Sil, 1% Col</th>
<th>0.29% Li/K Sil, 1% Col</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Poured</td>
<td>Kilogram</td>
<td>8.50</td>
<td>16.98</td>
<td>18.81</td>
<td>17.03</td>
<td>17.61</td>
<td>19.01</td>
<td>8.8</td>
</tr>
<tr>
<td>Hardness*</td>
<td>Pre-Pour*</td>
<td>77.5</td>
<td>73.5</td>
<td>85.5</td>
<td>76.0</td>
<td>78.5</td>
<td>85.0</td>
<td>80.5</td>
</tr>
<tr>
<td></td>
<td>Post-Pour*</td>
<td>33.3</td>
<td>24.7</td>
<td>29.8</td>
<td>64.0</td>
<td>44.2</td>
<td>45.5</td>
<td>15.3</td>
</tr>
<tr>
<td>Erosion Depth</td>
<td>Total (cm)</td>
<td>3.08</td>
<td>0.36</td>
<td>0.33</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td>cm/kg Iron</td>
<td>0.362</td>
<td>0.021</td>
<td>0.018</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>0.381</td>
</tr>
<tr>
<td>Sand Erosion</td>
<td>Total (gram)</td>
<td>44.19</td>
<td>12.30</td>
<td>7.92</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td>gram/kg Iron</td>
<td>5.20</td>
<td>0.72</td>
<td>0.42</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>&lt; Detect</td>
<td>6.61</td>
</tr>
</tbody>
</table>
4. Conclusion

The key physical and mechanical properties determined from the work herein are summarized in Table 4.3. Sodium silicate performed very well during TGA as it retained 78.7% mass to 800°C, yet this may contribute to the poor shake-out characteristics. DMA tests indicated that sodium silicate had the greatest storage modulus throughout the entire test, specifically having a 362.4 MPa storage modulus at 300°C, when collagen only possessed a 21.64 MPa modulus. Although sodium silicate distorted quickly during HDT, it was able to distort to 13.5 mm without core failure. Also, a modified sodium silicate bound core was able to experience molten iron pouring without eroding or losing sand integrity. During TGA, heat cured phenolic urethane retained 50% mass until 438.7°C, while also retaining a 188.9 MPa storage modulus at 300°C and also was able to distort to 13.5 mm without failure. This was similar to sodium silicate. Phenolic urethane was also able to experience molten iron pouring, while only eroding slightly.

All tests indicated that collagen alone would perform poorly as a core binder: it lost 50% mass by 328.3°C during TGA experienced the lowest storage modulus (19.76 MPa) value between 300°C and 400°C, collagen-bound cores only distorted 4.2mm before failure, and collagen eroded most significantly during molten iron pouring. This can be attributed to the low bond energy associated with hydrogen bonds. Conversely, the two novel collagen-silicate binder systems compared favorably to conventional foundry binder systems. During TGA, the novel binder systems retained 50% mass until 600°C or 646°C, while also retaining a 19.0 or 50.6 MPa storage modulus at 300°C. The alkali silicate-collagen binders also possessed a tan δ peak similar to sodium silicate. These novel binders were able to distort 13.5 mm without failure during hot distortion tests.
Most importantly, during molten metal erosion tests, the two novel-silicate binders experienced zero erosion.

The results herein demonstrate that collagen alone does not provide sufficient physical and mechanical properties to work as a core binder, which is attributed to the low bond energy attributed to hydrogen bonds (Stainsby, 1958, Emsley, 1980, Buhler and Ackbarow, 2007, IUPAC, 2006, Strong, 2008). However, when collagen is used in conjunction with lithium/potassium silicate or sodium silicate, a foundry binder that possesses favorable physical and mechanical properties is formed. Furthermore, the novel collagen plus silicate binders compare favorably to conventional modified sodium silicate and phenolic urethane. Yet, the novel collagen plus alkali-silicate cores withstand thermal distortion more favorably than phenolic urethane which can help prevent unwanted core behavior which contributes to casting defects. Overall, the novel collagen and silicate binders possess: superior capabilities to withstand distortion at high temperatures, appropriate mass retention at high temperatures as well as most importantly withstand molten iron erosion. Therefore, the results to date indicate that novel collagen-silicate binders possess physical and mechanical properties at high temperatures that are useful to foundries.
Table 4.3. Summary Table providing key data from DMA, HDT, TGA, DSC and Pilot-Scale Molten Iron Erosion Tests.

<table>
<thead>
<tr>
<th>Test</th>
<th>Parameter</th>
<th>Binder Material (along with 98-99% sand)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.87% Li/K Sil, 1% Col</td>
</tr>
<tr>
<td>Sand Erosion g sand / kg iron poured</td>
<td>Nil</td>
<td>nil</td>
</tr>
<tr>
<td>Erosion Depth (cm / kg iron poured)</td>
<td>Nil</td>
<td>nil</td>
</tr>
<tr>
<td>Hardness, Pre-pour</td>
<td>85</td>
<td>78.5</td>
</tr>
<tr>
<td>Hardness, Post-pour</td>
<td>45.5</td>
<td>44.2</td>
</tr>
<tr>
<td>Storage Modulus at 300°C (MPa)</td>
<td>48</td>
<td>72</td>
</tr>
<tr>
<td>Storage Modulus at 450°C (MPa)</td>
<td>179</td>
<td>164</td>
</tr>
<tr>
<td>T (°C) of start of Deflection (start of loss of stiffness)</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Percent Storage Modulus Retained at 300°C (%)</td>
<td>2.4</td>
<td>7.9</td>
</tr>
<tr>
<td>Percent Storage Modulus Retained at 400°C (%)</td>
<td>9.4</td>
<td>20.5</td>
</tr>
<tr>
<td>Tan Delta Peak</td>
<td>0.51</td>
<td>0.42</td>
</tr>
<tr>
<td>Tan Delta Peak T (°C)</td>
<td>342</td>
<td>344</td>
</tr>
<tr>
<td>Average time to 1 mm Distortion (seconds)*</td>
<td>83 ± 21</td>
<td>29 ± 14</td>
</tr>
<tr>
<td>Average time (seconds) to distortion of 13.5 mm (or to break-failure)*</td>
<td>152 ± 55</td>
<td>197±137</td>
</tr>
<tr>
<td>TGA</td>
<td>T (°C) at 10% mass loss</td>
<td>273</td>
</tr>
<tr>
<td></td>
<td>T (°C) at 50% Mass Loss</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>% Mass Retained at 750°C</td>
<td>43</td>
</tr>
</tbody>
</table>

*Hot Distortion Test data lists average and standard deviation for 10-15 analyses.
** For collagen: 71 seconds to break-failure at 4 mm average distortion.
***For phenolic urethane (hot cured), 3 samples broke before 13.5 mm distortion, while 10 samples did not even break at the maximum 13.5 mm distortion.
5. Acknowledgements

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0906271, Standard Grant, SGER/GOALI: Industry Presence on Campus: Cross-linking of Collagen Binders for Foundry Cores to Reduce VOC Emissions, 10/01/2009 to 12/31/2010

6. References


Chapter 5

Emission Characterization and Chemical Interactions of a Novel Collagen-Silicate Hybrid Foundry Core Binder

Abstract

Foundries within the United States aim to meet ever-more stringent air emission standards as production in many remaining foundries has increased due to the recent shut-down of many stateside facilities. However major contributors to foundry air emissions are conventional foundry core binders, which are responsible for up to 70% of foundries Volatile Organic Compound (VOC) emissions. A novel core binder that utilizes collagen, and alkali silicates possesses characteristics favorable for metalcasting. Collagen is a by-product of the meat-packing industry. Herein, conventional and novel foundry core binders air emissions were appraised using thermal gravimetric analysis mass spectrometry (TGA - MS). Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS) were utilized to characterize how collagen and silicate chemically interact. The analytical techniques indicate that cross-linking occurred between the carboxyl functional group innate to collagen and sodium silicate.

1. Introduction

Metalcasting is integral to American industry as castings are employed in nearly 90% of manufactured durable goods (AFS, 1998). Within the metal casting industry, the conventional process technologies release emissions, thus burden foundries aiming to meet ever-more stringent environmental standards. Therefore, the conventional technologies impart a significant financial burden on the industry (US DOE, 1999, U.S. Dept. of Commerce, 2008). Specifically, conventional core binders emit up to 70% of a foundries Volatile Organic Compound (VOC) emissions (Glowacki et al, 2003) and the
development of environmentally benign binders is identified as a critical research need (Cast Metal Coalition, 1998). Our recent work has demonstrated that a novel binder, composed of collagen and alkali silicates possesses physical and mechanical properties that are favorable for foundry utilization (Fox et al., 2011 – represented herein as Chapter 4). Herein, this novel binder is compared with conventional binders and appraised qualitatively for air emission potential via thermal gravimetric analysis mass spectrometry (TGA-MS). Also, fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were utilized to elucidate the chemical interactions between collagen and sodium silicate.

During metalcasting, foundries typically employ green sand molding in the outer mold to create the desired shapes and geometries. When more complex castings are produced, cores are the objects within a green sand mold that provide the geometry for cavities within castings; and cores are typically placed within the green sand mold. For example, when casting an engine block, the cavities that house pistons would be formed by placing cores in the mold. These sand cores generally contain 97-99% sand and 1-3% binder. Sand cores are conventionally held together with petroleum based adhesives, specifically phenolic-urethane or furans. These conventional cores have adequate strength at room temperature; yet also maintain structural integrity when exposed to molten metal. During metal pouring, the maximum temperatures experienced by cores range from 1440°C-1500°C at the molten iron interface, down to 50-300°C several inches away from this interface; with an exponential decline through the core (Wang et al., 2006). Paradoxically, after withstanding molten metal thermal exposure and subsequent cooling, the binder must then break down during shake-out, so that the sand can be easily
removed from the cast product cavities after the metal cools. Several conventional petroleum based binder systems, such as phenolic urethanes and furans, have been found to provide structural integrity, shakeout propensity, and casting quality. However, these phenolic urethanes and furan binders will ‘breakdown’ after metal solidification, and emit as much as 30-70% of a foundries VOC’s and Hazardous Air Pollutants (HAP’s) (Glowacki et al., 2003, Wang et al., 2007). Furthermore, VOC and HAP emissions increase proportionately with an increase in core-loading (Goudzwaard et al., 2003, Glowacki et al., 2003). Recent work has determined that VOC emissions for a collagen core binder are 70-95% less than phenolic-urethane (Wang et al., 2007, CERP, 2007). However, collagen alone does not provide the adequate thermal resistance when used as a core binder in iron castings, yet when collagen is coupled with alkali-silicates a core binder provides adequate thermal resistance for iron castings (Fox et al., 2011).

Collagen is the fibrous protein that strengthens skin, tendon and bones; and this triple-helical material has tensile strength greater than steel. The individual collagen strands are 200-500 nm long; and each polypeptide strand is comprised of a three amino acid repeating sequences. These typically include a repeating sequence similar to X-Y-Glycine; where Glycine comprises about 34% of collagen, while the “X” and “Y” include proline (12%), alanine (10%), hydroxyproline (10%), glutamic acid (7%), or other amino acids (Palfi et al., 2007; Eastoe and Leach, 1958, Stainsby and Courts, 1958). Gelatin also contains these same amino acid sequences, but is generally a shorter polypeptide strand. The strands in the helical structure, tropocollagen, are held together and aligned by hydrogen bonds (Kawahara et al., 2005). Any given hydrogen bond is relatively weak, but when the strands are helically coiled around one another, the cumulative
bonding strength can be considerable. However, as water penetrates the fibers, the hydrogen bonds are broken and this is what causes collagen to soften in water. At temperatures exceeding 60°C, these hydrogen bonds are broken, forming denatured collagen (i.e. gelatin); and this is when the polypeptide chains are free in solution (Kawahara et al., 2005). The adhesive that forms is hydrolyzed collagen (or gelatin), as an adhesive, these polypeptide chains re-align as water evaporates, and this causes a network of random alignments through hydrogen bonds (Hofmeister, 1878, Eastoe and Leach, 1958, Stainsby and Courts, 1958).

**Prior Studies of Pyrolytic Products**

Previous studies by Wang et al., have determined that aniline (C₆H₇N) is formed during the pyrolysis of phenolic urethanes. In comparison, pyrrole has been identified as a product of collagen core binder pyrolysis (Wang et al., 2007). Further, Dungan et al. and Lytle et al., have examined the thermal decomposition products of phenolic urethanes during pyrolysis by mass spectrometry. During these studies over 60 compounds have been identified, mostly consisting of benzene, toluene, phenol and various other volatiles (Dungan et al, 2005, Lytle et al., 1998). Others have performed studies of the pyrolytic products of proteins, amino acids and collagen (Smith et al., 1974, Higman et al., 1970). Some of the major pyrolysis products from collagen were found to be pyrrole, toluene, xylenese, benzonitrile, indole, pyridine, picoline, aniline, phenol and cresol (Higman et al., 1970). Pyrrole release from amino acids and proteins has been linked to the decarboxylation and dehydrogenation of proline (Higman et al., 1970). Proline is a predominate amino acid comprising collagen.
Collagen and Hydroxyapatite as Synthetic Bone

Collagen has the capability to be cross-linked with various organics such as glutaraldehyde (Harriger et al., 1997) or citric acid (Taguchi, 2006) for a broad range of purposes, such as soft tissue adhesion (Taguchi et al., 2004) or of particular focus, hard tissue adhesives. Hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) is one of the most biocompatible materials (Liao et al., 2005); and the author anticipated that the interactions of hydroxyapatite with collagen would offer similar chemistry as the interaction of alkali silicates with collagen. There is currently urgent work in the biomedical material industry to develop an improved collagen and hydroxyapatite based hard tissue material (Chang et al. 2001, Chen et al. 2005, Du et al. 2000, Landi et al. 2003, Tadic et al. 2002 and 2003, Wang et al. 2006 and Yunoki et al. 2007). In humans and other mammals, hard tissue is composed of approximately 70% hydroxyapatite and 30% collagen (Rhee et al., 2000). Attempts to form improved biomedical materials reflect similar approach as our methods by utilizing solution chemistry to initiate collagen cross-linking with hydroxyapatite. Fourier-transform infrared spectrometry by Rhee et al., 2000 and Kicuchi et al., 2001, found that nucleation of calcium phosphate originates with carboxyl groups on collagen, by interaction of Ca$^{2+}$ binding to –COO$^-$. Through use of FTIR, Zhang et al. (2003), confirmed the results of others, while also finding that carbonyl groups act as a nucleation site as well, with calcium working as a complexing agent. Bone types with varying organic matter content were heated to high temperatures and it was found that mass loss was directly related to the organic matter content in bones (Mkukuma et al., 2004). Of particular interest for this research is that high organic content bone types had significant mass loss in the range of 200-600°C.
Mkukuma et al., found that low organic content bone types had more significant mass loss in the range of 700-1500°C, consisting mostly of CO₂. Therefore, a collagen and silicate mixture is perhaps similar to the biomedical synthetic bone.

**Objectives and Hypothesis:**

The purpose of this study was to understand the pyrolysis pathways of conventional binders as well as the novel collagen alkali-silicate binder. Additionally, nitrogen is a key component of conventional phenolic urethanes and collagen as it comprises amino acids. Thus, the fate of nitrogen containing species was closely monitored. Herein, the decomposition of the novel collagen/alkali silicate binder was compared to both collagen (alone) and conventional phenolic urethane binders. Comparison to collagen alone elucidates how the collagen/alkali silicate binder withstands thermal decomposition. Our hypothesis was that since both sodium silicate (alone) and collagen (alone) release fewer VOCs than conventional phenolic urethane binders, a composite collagen/alkali silicate binder should likewise release fewer VOCs than conventional phenolic urethane. The second objectie was to elucidate the chemical mechanism by which collagen/alkali silicate binders had exhibited greater strength and less erosion when exposed to molten iron and elevated pyrolytic temperatures. The comparison of phenolic urethane to the novel collagen/alkali silicate binder should confirm the reduction in various emission species as reported by Wang et al., 2007.

2. **Materials and Methods**

2.1 **Materials**

Silica sand was provided by Wedron Silica Company (Wedron, IL), and had a specified AFS grain fineness number ranging from 67-73. The silica sand was sieved so
that all sand would pass through a US Mesh 30 sieve, yet be retained on a US Mesh 400 sieve. Sand was rinsed in 1500 gram batches with adequate distilled water and subsequently 1 L of deionized water. Sodium silicate was a modified sodium silicate provided by J.B. DeVenne INC. (Berea, OH). This modified sodium silicate formulation contained 42.5% by weight of dry solids. Collagen was provided by Entelechy (Plymouth, MI), and came as a dry powder. All proportions of collagen and sodium silicate are herein listed on a dry-mass basis. The phenolic urethane binder that was heat-set and cured by triethylamine (DMEA) was provided by Ashland Chemical Company (Columbus, OH); and came as a two-part binder that cured when mixed and heated. All proportions of phenolic urethane binder listed herein are based on an as-received mass basis.

2.2 Sample Preparation Overview

Samples for thermogravimetric analysis mass spectrometry (TGA-MS), were all prepared by mixing silica sand with binder. Specifically, bindered core samples were prepared by mixing (500 g) of washed foundry silica sand with the respective core binder composition for 90 seconds at Level ‘2’ Solid State Speed Control, in a Commercial Kitchen Aid Mixer, Model Number KSMC50S (St. Joseph, MI). The sand and binder mixture was hand packed in a 5”x5” box and cured at 110°C for 2 hours. The sample was then ground in a mortar and pestle into individual grains. Samples were stored in a desiccator until analyzed by TGA-MS.

Samples for X-ray photoelectron spectrometry (XPS) and Fourier Transform Infrared Spectroscopy (FTIR), were prepared by first sieving sand through 100 US Mesh (149 micron) sieve. Collagen was denttured and hydrolyzed at 70°C to form a gelatin
solution, and then mixed by hand with sodium silicate and 50.0 grams of sand. The samples were packed into a dogbone mold and cured for 1 hour in a 110°C oven. Following this hour-long cure, the samples were removed from the mold and ground into individual sand grains.

**Table 5.1. Sample composition summary table (on dry mass basis).**

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collagen</td>
<td>10 g Denatured and Dried Collagen</td>
</tr>
<tr>
<td>Sand + Collagen</td>
<td>100 g Sand + 1 g Collagen</td>
</tr>
<tr>
<td>Sand + Collagen + Sodium Silicate</td>
<td>100 g Sand + 1 g Collagen + 0.85 g Sodium Silicate</td>
</tr>
<tr>
<td>Sand + Sodium Silicate</td>
<td>100 g Sand + 0.85 g Sodium Silicate</td>
</tr>
<tr>
<td>Sand + Phenolic Urethane (Heat Cured)</td>
<td>100 g Sand + 1 g Phenolic Urethane</td>
</tr>
<tr>
<td>Sand + Phenolic Urethane (DMEA cured at HMAC)</td>
<td>100 g Sand + 1.1 g Phenolic Urethane + DMEA gas catalyst</td>
</tr>
</tbody>
</table>

### 2.3 Thermal Gravimetric Analysis with Mass Spectrometry

Approximately 400 mg of sand sample was placed in an alumina pan for thermal gravimetric analysis with mass spectrometry. The samples were placed in a TGA 2050 (TA Instruments, Newcastle, DE) and heated from room temperature to 1000°C at 10°C/min while being purged with high-purity argon. The effluent gas was analyzed by a mass spectroscopy instrument (Thermostar GSD 301T, Pfeiffer Vacuum Inc., Nashua, NH). The samples were analyzed for previously identified VOC and HAP emissions formed during foundry core binder pyrolysis as well as potential nitrogen containing emissions. Each sample was analyzed in duplicate.

### 2.4 Fourier Transform Infrared Spectrometry (FTIR)

Fourier transform infrared spectrometry attenuated total reflectance (FTIR-ATR) spectra were acquired on a Bruker IFS/66s (Bruker Optics, Billerica, MA) spectrometer equipped with an MVP-Pro Star Diamond ATR accessory (Harrick Scientific, Pleasantville, NY). Sample spectra were acquired in rapid scan mode using a DTGS
detector and by averaging either 100 or 400 scans at 8 cm⁻¹ resolution. All spectra were referenced to the spectrum of the bare diamond crystal and were plotted in absorbance units.

2.5 X-ray photoelectron spectroscopy (XPS).

Approximately 100 mg of binder-coated sand sample was spread out on aluminum foil. Double sided 3M tape, which is electrically insulated, was stamped on the sample to fully coat the tape with sample. The samples were then loaded into the XPS, a Kratos Axis Ultra (Kratos Analytical Ltd., Manchester, UK). The analysis chamber was placed under a vacuum to approximately 10⁻⁸ Torr range. The lens was set to hybrid mode and the pass energy was set to 80 eV for survey scans; and 20 eV for high-resolution scans. The step size was set to 0.5 eV for survey scans; and then to 0.1 eV for high-resolution scans. The samples were scanned for Na 1s, O 1s, N 1s, C 1s and Si 2p electron orbitals.

3. Results

3.1 Pyrolysis Emision Products of Thermal Gravimetric Analysis with Mass Spectrometry (TGA-MS)

Collagen (alone) versus collagen with alkali silicates pyrolysis emission products are compared in Figure 5.1. For most compounds monitored, both these binder systems exhibited similar responses when identical levels of collagen were used (1% on dry mass basis, refer Table 5.1). Both binder systems presented limited response for benzene, formaldehyde, aniline, phenol and xylene; and the significance of this is discussed below. However, during pyrolysis, both binders emitted hexane, pyrrole and toluene; and these three compounds were generally released between 300 and 500°C.
One significant difference between collagen (alone) and collagen with alkali silicates, when comparing carbon dioxide emissions (m/z = 44). Carbon dioxide release from collagen (alone) occurs from 200°C to 800°C. Collagen-with-alkali silicates also releases carbon dioxide in this temperature range, however, above 500°C, there is a ‘shift’ that occurs when alkali silicates are used. At 500°C, collagen (alone) begins to release significantly more carbon dioxide, whereas collagen-with-alkali silicates shifts upward, to approximately 570°C when it begins to release carbon dioxide at a similar rate. This is due to the linkages between alkali silicates and collagen that enhance binder thermal stability, as discussed below. Further, a significant difference between these two binder systems occurs when monitoring m/z = 30. The m/z = 30 signal can represent a host of compounds, including formaldehyde, ethanolamine, ethane, nitromethane, nitrogen dioxide and nitrogen monoxide. The major difference between collagen and collagen with alkali silicates occurs in the 500°C to 900°C temperature range. Within this temperature range, collagen alone demonstrates an increased m/z = 30 release, whereas, collagen with alkali silicates demonstrates a subdued response. The author pose that this subdued response from collagen with alkali silicates is due to the linkages between silicates and collagen, as discussed below. Thus, the compound that is exhibited during m/z = 30 is also critical to the interaction between collagen and alkali silicates, however, without further work, this cannot be fully confirmed.

That author also appraised to conventional phenolic urethane one that had been heat-cured and the other that had been cured with dimethylehanolamine (DMEA). These were both pyrolyzed to compare released emissions in Figure 5.2. Both binders released formaldehyde, carbon dioxide, hexane, pyrrole, benzene, toluene, aniline and phenol.
These compounds were released from 200°C to 800°C, with each compound demonstrating a unique temperature dependent profile. Specifically; formaldehyde was released between 200°C to 300°C, hexane was released from 200°C to 600°C, pyrrole was released from 300°C to 600°C, benzene was released between 400°C to 700°C, toluene was released between 400°C to 700°C, aniline was released from 350°C to 650°C and phenol was released from 200°C to 800°C. In general, for the compounds monitored, there did not appear to be significant differentiation between heat cured and dimethylethanolamine cured phenolic urethane pyrolysis emissions. The only exception was that the DMEA-cured sample appeared to release slightly more formaldehyde over all temperatures, more aniline released between 500°C and 600°C, and more carbon dioxide between 600°C and 800°C.

When comparing the TGA-MS responses, the author noted that both phenolic urethanes and collagen-containing binder systems released emissions during pyrolysis. However, phenolic urethanes tended to release a larger variety of compounds than did collagen containing binder systems (See further discussion below).
Figure 5.1. Thermal Gravimetric Analysis with Mass Spectrometry for collagen (alone) versus collagen-with-alkali silicates; both heated at 10°C per minute while under a 100% argon atmosphere.
Figure 5.2. Thermal Gravimetric Analysis with Mass Spectrometry for heat cured phenolic urethane, DMEA-cured phenolic urethane, and sodium silicate, all heated at 10°C per minute under a 100% argon atmosphere.
3.2 X-Ray Photoelectron Spectrometry (XPS)

X-Ray photoelectron spectrometry was performed on collagen-alone versus collagen-with-alkali silicate to analyze the nature of the chemistry for carbon and nitrogen atoms, as related to the carboxyl and amine functional groups innate to collagen. Interestingly, these XPS scans revealed that carboxyls were reconfigured to carboxylates for the collagen-with-silicate samples. This reconfiguration has been demonstrated in Figure 5.6 by the sub-peak formed at 289 eV; and is taken to represent sodium carboxylate linkages, which could enhance this binder system’s strength (see discussion below). This peak was absent from collagen samples-alone (Figures 5.4 and 5.5). Further, the carboxyl peak at 288 eV in Figures 5.4 and 5.5 decreases in Figure 5.6 due to consumption of carboxyls to form carboxylates. In contrast, these same XPS scans did not reveal any shift or change for nitrogen chemistry between collagen and silicate coated sand samples. Thus, XPS data did not detect that the amino functional groups interacted with sodium silicate.
Figure 5.3. X-ray photoelectron spectroscopy scan for the C1s orbital for collagen alone sample (no sand).
Figure 5.4. X-ray photoelectron spectroscopy scan for the C1s orbital for collagen (alone) and sand sample.
Figure 5.5. X-ray photoelectron spectroscopy scan for the C1s orbital for collagen and sodium silicate with sand sample.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR scans were performed to elucidate the chemistry of the collagen and sodium silicate binder system, specifically, the carboxyl and amino functional groups of collagen were of particular interest. The FTIR scan of collagen-with-silicate indicates a shift at 1715 cm⁻¹, as compared to collagen-alone (Figure 5.3). This shift at 1715 cm⁻¹ concurred with the data above, indicating that the alkali silicates induced carboxyl stretching.
Figure 5.6 FT-IR showing a shift at 1720 cm$^{-1}$, indicating C=O from the collagen carboxyl is interacting with sodium silicate and ‘stretching’. In Black is collagen only, Red is collagen with sand, Blue is collagen and sodium silicate coated sand.

4. Discussion

Herein, TGA-MS, FTIR and XPS were utilized to characterize emissions and understand chemical interactions for a novel collagen/alkali silicate core binder. The emissions from the collagen based binder demonstrate that less VOC’s are formed during analytical pyrolysis. Specifically, phenolic urethane released phenol, benzene, formaldehyde and aniline during pyrolysis, whereas the collagen based binders both did not form these degradation products, as tested herein. However, the collagen/alkali silicate core binder demonstrated an increased CO$_2$ release at 570$^\circ$C, when collagen alone demonstrated this increased CO$_2$ release at 500$^\circ$C. This TGA-MS response indicates the CO$_2$ is an important compound to determine the specific mechanisms that improve the
thermal resilience for the collagen/alkali silicate binder. Indeed, through FTIR and XPS analysis, there is carboxyl stretching that occurs between collagen and alkali silicates. The carboxyls present in collagen are converted to carboxylates in the presence of alkali silicates, as demonstrated by XPS with a sub-peak appearing at 289 eV (for carboxylate) and a subdued sub-peak appearing at 288 eV (for carboxyl). Similarly, FTIR confirms the carboxyl stretching by the response of collagen/alkali silicates at 1715 cm\(^{-1}\). This shift is similar to what occurs on the surface between acetic acid and sodium aluminoborosilicate glass fibers as described by Stapleton et al., 2010. Further, the increase in intensity at 1576 cm\(^{-1}\) is due to the asymmetric stretch of carboxyl groups. Similarly, at 1450 cm\(^{-1}\) the intensity increase is due to the symmetric carboxyl stretch (Jones et al., 1954 and Tafipolsky et al., 2009).

Further, this collagen and alkali silicate binder is similar to synthetic bone produced by the medical material industry. Specifically, an increased response of CO\(_2\) emissions is typical of higher inorganic content synthetic bones (Mkukuma et al., 2004), which is similar to the response of a collagen/alkali silicate binder examined herein. Additionally, there were less pyrolysis products of collagen-with-alkali silicates, as compared to conventional phenolic urethane. The TGA-MS results yielded similar trends as Wang et al., where collagen (alone) behaved the same as collagen-with-alkali silicates relative to the peak areas of VOC’s. This confirms the hypothesis that collagen-with-alkali silicates will yield less emission products than conventional phenolic urethane as suggested by previous work analyzing collagen alone (Wang et al., 2007). Additionally, synthetic bone demonstrates carboxyl stretching via linkages with calcium, confirmed via FTIR (Rhee et al., 2000 and Kicuchi et al., 2001, Zhang et al., 2003); whereas collagen
and alkali silicate carboxyl stretching were confirmed via XPS and FTIR. Carboxyl stretching initiated by sodium silicate stabilizes collagen at higher temperatures, providing an adhesive useful for the foundry industry, which also yields fewer pyrolysis products than conventional foundry binders.

5. Acknowledgements

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Chapter 6

Full-Scale Demonstration of a Novel Collagen Alkali-Silicate Core Binder

Abstract

Foundries within the United States aim to meet ever-more stringent air emission standards as production in many foundries has increased due to the shut-down of many stateside facilities. Major contributors to foundry air emissions are conventional petroleum based foundry core binders, which are responsible for up to 70% of foundries Volatile Organic Compound (VOC) emissions. A novel core binder that utilizes collagen, a by-product of the meat-packing industry, and alkali silicates possesses characteristics favorable characteristics for metalcasting. Herein, this core binder was tested using tensile strength, hot distortion testing and a full-scale casting demonstration. This novel collagen-alkali silicate binder possessed a tensile strength of nearly 300 psi, (at 0.98% dry weight binder) compared to a 215 psi tensile strength for 1.1% conventional phenolic urethane. Additionally, this novel collagen-alkali silicate binder withstood hot distortion longer than conventional phenolic urethane. Most importantly, the collagen-alkali silicate binder was also able to produce quality castings when utilized in a full-scale casting study.

1. Introduction

Metalcasting is integral to American industry as castings are employed in nearly 90% of manufactured, durable goods (Cast Metal Coalition, 1998). However, conventional core binders utilize petroleum based binders that are responsible for 30-70% of foundries Volatile Organic Compound (VOCs) emissions as well as release numerous Hazardous Air Pollutants (HAPs) (Glowacki et al., 2003, Wang et al., 2007). Recent
work has demonstrated that a novel core binder that contains collagen and alkali silicates possesses favorable thermal mechanical properties for metalcasting. Specifically, this novel core binder possesses a longer time until distortion than conventional petroleum based binders while also withstanding molten metal erosion (Fox et al., 2011). Herein, this core binder was appraised using tensile strength tests, hot distortion tests, core production, core blowing modeling and a full-scale casting demonstration.

Cores used in foundries should possess properties which enable them to form internal cavities in castings or portions of the exterior of castings. Historical requirements for cores, as per Dietert, mandate a core be strong enough following preparation to retain the desired shape. The core should be able to withstand molten metal erosion and resist deformation during metal pouring. It is also desirable that a core remains a high degree of dimensional tolerance through the metalcasting process. Additionally, cores should have low off-gassing, so as to prevent gases entering the liquid metal. Paradoxically, following casting, the core should disintegrate following casting solidification, so the core can be removed from the casting during shake out (Dietert, 1966). With contemporary environmental permitting and regulation, cores must also limit air pollutant emissions. During production, cores should be able to be produced without producing VOC’s or odors. Additionally, during storage cores should not leach compounds into the atmosphere that are regulated or odorous. Also, cores should limit air emissions during the pouring, cooling and shake-out phases of metalcasting. In summary, cores should be able to be easily formed, retain their geometry, resist molten metal erosion, resist distortion, limit off-gassing, breakdown following metal pouring, and limit air emissions from production to use.
An essential component of a core binder and sand mixture is the ability to form cores. For high volume core production, cores are conventionally formed through what can be visualized as ‘quasi-injection molding’. The mold used for production is typically called a ‘core box’. This core box consists of two parts, which are closed together when the sand and binder mixture are injected into the mold and following core curing the two parts are separated so the cores can be easily removed. During this ‘quasi-injection molding’ the sand and binder mixture is ‘blown’ with compressed air into a mold. This ‘blow’ process will compact the sand into the mold, ideally completely filling the mold cavity. The binder is then ‘cured’, typically via both heat and a gas catalyst. In the case of phenolic urethane resins, the gas curing catalysts are either triethylamine (TEA) or diemethylethylamine (DMEA) (AFS, 1987). These gas catalysts solidify the binder system. For water based binders, the cores are cured via heat, which radiates from the heated mold. Also, when curing a water-based binder heated air can also be forced through the core to accelerate heating the binder as well as remove vaporized moisture.

Cores are conventionally formed in core machines. After sand and binder have been mixed together, they are transferred to the sand chamber. The sand chamber retains the binder coated sand. The binder coated sand is fluidized in the sand chamber with compressed air and ‘blown’ into the corebox at pressures between 45 and 100 psi. The corebox is clamped together via pneumatics or hydraulics while cores are ‘blown’ and cured. At this point, the gassing manifold is transferred to the core box. The gas, either TEA or DMEA when using phenolic urethane, is then passed through the core box to cure the core. With collagen/alkali silicates; the author has used hot air as the curing gas.
When the cores have cured, the corebox is unclamped and opens, at this point the cores can be removed and stored for use in the casting process (AFS, 1987).

The distortion of cores at high temperatures is highly undesirable as this leads to increased casting defects. Core distortion can cause casting defects during pouring or metal solidification when the core moves or changes shape, resulting in a casting that possesses a distorted cavity. Core distortion at high temperatures is conventionally measured via hot distortion testing. Hot distortion was measured herein to appraise the novel low emission binder for resistance to distortion.

Until recently, core box venting configurations were adjusted for core blowing through trial and error. Recently, computation particle fluid dynamic (CPFD) modeling software has enabled coreboxes to be appropriately designed for ‘blowing’. An important component that must be adjusted during blowing is the corebox venting. There must be appropriately placed vents, with ample area to allow air, which fluidizes the sand to exit the corebox as the sand compacts. If the air is unable to exit the corebox, the sand can become re-suspended which causes lifting and results in low-density regions within the core (Yao et al., 2003). This phenomena can be modeled via CPFD and generally corresponds well to experimental results using coreboxes (Yao et al., 2003). Herein, the modeling of Hitachi Metals Automotive Components (HMAC) part 249 was performed with Arena-flow (Albuquerque, New Mexico). The modeling of part 249 was performed to assist in the retro-fit of a ‘retired’ shell core box to be compatible with binder coated sand. Shell coreboxes have minimal venting, as the sand that is blown is dry since it is coated with a resin. Whereas, conventional phenolic urethane coreboxes have increased venting since the binder coated sand requires more air for fluidization, which must be
vented from the core box. Similarly, water based cores require more venting than shell sand. Thus, the shell core box had minimal venting as it was received, however using the CPFD modeling software Arena-flow® assisted in determining where and how many vents to add to the former shell corebox.

Once cores are produced, they are generally stored on a core rack for a limited time before use. The core racks are moveable shelving systems, which enables cores to be readily moved from the core room to the molding line. In a conventional foundry line, cores will be placed in the green sand mold. The green sand mold containing the cores will be moved via a flask system or conveyer to pouring. At metal pouring, the mold is filled with molten metal and moved away from pouring. Typically, molds will cool for approximately one hour before they reach shake-out. At shake-out, the molds are vigorously shaken to remove the casting from the green sand mold. Additionally, the cores should be readily removable from the castings during shakeout. Ideally, the cores would shake-out so well that individual sand grains would enter the green sand system, replenishing the system for discarded waste green sand. Following shakeout, castings are shot blast. During shot blast, steel shot, or steel ball bearings are forced against the surface of the casting to remove any remaining sand or molding materials from the casting surface. Following shot blast the casting should be free of any molding materials, such as sand, clay or core debris. After shot blast, castings are conventionally segregated by part so that they can be machined. Following visual, robotic or laser inspection castings are machined to improve surface finish and dimensional tolerances. Depending on the casting, additional machining may be necessary to produce the final part.
2. Materials and Method

2.1 Tensile Strength

As previously mentioned, cores should be able to be strong enough to retain desired shape after preparation. The conventional method to measure strength is through tensile strength measurements; and these are conventionally tested with ambient-temperature cores. Tensile strength is measured by forming ‘dogbones’. These dogbones are then placed in a Simpson Gerosa universal sand test machine and pulled in tension until failure. The point at which the dogbone fails in tension is referred to as the core tensile strength. This test is the acceptable method to appraise if a core will retain the desired shape following preparation.

Samples were prepared by mixing 1.50 kg of sand with binder using a Kitchen Aid Mixer for 90 seconds at level ‘2’. The sand was then hand-packed into a 9-part open face dog bone mold. The samples were cured at 110°C for 1 hour. The samples were removed from the mold and tested for tensile strength, within 15 minutes of being removed from the oven. The samples were tested for strength using a Simpson Gerosa Universal Sand Strength Machine.

2.2 Hot Distortion Tests

For hot distortion testing (HDT), the samples were formed and tested as per Fox et al., 2011 (Also refer to Chapter 4). The samples were formed by hand packed cores, in a 16- sample wooden core box, which created candy bar-sized cores that were 15.24 cm long, 2.54 cm wide and 1.27 cm thick. In this core box, the bindered cores were cured at 110°C for 1 hour, with the exception of heat cured phenolic urethane which was cured for 24 hours. After curing, the cores were stored for 24 hours in a dessicator prior to testing.
Hot distortion tests were performed with a custom hot distortion test device. The samples were clamped in place with 2.54 cm of sample clamped on an iron ledge, the Bunsen burner flame was centered on the exposed 12.7 cm of sample and the micrometer monitored the deformation at a location that was 1.27 cm from the end opposite the clamp. This deformation was monitored up to a maximum of 13.53 mm. The samples were heated in the center of the test bar with a natural gas flame through 2.54 cm diameter perforated Bunsen burner, which had an adiabatic flame temperature of 1960°C at its source; and the perforated burner plate remained 2 cm from the bottom of the cantilevered sample. The micrometer transmitted deformation readings every second; and these readings were logged by the computer. For each binder condition, 15 samples were analyzed via HDT. The results exhibited inherent variability in both time to given deflection, and deflection at failure (See discussion below).

2.3 Core Making for Full-Scale Demonstrations

Sand was mixed with binder as is the conventional foundry practice and placed into the sand magazine of a Redford Carver core machine. The sand was blown into the multi-part core box. The part (part 249) formed has a five inch cube bulk area, with an extension approximately 3” long and ¾” in diameter. When blowing part 249 in this specific core box, the binder coated sand flows through the five inch cube and then into the 3” extension. The cores were cured in a warm core box, with curing acceleration aided by a Furness-Newburge INC Superheater System. Following curing, the cores were placed on a core rack. Core curing times were similar to those used in production.

As discussed in the introduction, cores were produced using a shell core box that was obtained from our full-scale foundry partner. Initial attempts using this shell core
The corebox had limited success, due to the fact that no additional venting was used to accommodate binder coated sand, specifically water-based binder coated sand. Herein, the ‘retired’ shell corebox was retrofitted with additional venting as per determinations through Arena-flow simulations. However, retrofitting a ‘retired’ shell corebox is not ideal as coreboxes for shell cores are generally configured differently than coreboxes for phenolic urethane or water-based cores. Specifically, since less air is required for shell cores, box configurations can be more rigorous in blow direction and distance, whereas phenolic urethane and water-based binder coreboxes are designed to minimize the rigors of core blowing. Additionally, shell coreboxes are generally heated at high temperatures from 500°F-550°F (260-288°C, AFS, 1987) and open and closed hundreds of thousands of times through their useful life, which can result in warping and wear. The corebox herein also was warped, which further confounded the ability to produce quality cores.

The improved venting aided production and overall core quality was improved, yet since the box was warped and originally configured for the shell process, additional venting and changes would be necessary to optimize the process. Specifically, many cores were produce that did not have complete filling, or high density, in the furthest region of the core, which is the very tip of the core.

The cores used for this study were between 25 and 33 days old and had ‘softened’ due to prolonged storage and exposure to humidity. The variation in core age was due to the different days that the cores were produced. Also, a handful of unforeseen conflicts necessitated this month-long delay, including weather which incapacitated plant production. It is necessary to point-out that humidity softening can be prevented through binder adjustment; however, the research team did not make this binder adjustment.
Additionally, the cores were produced near Cleveland, Ohio, placed on a core rack, then packed into plastic containers, transported 240 miles to Penn State, unloaded into cabinets at Penn State, then re-packed into 55-gallon drums, then shipped 120 miles to HMAC, unloaded onto core racks, then finally placed in a mold. Thus, the cores have been handled significantly more than if they were produced on-site.

2.4 Core Modeling

Due to the fact that a shell core box was used, core modeling was conducted to ascertain venting changes that would improve core making. Core simulations were modeled using Arena-flow software, available through Arena-flow, LLC, Albuquerque, New Mexico. Discussed herein, there are two simulations discussed. Simulation ‘A’, models core blowing for a core box with minimal vent area, as is common in shell core boxes. Simulation ‘B’, models core blowing for the same core box, but with increased vent area as to enable forming a core with a ‘wet’ binder. Specifically, while modeling with Arena-flow, the simulation ‘A’ parameters were: (a) Six Vents on face of core (bulk), (b) Sand: Wedron 520, (c) particle fraction 0.50, (d) Blow Pressure 517106 Pa (75 psi), (e) Feed volume fraction, (f) Blow 3 seconds, (g) 0.02 interval, (h) Flowability lowest allowed (slide-scale adjustable), (i) wipe-off 0.02 Binder fraction. simulation ‘B’ parameters: (a) Forty Vents in total, 36 on body of core (bulk), 4 vents in finger, (b) Sand: Wedron 520, (c) particle fraction 0.50, (d) Blow Pressure 517106 Pa (75 psi), (e) Feed volume fraction, (f) Blow 3 seconds, (g) 0.02 interval, (h) Flowability lowest allowed, (i) wipe-off 0.02 Binder fraction.
2.5 Casting Study

The HMAC casting process utilizes a Dansk Industri Syndikat A/S (‘DISA’, Denmark) molding line. This molding line utilizes a flaskless process. Green sand is blown into a chamber, and then steel patterns simultaneously impart an impression on the mold surface for the entire mold. The mold is then placed on the conveyer and pressed against all the other molds, such that the molds provide the essential support for the other molds, instead of using conventional flasks. Following mold formation, the molds are conveyed to metal pouring and then cooled for approximately 1 hour until the molds reach shake-out.

Upon shake-out, the castings described herein, were quarantined by diverting the molds through a shake-out process that replicates the rigors of approximately ½ of the conventional shake-out process. Herein, to fully quarantine the parts produced at HMAC, they were diverted from the conventional shake-out process. Following the shake-out process, the castings were put through primary shot-blast. There is the opportunity to use secondary shot-blast, however conventionally the parts herein are only processed through primary shot-blast. After the parts were processed through primary shot-blast, they were quarantined for visual inspection by machinists who work with part 249. As per the recommendation of the quality assurance department, the castings were analyzed in a blind quality study by production-finishing machine operators. The operators were guided by quality assurance personnel to select castings which would be able to be finished or castings which would be rejected before finishing. Thus, the evaluation of the castings were on a pass or fail scale. The castings that were deemed
able to be machined were considered ‘good’ and the castings that were deemed unfavorable were considered ‘scrap’.

3. Results and Discussion

3.1 Tensile Strength

To appraise how well cores retain their shape following production, tensile strength tests were performed. For a binder system that utilized 0.98% collagen plus alkali silicate (this was the same composition utilized in full-scale trials); nine dog bone samples possessed tensile strength range from 245 psi to 361 psi. The average tensile strength for the cores measured 294 psi, with a standard deviation of 38 psi. This compared favorably to the phenolic urethane tensile strength of 215 psi, when using 1.1% binder reported by Fox et al., 2008. The tensile strengths are compared in Figure 6.1.

Cores with 0.98% collagen-with-alkali silicates retained a tensile strength of nearly 300 psi, which compare favorably to the nearly 250 psi tensile strength demonstrated by 0.5% collagen-alone adhered cores (Figure 6.2). Cores prepared with 1.0% collagen can retain as much as 500 psi, exceeding the strength of 1.1% phenolic urethane by 2 times as much. Thus, the collagen with alkali silicate binder system possesses favorable strength at ambient temperatures.
Figure 6.1. Tensile strength for 0.98% collagen and alkali silicate cores compared to 1.1% phenolic urethane cores.
3.2 Hot Distortion Tests

To appraise the potential for core distortion during metal pouring and solidification, cores were tested using hot distortion testing. The core samples distorted as they were exposed to a natural gas flame in the hot distortion testing device. In a foundry setting, rapid distortion at high temperatures provides unwanted core behavior; possibly yielding casting defects. The conventional petroleum based binder can withstand a natural gas flame for approximately 40 seconds without distortion. However, the novel collagen and alkali silicate binder (0.33% collagen and 0.65% alkali silicates) can withstand a natural gas flame for over 50 seconds without distortion. Interestingly, once the collagen and alkali silicate binder begins to distort under thermal stress it continues to distort at a
lower rate than phenolic urethane (Figure 6.3). The phenolic urethane hot distortion is the same used in Fox et al., 2011.

![Graph showing distortion over time for different binders](image)

**Figure 6.3.** Hot Distortion tests, illustrating the distortion curve for the conventional petroleum based binder (phenolic urethane) and the binder as tested (collagen and alkali silicate).

### 3.3 Core Making

Cores were produced with the collagen and alkali silicate binder. The cores were able to be produced at a rate that is comparable to full-scale production; however, core pattern improvements such as venting can likely optimize production rates to cycle times identical to or even faster than those for conventional binder technologies. A good core is illustrated in Figure 6.4.
The cores often had low-density in the furthest region of the core as demonstrated in core modeling. The low density region occurred due to inadequate venting, since a shell core box was used. Shell sand requires much less air to fluidize than binder coated sand, thus significantly fewer vents are needed in shell. Since there were not vents in the most extreme point on the core (the most vertical section, pictured in Figure 6.4). This ¾” long and ½” region, which we shall call a ‘stem’, often did not completely fill, as inadequate venting likely refluidized sand in this region (as per Yao et al., 2003), which inhibited core compaction, which subsequently resulted in a low density ¾” and ½” ‘stem’.

Figure 6.4. A ‘good’ core produced by blowing the collagen and alkali silicate coated sand into a warm box.

3.4 Core Modeling

Computational particle fluid dynamic modeling from Arena-flow® software confirmed that a modestly vented corebox, such as a shell box, indeed creates low density
regions within the core. This ‘poor’ venting was simulated by placing only six vents along the bulk of the core. From this simulation, the core ‘stem’ seemed to be the most difficult region to fill within the core, Figure 6.5. However, when venting is increased along the bulk of the core and the ‘stem’ region, overall core density improves refer Figures 6.6 and 6.7. The increased venting contained more than 6 times as much venting surface area, by increasing the number of vents from 6 to 40. Overall, modeling confirmed that increased venting improves core production quality, which confirms that proper venting is essential to producing quality cores.

![Figure 6.5. Simulation ‘A’ isometric, demonstrating the lower density regions within the core when there is not adequate venting. Purple and Red hues indicate the densest regions, where blues indicate areas with minimal density.](image)
Figure 6.6. Simulation ‘B’ isometric, demonstrating the improved density within the core due to improved venting. Purple and Red hues indicate the densest regions, where blues indicate areas with minimal density.

Figure 6.7. Core Density, comparison between Simulation A (on left, six vents) and Simulation B (on right, 40 vents). Notice: Increased venting improves core density. Purple and Red hues indicate the densest regions, where blues indicate areas with minimal density.
3.5 Casting Study

After being stored between 25 and 33 days, the cores were transported to HMAC for full-scale testing. As previously mentioned, it is necessary to point out that at this point the cores had softened by 30% as per scratch hardness tests. This softening is due to humidity exposure during the prolonged storage. Despite some cores having softened and other cores not having a ‘stem’ with desirable density, over 200 cores were used in this full-scale demonstration.

The castings were produced in a multi-part green sand mold, with one core used for each part produced. The cores were placed in the green sand mold and moved along the DISA towards pouring. Iron was poured near 2520°F, with a pour time of 8-11 seconds. The castings were transported along the DISA line during the cooling phase. At shake-out, the cores were diverted, so as to be quarantined (Figure 6.8). To quarantine the castings, the parts were processed through a shake-out process that replicates about half of the conventional shake-out process (Figure 6.9). Following shake-out, the castings were processed through the conventional primary shot-blast process (Figure 6.10). Following the primary shot-blast process the castings were segregated to be analyzed by the quality assurance department.

The castings that were deemed able to be machined were considered ‘good’ and the castings that were deemed unfavorable were considered ‘scrap’. In typical operation, the finishing operators scrap between 0.5-5% of all castings due to core issues, for castings such as this, when the cores are employed within one day of core-making. When the time from making-to-casting increases to 6-10 days, the scrap rate increases by a factor of 3-5; and a full-scale foundry would not normally process conventionally-
bindered cores that had softened for 30 days (per communication with foundry personnel). At HMAC, there were two different cores evaluated by finishing machine operators. Core ‘type 1’ contained 0.98% as dry-weight of binder (0.33% collagen and 0.65% alkali silicates) to lake sand, as is the conventional aggregate for HMAC. Core ‘type 2’, contained 0.98% as dry-weight of binder (0.33% collagen and 0.65% alkali silicates) to Wedron silica. There were 86 castings analyzed that utilized core ‘type 1’, 121 castings analyzed that contained core ‘type 2’.

In the first full-scale attempt using cores containing the novel collagen and alkali silicate binder, the production finishing machine operators selected 21% and 24% castings as good quality, usable castings. There were 21% (of 86 castings analyzed) that were ‘good’ castings made with the ‘type 1’ cores, containing collagen and alkali silicate binder with lake sand. There were 24% ‘good’ castings (of 121 castings analyzed) produced with ‘type 2’ cores, containing collagen and alkali silicate binder with Wedron silica.

The cores also exhibited other favorable characteristics during the casting process. Specifically, cores were able to be removed easily through the shake-out process. Additionally, the cores produced a satisfactory surface finish. Further, the cores were able to produce castings that did not have veining, even despite the fact that no anti-veining additive was utilized (Figure 6.11 and 6.12). The conventional petroleum based binder can produce veining in the castings (Figure 6.13). The cores did not exhibit any erosion from molten iron.

The cores did produce many scrapped castings. However, these scrapped castings were not directly attributed to the binder. Scrapped castings were due to poor filling of
the core during core-making from using a shell-box. Also, the cores did not produce an excellent surface finish due to the fact that the cores were softened from humidity during prolonged storage. Lastly, the cores were handled many times and did not fit green sand cavity ideally, as there was some metal penetration at the green sand and core sand interface.

Figure 6.8. Mold drop from the DISA when using the collagen/alkali-silicate binder. Notice: the steam has no colored hue from binder off-gassing, as compared to the typical phenolic urethane resins releasing a blue hue.
Figure 6.9. An example casting following shake-out, which was equal to about one-half of the conventional shake-out process.

Figure 6.10. An example casting following shot-blast. This casting only experienced primary shot-blast. Notice: The sand on the surface of the casting from shake-out is now fully removed.
Figure 6.11. An example of a casting deemed ‘good’, by finishing operators that was produced using a collagen and alkali silicate binder. Notice, there is no veining in the casting, with no anti-veining additive used.

Figure 6.12. An example of a casting deemed ‘good’, by finishing operators that was produced using a collagen and alkali silicate binder, shown next to a collagen and alkali silicate core.
4. Conclusions

The work herein has demonstrated that a collagen and alkali silicate binder can produce good parts when casting iron without exhibiting molten metal penetration. Favorably, this binder withstands thermal stress longer than phenolic urethane without distortion as demonstrated by hot distortion tests. Additionally, when using 0.98% solid binder content of collagen and alkali silicates, the cores obtained a tensile strength of nearly 300 psi, which is 80 psi greater than 1.1% phenolic urethane cores. Also, this novel collagen and alkali silicate binder can produce castings without veining, without the use of veining additives. These cores also exhibited excellent shake-out properties as the cores were removed in one-half the shake-out time as the conventional shake-out process at HMAC.
5. Acknowledgements

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6. Literature Cited


The loosely catalogued industry belief that collagen alone does not withstand molten iron was confirmed via erosion tests on cores containing only collagen. However, the thermal resistance of collagen can be improved through cross-linking, as demonstrated with glutaraldehyde during thermal gravimetric analysis (TGA). Yet, aldehyde use can be avoided and alkali silicates can be coupled with collagen, which yields a material which closely mimics the thermal gravimetric ‘fingerprint’ of phenolic urethane. Further, this collagen/alkali silicate binder resists distortion at higher temperatures better than sodium silicate or phenolic urethane. Additionally, this collagen/alkali silicate does not harden at high temperatures as sodium silicate demonstrates during Dynamic Mechanical Analysis (DMA). During thermal gravimetric analysis mass spectrometry analysis (TGA-MS), the collagen/alkali silicate binder experiences an increased CO$_2$ release at 570°C, where collagen alone experiences a similar increase in CO$_2$ release at 500°C. FTIR and XPS scans indicate that carboxyls are converted to carboxylates when collagen is coupled with sodium silicate. This conversation and interaction imparts improved thermal stability for the collagen component of the novel binder system. When tested at full-scale this binder withstood molten iron erosion and produced “good” castings. Albeit, a poor performing core box and prolong storage time decreased the overall yield of “good” castings, yet the initial full-scale demonstration of the collagen/alkali silicate binder produced “good” castings.
Herein, it was demonstrated that a novel waste green sand reclamation system can provide core sand usable at the full-scale, lessening the solid waste stream at foundries. Also, a novel collagen/alkali silicate core binder was conceptualized, analyzed and tested at the full-scale. The novel collagen/alkali silicate binder demonstrated properties that are favorable for foundry operators, while also yielding less emission products as compared to conventional petroleum based binders.

This work also had the following contributions to science and engineering:

● Developed novel low-emission core binder with superb shake-out characteristics, no veining, improved resistance to distortion and odorless production.

● First known analysis of cores with Dynamic Mechanical Analysis (Storage Modulus and Tan Delta).

● Determined that carboxyl stretching is one of the key binding mechanisms between novel collagen/alkali silicate binder (demonstrated through FTIR and XPS).

● Confirmed that collagen alone cannot withstand molten iron erosion alone However, Collagen plus alkali silicate could quite favorably resist molten iron erosion.

● Determined that ultrasonic-cavitation device can reclaim sand that can be utilized in core production to yield quality castings at full-scale production.
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