2015

Preliminary investigation into the cause of pinhole porosity in aluminum metal castings from serpentine impurities in olivine sand

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PRELIMINARY INVESTIGATION INTO THE CAUSE OF PINHOLE POROSITY IN ALUMINUM METAL CASTINGS FROM SERPENTINE IMPURITIES IN OLIVINE SAND

An Abstract of a Thesis

Submitted

in Partial Fulfillment

of the Requirements for the Degree

Master of Science

Brodie J. Biersner

University of Northern Iowa

December 2015
ABSTRACT

The problem addressed in this study is how contaminates in the foundry molding aggregate olivine, affect aluminum castings during the casting process. This research will concentrate on hydrated contaminates, specifically the mineral serpentine. The purpose of this research is to better understand how hydrated minerals contribute to the generation of pinhole porosity defects during the casting process. Understanding how impurities in foundry aggregates affect the casting process would aid in the reduction of scrap caused by core and molding sands, ultimately providing savings to the casting manufacturer.

A foundry grade olivine was compared to a new source of olivine to determine how much pinhole porosity would be produced on a given casting sample based on purity and sourcing of the olivine aggregate. Various testing methods were used for the project: acid demand value, pH, grain fineness number and screen distribution, loss on ignition, differential scanning calorimeter/thermo gravimetric analyzer (DSC/TGA), chemical analysis by x-ray florescence, and the casting trial.

Results indicated there were differences in a given control sample of olivine in the amount of weight loss, screen distribution/GFN, and ADV, as compared to samples tested in which potentially contain hydrated minerals. The predominant relationship to pinhole porosity was results from GFN. The smaller the olivine sand grain became, the greater propensity for pinhole defects.

This increase in fineness levels also corresponded to increases in the LOI and acid consumption of the aggregates. Variation in grain sizing from sample to sample was not
designed into the original testing parameters. A clay bond of 8.00% bentonite based on sand was used for all samples. Resulting in the potential for an improper amount of clay bond to compensate for the increased surface area of the finer sand, leading to increased pinhole defects in the castings from potentially un-bonded particles.

Casting results indicated finer grained olivine aggregates had the greatest amount of pinhole porosity. Results were inconclusive in determining if serpentine was generating the pinholing porosity on the aluminum castings. Differences in grain distributions between samples resulted in finer olivine sand having an increased amount of surface area. Reducing the overall clay/sand ratio and introduced the potential for sand grains to break from the mold prematurely and enter the casting during the liquid state, creating a pinhole. The result was aluminum castings that contain sand grain entrapment, causing the majority of the pinhole porosity.
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Entitled: PRELIMINARY INVESTIGATION INTO THE CAUSE OF PINHOLE POROSITY IN ALUMINUM METAL CASTINGS FROM SERPENTINE IMPURITIES IN OLIVINE SAND

has been approved as meeting the thesis requirement for the

Degree of Master of Science

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Date  Dr. Kavita R. Dhanwada, Interim Dean, Graduate College
DEDICATION

Dedicated to my Grandparents: Jim and Berdie Biersner as well as Chris and my late Grandmother Lucy Bolhuis. They have encouraged me from the start to continue my education.
ACKNOWLEDGMENTS

The author would like to express his appreciation for the following people:

First I would like to thank my wife Heidi, for her kindness, support, and encouragement to finalize my research project. Without the support of my friends and family, this would not have been possible.

And a special thanks to Jerry Thiel, Director of the Metal Casting Center, and Sairam Ravi, Project Manager of the Metal Casting Center for their support and allowing use of the metal casting center’s resources and testing equipment to make this project possible. Thanks to all the students at the MCC to assisted in evaluating the castings for this project.

A thank you to Kris Boss and John Deere Casting Center of Excellence for allowing use of the 3D stereoscopic microscope to capture clear images of the aluminum casting defects.

Finally, I would like to thank my Graduate Advisory Committee, especially Dr. Scott Giese, for all of their support and patience as I completed this project.
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CHAPTER 1
INTRODUCTION

Subject of the Study

Metal casting is believed to have been practiced for more than 5500 years utilizing natural occurring metals: copper, silver, and gold (Kaufman & Rooy, 2004). Today this process continues to be essential component in the advancement and continuation of the civilized world. More than 90% of all manufactured goods and capital equipment use a casting as a component or rely on the casting as part of their manufacturing process (Spada, 2008).

Today’s metal casting process is a science that requires the understanding of how liquid metals behave chemically, mechanically, and physically. A variety of metals and alloys have been refined and utilized through human intervention and developed to meet the requirements requested by the end user of a casting. This thesis will specifically focus on the interaction of aluminum alloys and olivine sand used for the metal casting process.

Some of the first aluminum alloys were cast in the United States. One of the first recorded cases of an aluminum casting being produced in the United States was by Colonel William Frishmuth. His foundry was located in Philadelphia, Pennsylvania, and in 1876 was the only one utilizing aluminum. Frishmuth was offered the opportunity to produce the pyramid cap on top of the Washington Monument. On November 12, 1884 the cap was successful produced out of aluminum.
The casting weighed in at 2.85kg (6.28lbs.). Before the casting of the monument’s cap no one completely understood how to cast aluminum. The alloy was only developed 5 years earlier in Europe. Frishmuth discovered he couldn’t use an ordinary sand mold to produce the casting, and had to have an iron mold made (Binczewski, 1995). Advancements have been made in regards to pouring aluminum, and the material can easily be poured into sand molds today.

There are a variety of aggregates that can be used to produce a sand mold. The aluminum foundry industry has the option to utilize an aggregate known as olivine for the production of sand molds to manufacture aluminum castings. A sand mold will provide an empty cavity of which liquid aluminum is poured into and, upon solidification, produce a casting. Olivine is used because of the superior surface finish it provides to the aluminum casting and its ease of use, when compared to other foundry aggregates physical and chemical characteristics.

Olivine is not manufactured but rather purified through different mining processes. Nature plays a role in availability of olivine along with the overall purity. Variables such as the location of the mineral deposit, concentration of impurities, and the type of impurities all play a role in the mining site. Current production rates are depleting olivine deposits resulting in a reduction of its availability. This requires the suppliers of olivine to enter into new territories within the mine site. Moving to a new location can produce changes in the amount of impurities, or accessory minerals, and thus can produce a lower grade olivine.
The olivine material for this study was from a new mine site. It currently was not producing acceptable casting results for the foundry industry. Foundries were reporting an increase in casting defects, particularly a surface defect on the aluminum casting known as pinhole porosity.

The operators of the mine sent samples of the new mining areas to be tested at the University of Northern Iowa’s (UNI) Metal Casting Center (MCC). At the MCC they conducted a series of casting tests utilizing five different olivine products from various mine sites to qualitatively evaluate the amount of pinhole porosity produced from each sample. The results from the test castings produced from the various olivine samples, using an aluminum alloy, concluded that the olivine material was unfit for foundry applications. The results showed excessive amounts of pinhole porosity on the surface of the castings. It was hypothesized that these pinholes were produced by an accessory hydrated mineral within the olivine aggregate known as serpentine.

It came to the attention of this researcher that this defect couldn’t be specifically related to just olivine, and better testing methods, other than casting trials, needed to be developed in order to capture the effects of hydrated minerals before the material could be used in the casting process. Pinhole porosity defects can occur quite frequently in the casting industry. While there are other sources that can cause pinhole porosity defects, there is no test that could definitively determine if pinhole defects are derived from the molding media. Many of the aggregates used for the foundry industry are naturally occurring and could easily contain similar types of hydrated minerals.
Using the five samples that were provided for the casting study, research was conducted utilizing the only method currently used and accepted by the foundry industry, the Loss on Ignition (LOI). This information will be compared to testing conducted with analytical equipment to better understand the mechanisms that were contributing to the generation of this casting defect on the surface of aluminum castings. The results will be correlated to aid foundries to predict the amount of hydrated impurities in a potential casting aggregate. The results could then be correlated to current foundry testing techniques and lab equipment to determine if a foundry could test current sand supply for hydrated minerals. If a testing method can be found, any pin holing defects related to hydrated minerals would be eliminated before these aggregates are used in the casting process.

**Statement of the Problem**

The problem addressed in this study was to provide a preliminary understanding of the thermal breakdown of the hydrated mineral serpentine in a foundry grade olivine and how this mineral generates pinhole defects on cast aluminum surfaces.

**Statement of Purpose**

The purpose of this research was to better understand how hydrated minerals, specifically serpentine, can contribute to the generation of pinhole porosity defects when utilizing the olivine aggregate. Understanding these types of impurities in foundry aggregates used in the metal casting industry would aid in the reduction of scrap caused by core and molding sands, ultimately providing savings to the casting manufacturer.
The following objectives were determined for this study:

- Research will utilize analytical equipment to evaluate various olivine samples to state the presence of the hydrated mineral serpentine.
- Define the temperature of thermal degradation of the hydrated mineral.
- Try to correlate the current foundry procedures to the analytical results to understand if the current techniques and equipment available in foundry operations could be used to identify and/or predict porosity defect generation from hydrated minerals.

**Assumptions and Research Limitations**

Due to the limited amount of research that has been conducted on hydrated minerals in nonferrous castings the following limitations were established:

1. The samples provided are representative of the respected mine site operations. The samples were provided by the producers of the olivine mineral. Sample buckets provided were gathered from the mine following their recommended sampling procedures.

2. The clay bond used for the molding process does not contribute or affect the pinhole porosity results. Future testing can be utilized to understand the relationship between bonding mechanisms and hydrated minerals.

3. Due to the limitations of standardized samples for olivine, i.e. Magnesium, silica, and iron, on the x-ray florescence equipment, a nonstandardized option was used
on the equipment. It is assumed that the nonstandard option would provide repeatable results for all five samples that were tested in this study.

4. It is assumed that a certain percentage of serpentine is contained within the base olivine aggregate.

**Hypothesis and Research Questions**

If the hydrated mineral serpentine is contained within olivine, then pinhole porosity defects will occur on the surface of the casting due to higher temperatures decomposing the serpentine mineral, releasing water vapor when liquid aluminum is poured into a mold.

1. At what temperature are these hydrated minerals breaking down?
2. At what concentration do hydrated minerals affect aluminum casting surfaces?
3. What resources could a foundry utilize to check for hydrated minerals in olivine?

**Definition of Terms**

*Active Clay* — amount of clay that is able to absorb water and be used as a bonding mechanism in producing sand molds

*Binder* — The bonding agent used as an additive to mold or core sand to impart strength or plasticity in a "green" or dry state.

*Cope* — The top half of a horizontally-parted mold.
**Dead Clay** — Clay that has had the chemically bonded water removed from the lattice structure of the material. This is due to the heat produced from the casting process.

**Differential Scanning Calorimeter (DSC)** — An analytical piece of equipment that monitors the amount of change in energy required to heat at a constant rate utilizing a known standard.

**Differential Thermal Analysis (DTA)** — is a thermo-analytic technique, similar to differential scanning calorimetry. The results from testing are compared to temperature differences from a referenced sample.

**Differential Thermogravimetry (DTG)** — A continuous recording of mass changes in a sample. It is a function of a combination of temperature with time, and additionally of pressure and gas composition.

**Drag** — The bottom half of a horizontally parted mold.

**Foundry** — A workshop or factory for casting metal.

**Green Sand** — Moist, clay-bonded molding sand.

**Ladle** — A container used to transfer molten metal from the furnace to the mold.

**Mesh Size** — A unit of measure that is used in determining the particle size distribution of a granular material.
**Mold** — Normally consists of a top, the cope, and bottom, the drag, made of sand, metal, or any other investment material. It contains the cavity into which molten metal is poured to produce a casting of definite shape.

**Mass Spectrometry (MS)** — An analytical tool used for measuring the molecular mass of a sample.

**Nesosilicate Group** — The simplest of all the silicate subclasses, the Nesosilicates include all silicates where the \((\text{SiO}_4)\) tetrahedrons are unbonded to other tetrahedrons. Nesosilicates, which are sometimes referred to as orthosilicates, have a structure that produces stronger bonds and a closer packing of ions and therefore a higher density, index of refraction and hardness than chemically similar silicates in other subclasses. Consequently, there are more gemstones in the nesosilicates than in any other silicate subclass.

**Olivine** — An olive-green, gray-green, or brown mineral occurring widely in basalt, peridotite, and other basic igneous rocks. It is a silicate containing varying proportions of magnesium, iron, and other elements.

**Phenolic Urethane No Bake** — A binder system that is utilized in the foundry industry. It is a two part system with a liquid catalyst that bonds sand grains together and produces sand molds and cores.
Phyllosilicate Group — Phyllosilicates are sheet silicate minerals, formed by parallel sheets of silicate tetrahedra with Si$_2$O$_5$. Certain types of clays fall within this group of minerals.

Permeability — The property of a mold material to allow passage of mold/core gases during the pouring of molten metal.

Porosity — Holes in the casting due to gases trapped in the mold, the reaction of molten metal with moisture in the molding sand, or the imperfect fusion of chaplets with molten metal.

Serpentine — A group of minerals having the general formula (Mg,Fe)$_3$Si$_2$O$_5$(OH)$_4$.

Shakeout — The process of separating the solidified casting from the mold material.

Thermogravimetry (TG) — See Thermogravimetric Analysis.

Thermogravimetric Analysis (TGA) — A method in which the mass of a sample of material is measured as a function of temperature.
**X-Ray Diffraction (XRD)** — An analytical technique providing information about the crystallographic structure, chemical composition, and physical properties of materials by observing the diffraction or scattering pattern produced by a beam of X-rays hitting the sample.

**X-Ray Fluorescence (XRF)** — A non-destructive analytical technique used to identify and determine the concentrations of elements.
CHAPTER 2

REVIEW OF LITERATURE

Introduction

The literature review is divided into two parts. The first part is devoted to explaining the physical and chemical requirements needed for a casting aggregate, along with a description of the more common types of mineral aggregates that are used for the foundry industry. The second part is a description of the olivine sand systems’ physical and chemical characteristics along with an explanation into the serpentine mineral impurity that olivine aggregates can contain.

Sand Molds in Metal Casting

Sand Mold Design

There are many molding methods available to produce a metal casting. The majority of metal castings however are produced with sand molds. This method for the production of metal casting has advanced over the years—from the materials utilized to the types of molding equipment and processes. Historically there were a lot of manual labor required for the production of a sand mold. Today high speed molding machines are used with minimum amounts of human labor required (Schleg, 2003).

For sand casting to be successful for foundry applications certain criteria must be met. The principal feature is good compatibility between the binder system being used and the sand aggregate chosen. This combination must also be compatible with the metal alloy being used to produce the casting.
Functions of a Sand Mold

There are multiple purposes for a sand mold. The main purpose of a mold is to hold liquid metal in a specific shape until it is solidified. Sand molding can be broken down into two main categories: permanent and expendable. Permanent molds can be reused after the casting is solidified and removed, while in the expendable process the mold is destroyed. There are two methods that are predominant in expendable mold processes.

One process uses an aggregate with a polymer/plastic and mixes the products together and allows the polymer to harden, or react. The other process mixes an aggregate with a mixture of bentonite clay and water. Known as green sand molding, this process produces the greatest amount of castings by weight (Schleg, 2003).

Historically, the most widely used aggregate in the foundry industry is silicon dioxide (SiO₂), commonly known as silica sand. Silica sand, in the form of quartz particles, is used because it is the most abundant mineral in nature, easily mined, low cost to produce, available in various grain sizes and distributions, along with being an excellent refractory (American Foundrymen's Society, 1962). Other aggregates used are olivine ((Mg,Fe)₂SiO₄), chromite (FeCr₂O₄) and zircon (ZrSiO₄) sands. This is because of their resistance to react to the liquid metal. These aggregates also have a higher fusion point, and lower thermal expansion, when compared to traditional silica quartz (Yamamoto, Iwahori, Yonekura, & Nakamura, 1979).
Requirements for an Aggregate to be used for Sand Molding

All sand aggregates used for the foundry process will have to meet certain criteria to produce a satisfactory casting. Every foundry will have their own requirements to produce a casting to the specifications that the end user requests. The majority of these foundries will pay attention to the following characteristics when choosing a base sand for their foundry sand system: acid demand value (ADV), clay content, Grain Fineness Number (GFN), grain shape, loss on ignition, moisture, and pH.

Acid Demand Value (ADV)

The ADV was a test initially designed for acid set binder systems. This test is used to measure the reactivity level of any insoluble acid reactive materials found within the foundry sand. Insoluble materials within the sand include carbonate minerals and metal oxides (Hoyt, 2012). ADV can measure acid consuming materials that are not water soluble. This phenomenon is a limitation of pH testing. pH (acidity or alkalinity) is only affected by water soluble materials present in the sand. ADV is determined in the foundry industry following the American Foundry Society’s procedure AFS 1114-00-S.

Clay Content

Clay content is determined in the foundry industry following the American Foundry Society’s Clay Content procedure AFS 2110-00-S. The test is used to determine the percentage of clay and other particles that settle at a rate of less than one inch per minute in water. Typically these are materials under 20 microns. Clay testing was
originally designed to monitor the total amount of total clay in the green sand molding process. It determines how much clay, dead and active clay, is in a given sand system.

Clay content testing has evolved to also be used in chemically bonded sands to monitor clay fines within the aggregate, before it is mixed with a resin polymer. The closer the clay content is to 0.0%, the cleaner the sand. Lower values correlate to the amount of surface area from fine particulate matter that would be required for the resin to coat. The increase in clay content will require more resin to coat each individual particle, because of this increased surface area. The clay content test is helpful for a foundry when sand is shipped to them. Typically a trucking container ships a variety of goods, i.e. cement, sea shells, oil, lime, fertilizer, flocculants, etc. The fine material can easily be picked up from the shipment container and cause issue within the molding and casting processes (Hoyt, 2012).

Grain Distribution and Grain Fineness Number (GFN)

Sand is a material, regardless of chemical composition, that falls between 1/12-1/500in. (0.05-2.0mm) or 10-250 mesh (Hoyt, 2012). Due to this range for sand, there will be an associated binomial distribution associated with molding aggregates. This distribution is important to consider when using sand for a foundry application. Grain distribution can also be referred to as a screen distribution or particle size distribution. It is important to understand the distribution. To give a value to this sieve distribution, the foundry industry uses what is known as grain fineness number (GFN). GFN is
determined in the foundry industry following the American Foundry Society’s GFN procedure AFS 1106-00-S.

A grain fineness number is an average number that refers to how fine or coarse the average sand grain is in a given sample. This is a test approved by the American Foundry Society to determine the average particle size of a sand system to be used for the sand molding process. The larger the GFN number, the finer the sand. Both GFN and screen distribution have to be understood, one cannot be substituted for the other. F. Schleg stated that, “A blend of marbles and dust may give an acceptable AFS GFN, but it is easy to imagine what the casting surface would look like and other casting defects that may result.” If the results of testing a sample contain 10% or more sand by total weight, it is considered a screen in the particular distribution. Typically a 3 to 5 screen distribution is required to produce an acceptable casting. Typical range for grain fineness is 25 to 170 (Schleg, 2003).

A finer particle size distribution will give a better surface finish. However, using a finer particle size distribution inhibits the gases from escaping during the pouring process where as coarser particle sizing would allow gases to escape, but at the expense of providing a rough surface finish.

**Grain Structure (Shape)**

The shape of the sand grain also affects the quality of a casting. Grain shape is a qualitative measurement that breaks down essentially into three components: angular, sub-angular, and rounded (Schleg, 2003). A comparison between angular and rounded
grains can be found in Figure 1. The properties provided by an angular shaped sand is higher permeability, lower heat transfer, and higher binder demand. Rounded grain shapes with require less binder, provide a higher heat transfer rate, lower metal penetration, a smoother casting finish, but a decrease in the amount of permeability (Hoyt, 2012). This can be seen in Figure 1, where the interstices are smaller when compared to an angular grain.

![Figure 1. Comparison of angular grains to round grains for the sand casting process Reproduced from Hoyt, 2012.](image)

**Figure 1.** Comparison of angular grains to round grains for the sand casting process Reproduced from Hoyt, 2012.

**Loss on Ignition (LOI)**

Loss on Ignition testing is used to measure the total amount of combustible material within a sand sample. This is done by measuring the weight loss or gain of a given material when placed in an oven at 982°C (1800°F) for a minimum of two hours. This weight loss includes loss due to volatilization of organics, removal of chemically bound water, and losses due to dissociation of inorganic compounds (AFS Mold and Core
Weight gains found in LOI testing can be attributed to the oxidation of metals in an oxidizing atmosphere (Viti, 2010). Aggregates such as Chromite can exhibit this behavior, due to the iron content in the mineral.

Foundries use the loss on ignition testing to control the combustible material within the sand system. The testing is used to manage green sand systems, chemically bonded sand systems, additives, and reclaim sands. Each system has a range that has been determined by the foundry as an acceptable level of combustible material within the sand system. Excessive amounts of organic materials in foundry sands is problematic, typically the outcome is gas porosity defects in the castings (Love & Ramrattan, 2011).

The disadvantage of the LOI testing is the amount of time required to run the test. It can take up to three hours to complete the test, between heating the sample and cooling. A few advancements have been suggested to speed up the testing. One of these advanced methods uses a microwave furnace to heat the sample to the required temperature. The microwave oven reduced the heating time from two hours down to twenty minutes (Laitar & Cabanaugh, 1995).

**Moisture**

This is a simple quantitative measure to determine the amount of moisture contained within the aggregate used for the foundry. The test is typically conducted between 220°F to 230°F (104°C to 110°C). It is typically performed by using forced hot air through a specially designed pan for five minutes (Schleg, 2003). The moisture in the sand can affect both the green sand system and resin bonded sand systems. Too much
moisture in green sand can degrade performance of the green sand, too little can also
produce the same degradation in performance. For sand being coated with a resin,
moisture levels over 0.2% can degrade performance, due to chemical reaction between
the water and binder system being used.

**pH**

pH is the logarithm of the reciprocal of the hydrogen ion concentration in an
aqueous solution (Hoyt, 2012). The more hydrogen ions present in water, the more
acidic the aqueous solution. Lowering the amount of hydrogen ions, or increase in
hydroxides within the water solution, the higher the pH. pH is a scale that measures
between 0 and 14. Knowing the pH of aggregate is important because most binder
systems requiring a shift in pH to start the reaction. If an acid cured binder system is
used with basic pH sand it would require considerably more acid catalyst to react the
binder, as compared to a neutral pH aggregate. The acid in turn would have to neutralize
the basic components decreasing the amount of a required to create the polymer.

**Gas Porosity in Castings**

Gas porosity is a process by which pressures generated in the core or mold are
greater than the pressures in the liquid metal thus pushing gases into the liquid metal
generating a cavity in the casting. Typical shapes of gas generated defects are spherical,
flattened or elongated (American Foundry Society, 2000). Gas defects are developed
primarily in two ways-entrapped gas and soluble gas.
Entrapped gas is produced from core and mold binders. Organic materials decompose when exposed to the heat of the molten metal. When higher percentages of resin is added to foundry sand to make molds and cores, a greater volume of gas is generated from them during pouring. This is a product of the resin system decomposing, and generating gas. The resulting increase in gas also increases the chances for a porosity defect. When the decomposition products from resin, in the form of gas, is displaced in a mold cavity by liquid metal, it is put under pressure. This gas then has to find a path in which to escape the liquid metal entering the sand mold cavity. It does this by finding the path of least resistance.

Ideally, the permeability of the sand, along with proper venting techniques, should permit the path of least resistance for the gas, and safely move the evolved gases away from the casting interface. However, if the pressure generated in the mold is greater than the metallostatic pressure of the liquid metal, gas will escape through the liquid metal. During solidification, the gas entrapped within the liquid metal becomes a defect. Other contributors to forming this type of defect are: pouring temperature, pouring velocity of the metal, tooling design, and permeability of the sand.

Another way gas defects form is through the soluble gas process. This defect is formed from gases that are dissolved within in molten metal. Liquid aluminum is capable of dissolving hydrogen. The liquid phases of all metals have the ability to hold greater amounts of gas in a solution than the solid metal can. This gas is then released
during solidification, nucleating a gas bubble, and forming gas porosity defects (Kay, Magel, & Spada, 2001).

This study is working with gas defects that are only on the surface of the casting. The two types of gas defects, mentioned above, are further broken down into two major categories. “Blows” which are large voids in the castings and pinholes which are small numerous holes in the casting. Most gas porosity related defects are determined by their location relative to the mold, the shape of the casting, and casting conditions (Yamamoto et al., 1979). Pinhole porosity defects in metal castings typical range is 1 ~ 5 mm in size on the surface of the casting. Defects of this nature reduce the reliability of the part and increase production cost due to their repair.

**Primary Aggregates used in Sand Molding**

To be successful, a foundry cannot dig up a sand from the ground and use it for their molding process. As described previously, certain sand properties are desired in order to produce a quality casting. This section will describe some of the more common types of aggregates used for the foundry industry. All of the materials listed below exhibit a physical and chemical requirement needed to produce a casting. Each aggregate provides a unique characteristic that can provide certain advantages, or disadvantages, depending on the metal alloy being used.

**Silica (Quartz)**

One of the most common aggregates used in the foundry industry is Silica, SiO$_2$. Sometimes referred to as quartz, it is the most abundant mineral in nature making the
material readily available for a foundry. However, silica must be able to pass the physical and chemical characteristics as described earlier. Silica’s advantages for mold production consist of being easy to extract from the mining source, inexpensive to process as the mine, and it material properties to satisfy the refactoriness, hardness, and abrasion resistance required for the molding and core making processes. Silica is also available in a variety of sizes, sub angular to round, and various screen distributions. The material exhibits a high refactoriness. This resistance to heat also provides protection from many metal alloys reacting with the sand and acid slag attacks, Table 1 (American Foundrymen's Society, 1962).

Table 1.
*Physical Characteristics of aggregates used for sand molding and core production Table produced with information from Schleg, 2003 and Hoyt D., 2006.*

<table>
<thead>
<tr>
<th>Property</th>
<th>Silica</th>
<th>Olivine</th>
<th>Chromite</th>
<th>Zircon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>White/Brown</td>
<td>Green</td>
<td>Black</td>
<td>White</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2.65-2.67</td>
<td>3.27-3.37</td>
<td>4.3-4.5</td>
<td>4.6-4.7</td>
</tr>
<tr>
<td>Bulk Density</td>
<td>95-97</td>
<td>98-103</td>
<td>156-165</td>
<td>152-183</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>0.018</td>
<td>0.0083</td>
<td>0.0045</td>
<td>0.0037</td>
</tr>
<tr>
<td>Temperature Reaction</td>
<td>Acidic</td>
<td>Basic</td>
<td>Basic/Neutral</td>
<td>Slightly Acidic</td>
</tr>
<tr>
<td>Shape</td>
<td>Varied</td>
<td>Angular</td>
<td>Angular/Rounded</td>
<td>Rounded</td>
</tr>
</tbody>
</table>

There are other characteristics that can determine the type of silica sand that is used for the foundry industry. The location in which the silica is mined can change the overall purity and physical characteristics. Most foundry grade silica is primarily extracted from the St. Peter deposit found within Illinois and Missouri. Silica containing appreciable amounts of iron oxide can be further classified into bank sands
and lake sands. Bank sand are from dried up riverbeds or along the banks of an active river. Lake sands are from the dunes surrounding the Great Lakes. Typically this type of sand is extracted from Lake Michigan. These sands will contain impurities such as iron oxides, rootile (roots from trees), calcium carbonates, and other types of impurities. These impurities can cause issues for the foundry and cannot be used for certain types of chemical bonding core making processes (Schleg, 2003).

**Zircon**

Zircon, ZrSiO$_4$, is the most widespread occurrence of Zirconium in nature. This sand naturally occurs in a combination with other minerals, such as Ilmenite, rutile, chromite, garnet, and other trace minerals. Typically the grade of zircon supplied for foundry use is guaranteed to contain at least 66% zircon. Zircon is considered a specialty sand for the foundry industry. The reasoning for this designation is that it has unique advantages over silica which can include a high refractory value, high conductivity, high density, low expansion, and a resistance to being wetted by liquid metal, Table 1. (American Foundrymen's Society, 1962).

**Chromite**

Chromite is another specialty sand for the foundry industry and is primarily mined out of Africa. Typically chromite is a sub angular grain that provides good chilling characteristics, a high refractoriness, and lower thermal expansion, when compared to silica sand, Table 1 (Schleg, 2003). Recently there has been a domestic source of chromite released for the foundry that is unique. Instead of being a crushed product
derived from rock, like the traditional African chromite, this product comes from an alluvial site in Oregon (Hoyt, 2006).

History of Olivine in the Foundry

Olivine was originally used in the foundries for the production of refractory bricks and ramming mixes (Redeker, 1971). Olivine primarily come from dunites, an igneous rock. Minor deposits exist as alluvial deposits, natural sand deposits. Norwegian steel foundries first attempted using crushed olivine as a molding aggregate in 1927-1928. It provided an acceptable surface finish on the steel castings, especially for high chromium-nickel steels, but the cost was higher than silica.

Olivine’s popularity grew in the early 1940s as a molding aggregate because of silicosis, which occurs from long term effects of breathing silica dust. Research in the 1940s exposed rabbits and rats to silica dust and olivine dust. The results from the testing concluded that olivine dust appeared to be less dangerous than silica. It was presumed that the risk of silicosis was reduced because the olivine contains MgO that is chemically bonded to the silicon dioxide as compared to using pure silica sand (Sissener & Langum, 1952).

Olivine Sand Properties

Olivine is an angular sand that is available typically from 60 to 120 AFS GFN (Schleg, 2003). Olivine is a silicate mineral, more specifically in the neosilicate group. It is in the Orthorhombic system with a crystal class of 2/m 2/m 2/m (Hurlbut Jr. & Klein, 1977). Olivine is a magnesium-iron-ortho-silicate solid solution with end members of
fayalite (Fe$_2$SiO$_4$) and forsterite (Mg$_2$SiO$_4$) (American Foundrymen's Society, 1962). Generally the term Olivine is used when 10% or less of the mineral is fayalite (Viti, 2010). The two components in olivine have different melt points. Forsterite has a melting point of 1890°C (3434°F), and fayalite melts at 1205°C (2201°F). The fusion of the two materials is dependent of the two components (Hurlbut Jr. & Klein, 1977). Figure 2 is a phase diagram for the olivine system showing how the addition of fayalite reduces the overall melt point of the olivine mineral.

![Phase diagram of olivine](image)

*Figure 2. Phase diagram of olivine. Reproduced from (Hurlbut Jr. & Klein, 1977).*

The thermal expansion of olivine sands is less than quartz. This low thermal expansion is desirable in metal casting because olivine does not experience a rapid expansion to a slow contraction, which is a contributing factor to expansion type defects in silica sand. This effect is displayed in Figure 3.
Figure 3. Expansion rate of olivine compared to quartz. Reproduced from American Foundrymen's Society, 1962.

Olivine is a basic or alkaline refractory. When mined it can contain impurities, depending on location, such as enstatite, magnesium amphibole, magnesite, phlogopite, corundum, serpentine, talc, vermiculite, chlorite, and chromite (Sissener & Langum, 1952; Redeker, 1971).

Origin and Production of Olivine Sands

Olivine is native to the Twin Sisters area in the Cascade Range in Washington. It occurs as rock and boulders in its natural state. Another predominate location in the United States is San Juans, Washington. These olivine mining sites were the main source for North American foundries in the 1950s and 1960s. The aggregate is also deposited in North Carolina (American Foundrymen's Society, 1962).
Worldwide the mineral is primarily mined in Norway. Norway is the largest exporter of olivine. In order of olivine production following Norway is Japan, Spain, United States, and Italy (Kramer, 2001). Minor deposits exist as alluvial deposits. Majority of olivine comes from dunites and are ground down to grain fineness required for metal casting. Olivine sand is mixed and treated the same way as silica sands (American Foundrymen's Society, 1962).

**Serpentine**

Serpentine is a silicate mineral like olivine but is in is in the phyllosilicate group. Most members of this classification are hydroxyl bearing (Hurlbut Jr. & Klein, 1977). Serpentine composition can be varied but follows a chemical composition close to Mg$_3$Si$_2$O$_5$(OH)$_4$. There are different variations of serpentine. The variations of serpentine include: Antigorite, lizardite, polygonal serpentine and chrysotile (Viti, 2010).

Research conducted by Cecelia Viti utilizing thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA) determined that there were variations in the ranges of water released depending on the type of serpentine during the thermal decomposition process. Viti conducted experiments with the various serpentines in an air atmosphere with a flow rate of 20 mL/min. A Pfeiffer mass spectrometer was coupled to the TG to detect water vapors from the decomposing material. Viti used atomic masses of 17, 18, 19, and 20. Results showed a decomposition temperature range for serpentines between 550-800°C. The heating of serpentine breaks down into three separate components as shown in Figure 4. Two of the
decomposition products are mineral based, forsterite and quartz. A third component is water. This particular method of decomposition is referred to as dehydroxylation (Viti, 2010).

Viti’s study evaluated various forms of Serpentine. Each type of serpentine studied provided a different range in which dehydroxylation started. Specific break down of the various serpentinaes is as follows: Antigorite breaks down between 715-720°C, Lizardite 708-714°C, Polygonal Serpentine 685-691°C and Chrysotile 650-654°C. It was discussed by Viti that most of the time serpentinaes will be intermixed and will have structural variances. Different ramp rates along with different aggregate sizes were trialed with this study and was concluded that the same rate of decomposition occurred, no matter the heating rate or change in aggregate sizing (Viti, 2010).

<table>
<thead>
<tr>
<th>Serpentine</th>
<th>700°C</th>
<th>Forsterite</th>
<th>Quartz</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg₃Si₂O₅(OH)₄</td>
<td>→</td>
<td>3 Mg₂SiO₄</td>
<td>SiO₂</td>
<td>4 H₂O</td>
</tr>
</tbody>
</table>

*Figure 4.* A chemical breakdown of serpentine into forsterite, quartz, and water.

Viti’s study concluded that not only are the temperatures at which dehydroxylation takes place different, but the overall weight losses, and exothermic and endothermic peaks, picked up by the DTA, were different for each sample. Figure 5 gives the results from Viti’s paper on the results from the DTA, DTG, and DTA. The
amount of weight loss for each purified sample of serpentine was between 12-14% total weight loss heated to 990°C (Viti, 2010).

Results in Figure 5(a) show the thermal decomposition. Each type of Serpentine had a different amount of weight loss. All of the weight loss measured was confirmed with the attached mass spectrometer as being water released from the serpentine minerals. Figure 5(b), provides the results from the DTA, which is similar to DSC. DTA monitors energy changes or transformations associated with the serpentine minerals; such as glass transitions, crystallization, melting and sublimation. Figure 5 shows that each mineral had an energy change during heating. However, the changes in energy state occurred at different temperatures ranges between 550-800°C. The DTA analysis also shows a thermal degradation of the various serpentine samples tested, Figure 5(c).

Mass spectrometry results from Viti detected water vapor from the various types of serpentine, confirming that the weight losses in serpentine are exclusively associated to the dehydration processes. Results from the mass spectrometer and the trends observed in the DTG and DTA results were in good agreement and determined that the water loss occurred in two steps. It also corresponded to the weight loss results from the TG that occurred between 550-800°C.
Figure 5. (a) Comparison among TG curves or antigorite (ATG), lizardite (LIZ), polygonal serpentine (POL), and chrysotile (CHR) in the 550-850°C range. (b) comparison amount DTG curves of antigorite, lizardite, polygonal serpentine, and chrysotile in the 550-850°C range. (c) Comparison among DTA curves of antigorite, lizardite, polygonal serpentine, and chrysotile in the 550-850°C range. (Viti, 2010)

Foundry Practices with Olivine Aggregates and High Purity Serpentine Aggregates

The serpentine mineral was trialed as a foundry molding aggregate in 1996. G.L. Datta, S.K. Ghosh and G.H. Iyer (1996) trialed iron and steel castings with raw serpentine and calcined serpentine. Raw serpentine rocks were crushed and screened to a +60 and -30 mesh size. Molds were prepared using the green sand process with 5% bentonite clay and 6% seacoal. The calcined serpentine was heated to 1300°C before being crushed to fine particles. Casting results from the raw serpentine showed an
increased amount of penetration defects along with the generation of small gas cavities on the surface of iron castings. G. Datta, et al. believed the reasoning for this generation was from the presence of hydrated water in the raw mineral. It was concluded that calcined serpentine, with the removal of the high concentration of fines, had the potential of being used as a molding aggregate to replace olivine sands. The aggregate that was not calcined produced a rough casting surface finish, due to the porosity defect.

Similar conclusions were produced at the Toyota Central Research Laboratory. They studied the phenomena of pin holing defects related to foundry olivine sands and how pinhole porosity increased when these sands were used (Yamamoto et al., 1979). They developed a test to determine gas pressures that were generated inside a phenol resin shell sand olivine core. Their study used untreated olivine and compared it to different calcined olivine sands at 200°C (392°F), 600°C (1112°F), 800°C (1472°F), and 1000°C (1832°F) for five hours. Sands were coated in a phenol resin binder, known as the shell molding process. Samples were then tested in two different casting materials, iron and steel.

Results of the study showed a reduction in the amount of pinhole porosity, almost by half when castings were poured at temperatures of 1540°C (2804°F) and using the heat treated sand of 800°C (1472°F; Yamamoto et al., 1979). Measuring the gas generated from the various sands, they found olivine sand heated beforehand produced about 7ml/l less gas then the untreated olivine. The Toyota research team utilized x-ray diffraction on the samples and identified the sand preheated at 800°C and 1000°C
as $2(\text{Mg, Fe})\text{O}^*\text{SiO}_2$ and $\text{MgO}^*\text{SiO}_2$. XRD results from the untreated olivine and olivine treated to $600^\circ\text{C}$ had additional compositions beyond the $2(\text{Mg, Fe})\text{O}^*\text{SiO}_2$ and $\text{MgO}^*\text{SiO}_2$. $3\text{MgO}^*\text{SiO}_2^*2\text{H}_2\text{O}$ was the resulting extra peak, which corresponds with Serpentine. Toyota research team had concluded that serpentine was decomposing around $600^\circ\text{C}$ and was completed the decomposition process at $800^\circ\text{C}$.

Comparing the XRD results to the gassing results the Toyota research lab found a correlation between heated sand, chemical composition, and gas generation. It was deduced that serpentine was generating the gas due to the dehydration of the material. They measured the amount of water vapor coming off the olivine aggregate with the increase in temperature. At $600^\circ\text{C}$ there was a 0.62% water loss and at $800^\circ\text{C}$ this amount was reduced to 0.16%. It was also discovered that this dehydration reaction was rapid. Placing olivine sand with the serpentine contaminate into a furnace at $800^\circ\text{C}$ for three minutes completely dehydrated the material (Yamamoto et al., 1979).

In 1971, the Minerals Research Laboratory in North Carolina conducted a study to effectively eliminate the amount of serpentine in olivine sands and obtain lower ignition losses for use as foundry sand. European producers were using rotary kilns to calcine the olivine. It is difficult to heat this mineral, due to the reaction of oxygen with iron in the fayalite side of the olivine, resulting in an oxidation of the iron. Oxidation of the aggregate introduced an increase in surface area which resulted in the foundries to increase the total amount of binder required to stick the sand grains together. In 1971, Immo Redeker looked into the cost of calcining the olivine mineral to remove the
serpentine. Another downside to calcining the olivine is the associate costs. At that time, it would cost approximately $1.28/ton to process the olivine using oil and around $3.50/ton to process using electric. Redeker also concluded that the advantage of calcining olivine sand that contains serpentine is that it will completely eliminate water from crystallization and improve the overall properties for use in foundry applications (Redeker, 1971).
CHAPTER 3
RESEARCH METHODOLOGY

Introduction

Fives samples of olivine were sent to the University of Northern Iowa. Samples were sent for casting evaluation to determine how much pinhole porosity would be produced on a given sample. Further analysis was done in this study to better understand the trends that could be utilized to determine that a foundry aggregate would produce pinhole defects in aluminum castings. Testing for this study included acid demand value, pH, grain fineness number and screen distribution, loss on ignition, differential scanning calorimeter/thermo gravimetric analyzer (DSC/TGA), chemical analysis by XRF, and results from a casting trial.

Differential scanning calorimeter/thermo gravimetric analyzer (DSC/TGA) was the primary focus of this project to determine at what temperature the mineral breaks down and releases water vapor within the base olivine material that is theorized to release a gas bubble generating a gas pinhole porosity defect. Other testing associated with the experiment is to correlate this result to determine if a foundry using current testing techniques could pinpoint a sand material that wouldn’t be satisfactory for their molding operations. The results of the experiments are observed and discussed in Chapter 4.
Experimental Procedures Sample Selection and Preparation

Olivine samples were provided by Unimin Corporation. The olivine samples labeled LE75, LE80, LE105 and LE120 were all from the Sibelco Nordic mine at Aheim, Norway. The Hamilton sample was from the Unimin plant at Hamilton, WA. Olivine feedstock for processing at Hamilton was mined by the Olivine Corporation from their Swen Larsen quarry in the Twin Sisters Mountain Range in Whatcom County, WA. Samples were screened at the respected facilities and sent in 5 gallon pails to the University of Northern Iowa. Table 2 gives a typical chemical composition range of olivine sand.

<table>
<thead>
<tr>
<th>Elemental Oxide</th>
<th>SiO₂</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage (%)</td>
<td>40.0-41.2</td>
<td>47.6-48.5</td>
<td>0.1-0.6</td>
<td>7.4-8.0</td>
</tr>
</tbody>
</table>

Acid Demand Value

The first step in this study was to determine the physical characteristics of the olivine sand samples. Testing for acid consumption in the olivine sand started with splitting each sample down to the appropriate amount of sand following the AFS Mold & Core Handbook testing procedure AFS 1101-00-S. The purpose of ADV is to determine how much acid can be neutralized by the aggregate. Utilizing this test will aid in determining if hydrogenated minerals, such as serpentine, had an effect on the olivine aggregates ability to consume acid. Samples were prepared by splitting the sand down to
the recommended amount for ADV testing. Deionized water was used for each experiment. Each sample was titrated following the AFS procedure for determining acid consumption by an aggregate, AFS 1114-00-S. The olivine was allowed to soak in a 0.1M solution of hydrochloric acid and then back titrated after 5 minutes of mixing with 0.1M sodium hydroxide until a reading of neutral, pH 7, was established.

pH

pH is a test that is used to determine the acidic or alkaline nature of the olivine sand material. The determination of pH followed AFS 5113-00-S. pH was used to determine if hydrogenated minerals, such as serpentine, had an effect on the overall pH of the base aggregate olivine. Samples were prepared by splitting the sand down to the recommended amount for pH testing. Deionized water was used for each experiment.

Grain Fineness Number (GFN) and Screen Distribution

Screen distribution testing provides an understanding about the sizing of the grains on a particular sample. Sizing of the sand could indicate what is generating the pinhole porosity defects. Sands with higher fines, small sand grains greater than 140 mesh screen, often contain higher amounts of impurities. If the sand contains higher amounts of finer materials, this could be used to correlate hydrated minerals in the sand. Screen distribution testing determines the sieve distribution of the sand samples that were provided. A sample was split using the recommended procedure for splitting down a sample to a 45-75 gram sample for screening analysis. The testing procedure reflected
that of AFS 1105-00-S. Each sample was tested for a total of 15 minutes before being analyzed.

**Table 3.**

*Sample calculation to determine grain fineness number (GFN). GFN result from calculation example is 62.01 Reproduced from AFS Mold and Core Test Handbook, 2001.*

<table>
<thead>
<tr>
<th>ASTME-11 Sieve Size</th>
<th>Percent Retained on Sieve</th>
<th>Multiplier to Calculate GFN</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.00</td>
<td>0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>12</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>0.00</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>30</td>
<td>2.00</td>
<td>0.20</td>
<td>0.40</td>
</tr>
<tr>
<td>40</td>
<td>2.20</td>
<td>0.30</td>
<td>0.66</td>
</tr>
<tr>
<td>50</td>
<td>14.40</td>
<td>0.40</td>
<td>5.76</td>
</tr>
<tr>
<td>70</td>
<td>34.00</td>
<td>0.50</td>
<td>17.00</td>
</tr>
<tr>
<td>100</td>
<td>32.70</td>
<td>0.70</td>
<td>22.89</td>
</tr>
<tr>
<td>140</td>
<td>13.20</td>
<td>1.00</td>
<td>13.20</td>
</tr>
<tr>
<td>200</td>
<td>1.50</td>
<td>1.40</td>
<td>2.10</td>
</tr>
<tr>
<td>270</td>
<td>0.00</td>
<td>2.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Pan</td>
<td>0.00</td>
<td>3.00</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Total =</strong></td>
<td><strong>100.00</strong></td>
<td>N/A</td>
<td><strong>62.0</strong></td>
</tr>
</tbody>
</table>

Table 3 shows the standard procedure for determining the grain fineness number based on the percent retained from screen distribution testing. This retained percentage is then factored by a multiplier and the product from each screen is added up to give the GFN number. This procedure followed AFS 1106-00-S.

**Loss on Ignition**

Three representative samples of each aggregate were tested and averaged. This is the only test in the AFS Mold & Core Handbook that is used and accepted by the foundry industry to measure the amount of chemically bound water in foundry aggregates.
**Differential Scanning Calorimeter/Thermo Gravimetric Analyzer (DSC/TGA)**

A thermal analysis was conducted on all 5 samples utilizing a DSC/TGA. A Mettler Toledo, TGA/DSC 1 STAR® System, Differential Scanning Calorimeter (DSC) coupled with a Thermal Gravimetric Analyzer (TGA). A Pfeiffer Mass Spectrometer, model: Thermostar™, was attached to the DSC/TGA. This analytical piece of equipment was utilized to better understand the hydrated mineral breakdown. With the understanding that a hydrated mineral will decompose at high temperature, it would be valuable to the metal caster to understand when this reaction occurs.

The TGA provides the amount of weight loss per unit increase in temperature. The DSC analyzes any phase changes or chemical reaction occurring during the heating process. Samples were heated from room temperature to 1200°C at a rate of 20°C per minute. Heating occurred under a nitrogen atmosphere, which was supplied at 80mL/min. Each olivine sand sample was tested five times for statistical analysis. Gases that are produced from the decomposition are sent to the attached mass spectrometer and related to the unit increase in temperature.

A repeatability study was established for the DSC/TGA. Each sample of sand was split down to a 25-50gram sample of base aggregate. From there an 80mg specimen was placed into the DSC/TGA unit. Each of the five olivine aggregates were tested a total of 5 times on this piece of equipment. The data gathered from each sample was then normalized for data analysis.
Chemical Composition

The five samples selected for this experiment also underwent a chemical analysis. Chemical Analysis was achieved by using X-Ray Florescence (XRF). This equipment was made available by the University of Northern Iowa’s Department of Earth Science. Results from the XRF was used to understand the basic elements in the olivine samples along with the ratios of the elements. Each sample of olivine contains impurities, such as chromite, talc, silica, and serpentine. A XRF analysis was conducted before and after running an LOI sample. It was thought that there may be a correlation between Iron or Magnesium that would be detected by the XRF and related to the TGA/DSC result.

Casting Trials

The casting that was used for the trial measures 2”x3”x.25”. Figure 6 shows the layout of the casting and the gating system that was used for producing all samples used in the olivine sand testing. A total of 10 samples were produced based on the five olivine aggregates. Each batch was produced in a Simpson Gerosa Lab muller. Batch molding occurred in increments of 50 lb. were produced which included 8% western (sodium) bentonite, the selected aggregate to be tested, and potable water. Water was added to the mix until a compactability of 40-45% was attained.
Foundry grade A356 aluminum was used in this study. The aluminum was melted using a No. 25 clay graphite crucible in a tilt pour gas fired furnace. The metal was tapped out of the furnace at 1500°F and samples were poured at 1400°F. The molds were allowed to cool for 15 minutes before shakeout. The casting samples were then rinsed with water to removed excess molding sand.

Visual Analysis

Analysis of the casting involved surface and subsurface analysis of the castings. Visual method testing was to qualitatively determine the amount of pinholes on the
casting surfaces. Duplicates of each casting were produced, so an average was determined on the amount of pinholes on the casting surface. A statistical average was determined by counting the number of pinholes in each row. Three students were asked to count the number of visual pinholes on the surface of both cope and drag of the casting. The casting had five rows on the cope surface and five rows on the drag surface. Each row was summed and averaged. Results from each evaluator were then averaged. Finally the cope and drag surfaces were averaged into a final number for each casting. This provided a value on the number of pinholes per casting. This procedure was conducted for all the casting aggregates used in this study.

Pinhole porosity is not only a means for possible mechanical failure; it can also provide a cause for scrapping the casting due to the visual appearance of the casting. A qualitative result was also provided to determine the visual result of the casting based on the starting aggregate. The second measure was to visually inspect the castings and rank them in order from best surface quality to worse surface quality. This was strictly based on surface quality, rendering null the presence of pinholes. Analysis of the cast surface was done by utilizing a cast surface comparator. The block that was utilized was a Teledyne cast products unit, Part No. PCT-65-001. Castings were placed directly beside the comparison device which gives a “C” value to the roughness of the cast surface. Each casting was measured and an average C value was produced. This block would provide a common reference for each casting being analyzed.
A Zeiss stereomicroscope was used to visually analyze the pinhole defects on the casting surface. The microscope was provided courtesy of the John Deere Waterloo Works. The close up visual will be used to understand the type of defects that are formed on the surface of the aluminum castings. As discussed in Chapter 2, the type of defect that is formed on the surface of the casting can aid in the determination of the defects source.
CHAPTER 4

RESULTS AND DISCUSSION

Chapter 4 will comprise all results from testing the five olivine aggregates used for this experiment. Each of the testing methods discussed below followed the procedures as discussed in Chapter 3. This chapter will start with physical characterization from the base aggregate testing that is traditionally done in the field. These results will then be correlated with analytical equipment: TGA, DSC, and MS. Both methods can then be used in correlation with casting results. A discussion will follow the presentation of the results in order to determine if a test could be developed for foundries to identify the potential for gas generating aggregates, such as serpentine.

Base Aggregate Testing

Loss on Ignition (LOI)

Five grades of Olivine sand were examined to determine if there were variances in combustible material between the control sample, Hamilton, and the five grades of olivine that may contain hydrated minerals, such as serpentine. Figure 7 provide the result from LOI testing and shows that each sample had a varying level of combustibles. The lowest reported LOI was Hamilton, at 0.27%. LE80 and LE75 olivine samples had 0.58% and 0.60% combustibles respectively. LE105 had the greatest amount of weight loss with 0.84% loss. LE120 had a total weight loss of 0.80%. Outside of the Hamilton sample which is the controlled olivine sample, the ranges gathered from LOI testing are
consistent with literature that reported olivine aggregates with serpentine, having losses around 0.62% at 600°C (1112°F), (Yamamoto et al., 1979).

![Loss on Ignition (LOI) Results](image)

*Figure 7.* Loss on Ignition results from the five samples that were tested for this study. LE105 and LE120 had the greatest amount of weight loss.

**Chemical Composition**

The five olivine aggregates were analyzed for the chemical composition using x-ray florescence. Data obtained from the XRF was processed and an average was developed for the chemical composition of the various samples. Results from the XRF tests are represented below in Table 4.
Table 4.
Chemical composition results from XRF testing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>SiO₂</th>
<th>K₂O</th>
<th>CaO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Fe₂O₃</th>
<th>NiO</th>
<th>ZnO</th>
<th>Ag₂O</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>LE75</td>
<td>37</td>
<td>48.2</td>
<td>0.19</td>
<td>0.346</td>
<td>0.619</td>
<td>0.148</td>
<td>11.72</td>
<td>0.639</td>
<td>0.0072</td>
<td>0.85</td>
<td>99.7</td>
</tr>
<tr>
<td>LE80</td>
<td>39</td>
<td>45.5</td>
<td>0.086</td>
<td>0.29</td>
<td>0.453</td>
<td>0.172</td>
<td>13.09</td>
<td>0.71</td>
<td>0.008</td>
<td>0.92</td>
<td>100.2</td>
</tr>
<tr>
<td>LE105</td>
<td>39</td>
<td>45.3</td>
<td>0.13</td>
<td>0.407</td>
<td>0.492</td>
<td>0.164</td>
<td>12.76</td>
<td>0.699</td>
<td>0.0054</td>
<td>0.89</td>
<td>99.8</td>
</tr>
<tr>
<td>LE120</td>
<td>37</td>
<td>46.5</td>
<td>0.06</td>
<td>0.623</td>
<td>0.537</td>
<td>0.177</td>
<td>13.59</td>
<td>0.72</td>
<td>0.0097</td>
<td>0.9</td>
<td>100.1</td>
</tr>
<tr>
<td>HAMILTON</td>
<td>39</td>
<td>44.3</td>
<td>-</td>
<td>0.22</td>
<td>0.518</td>
<td>0.186</td>
<td>14.11</td>
<td>0.741</td>
<td>0.0083</td>
<td>0.93</td>
<td>100.0</td>
</tr>
</tbody>
</table>

As mentioned in Chapter 3, a non-standard analysis was used for the XRF testing. The averaged values from the XRF analysis indicated the chemistry of the five samples fell within the specifications described for an olivine aggregate. Based on the described composition for Olivine, found in Chapter 3, the silicon dioxide and iron oxide content was slightly higher than what is to be expected.

Magnesium oxide (dolomite) content average was 8.00% lower than what was reported by literature. A possible explanation could be due to the equipment’s non-standard option being used. It can also be suggested that these aggregates contain a higher concentration of fayalite. The higher concentration can be assumed because forsterite is the magnesium bearing mineral within the olivine structure. Only X-ray diffraction could provide the proper information on identifying the crystalline structure of the olivine aggregate, and provide an explanation for the discrepancy from the typical chemistry of Olivine.
pH

pH results were within the range expected of an olivine sand system. Results from the pH analysis can be found in Table 5. Each olivine sand sample produced an alkaline pH. The alkaline reading is typical for the olivine aggregate.

Table 5. Comparison of the pH results from the different olivine samples tested.

<table>
<thead>
<tr>
<th>Sand</th>
<th>LE75</th>
<th>LE80</th>
<th>LE105</th>
<th>LE120</th>
<th>Hamilton</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>9.87</td>
<td>10.10</td>
<td>9.98</td>
<td>9.90</td>
<td>9.50</td>
</tr>
</tbody>
</table>

Grain Fineness Number (GFN) and Screen Distribution

GFN results established that the olivine sand samples used for this study were of three different sieve distributions, as illustrated in Figure 8. Hamilton sand was classified as a four screen, LE80 a two screen, and the remaining samples followed closer to a three sieve distribution. Utilizing the grain fineness number calculation it was determined that a fifty-five point variation existed between the five samples. LE120 was the finest material, or a material with the highest amount of surface area with a value of 113 GFN. LE75 was the coarsest aggregate, or material with the lowest amount of surface areas, reporting a value of 58 GFN. Results from the GFN calculation can be found in Table 6.
Based on the physical property analysis thus far, the screen distribution and results from the LOI have a relationship. As Higher LOI values as observed with an increase in the GFN. As discussed in chapter two, finer sieve screen sands can have a tendency to produce more entrapped gas defects. The combination of the finer screen distribution and the olivine material having a higher loss on ignition. Compared to the coarser olivine aggregates could be a factor into the contribution of pinhole defects between each olivine sample.

This finer material may contain more impurities as well. Material that ends up in the pan could be material picked up during transport of the raw material, or other minute impurities that are from processing the olivine into an industrial sand product. The results from the screen analysis and LOI provide insight that the materials with a higher
concentration in fines also showed to be a material that was more combustible. This relationship could increase the possibility of pin holing to occur on the surface of the aluminum castings.

Table 6.

<table>
<thead>
<tr>
<th>Sand</th>
<th>LE75</th>
<th>LE80</th>
<th>LE105</th>
<th>LE120</th>
<th>Hamilton</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFN</td>
<td>58</td>
<td>66</td>
<td>91</td>
<td>113</td>
<td>78</td>
</tr>
</tbody>
</table>

Acid Demand Value (ADV)

Table 7 provides the results from the acid demand testing. The findings show that sand materials with a higher GFN, such as LE105 and LE120, Table 6, also have the higher acid demand value. As compared to sand samples with a lower GFN. LE105 and LE120 also had a higher LOI, Figure 7 as compared to the rest of the samples, along with a higher amount of fines, Figure 8. All three variables could be an indicator to the amount of pin holing generation on the surface of the castings. Based on the three reported tests it could be theorized based on the data collected that LE105 and LE120 contain an impurity that yields a high surface area, and has the ability to neutralize acid and is easily susceptible to combustion, as compared to the total makeup of the olivine aggregate.
Table 7. Comparison of the acid demand value (ADV) results from the various olivine samples tested.

<table>
<thead>
<tr>
<th></th>
<th>Sand</th>
<th>LE75</th>
<th>LE80</th>
<th>LE105</th>
<th>LE120</th>
<th>Hamilton</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADV</td>
<td>11.5</td>
<td>19</td>
<td>27</td>
<td>28.5</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

TGA/MS Results

Analysis using the TGA started with the control sample, Hamilton. The result from testing showed that Hamilton had a total weight loss between 0.7-0.8% at 1200°F. The TGA sample repeatability appeared to be consistent. The samples tested didn’t show a large deviation between the samples tested on the TGA. Samples of Hamilton had a weight loss in the ranges of 0.7% to 0.9% at 1200°C.

*Figure 9.* Five curves that were developed from thermal gravimetric testing with Hamilton.
The next sample analyzed for the repeatability study was LE75. This sample had an ADV and pH that was similar to the control sample of Hamilton. Comparing the results from the TGA to the traditional physical property testing done within a foundry show that Hamilton had the lowest LOI, Figure 7. Also, this sample was at the midpoint in regards to the grain size, with a GFN of 78, Table 6. LE75 had a three screen distribution, same as Hamilton. LE75, however, had a slightly coarser grain size, and a slightly higher LOI, than the Hamilton control sample.

LE75, weight in Figure 10 showed a gradual loss until reaching temperatures between 550-600°C. From 600°C and continuing into higher temperatures the material changed the rate at which loss weight occurred. The slope of which the weight loss occurred increased slightly until the end of testing at 1200°C. Each of the LE75 samples analyzed produced a range in the total weight loss between each sample. The range between each of the five samples of LE75 was between 0.80-1.10% at 1200°C. LE75’s range of weight loss is larger than the control sample of Hamilton. Comparing the sample to Hamilton, LE75 had a higher LOI in the traditional physical property testing, the coarsest overall GFN and a significant amount of pan fines at 1.34%. LE75’s ADV however was similar to Hamilton, Figure 7. Overall, the weight loss found from the TGA was comparable to the LOI trend found in Figure 7. The temperature ranges in which the weight loss occurred was similar to the weight losses found in literature for the hydrated mineral serpentine. Both Viti (2010) and Yamamoto et al.. (1979) concluded that weight losses for serpentine occurred between 500-800°C.
Figure 10. Five curves that were developed from thermal gravimetric testing with LE75.

The next olivine aggregate tested by the use of the TGA was LE80. Reviewing the standard physical property testing, this sample had an LOI that fell in-between Hamilton and LE75. LE80 was also a slightly finer sand, GFN 66, falling in-between Hamilton and LE75. The ADV of this sample was slightly higher than LE75 and Hamilton. Results from the TGA testing, Figure 11, had a decomposition slope similar to LE75.

The amount of weight loss increased for LE80 at 600°C. Again, the same result occurred after reaching a temperature range of 600-700°C. The sample showed a measurable amount of variation between each LE80 sample. LE80 had total weight loss that was similar to LE75, at 0.80-1.10% at 1200°C. Again, the LOI followed the same trend in combustibles. Falling within the same weight loss range as LE75.
Figure 11. Five curves that were developed from thermal gravimetric testing with LE80.

Total weight loss evaluated on the next TGA sample, LE105, was greater than LE75 and LE80. Its decomposition also followed the same trend as the previous TGA samples tested. The range of LE105 weight loss between the samples tested, varied less, per LE105 sample tested, than the previously two stated olivine sands, and the control sample. Overall, the total weight loss for the LE105 sample ranged from 0.2-0.3%.

Comparing the results to standard physical property testing, LE105 followed the same trend. This material has one of the highest LOIs, second highest GFN, and ADV. The pan fines from this sample came in at 4.05%. Testing showed it was a material that had a higher surface area and a higher tendency to neutralize acids. LE105 also showed the greatest amount of weight loss. This trend also followed in the TGA analysis.
Figure 12. Five curves that were developed from thermal gravimetric testing with LE105.

The final sample, LE120, had a weight loss from thermal gravimetric testing that closely reflected the weight loss of LE105. This sand sample also had a tight range in the amount of weight loss, when compared to the variation found in LE75 and LE80. During the standard physical property testing, LE120 contributed the highest LOI, GFN, and acid neutralizing capability. It also contained the highest amount of pan fines at 4.71%.

Figure 13 shows that the overall weight loss for this sample was between 1.10% - 1.30%. The highest amount of weight loss between all the samples analyzed on the TGA, and LOI testing.
Figure 13. Five curves that were developed from thermal gravimetric testing with LE120.

Figure 14 compares each olivine sand system trialed with the TGA. Averaging the samples from the repeatability analysis and plotting the results with error bars that show the standard deviation overtime between each sample reveals how each sample reacted slightly different when introduce to heat up to 1200°C. The results from testing show that each sample provided a different amount of weight lost. In order from lowest to highest amount of weight loss is as follows: Hamilton, LE75 and LE80 had the same amount of weight loss, LE105 and lastly LE120. The total weight loss found on the TGA as discussed, corresponded to the weight loss from LOI testing. The temperature range that the samples were analyzed at are higher than the pouring temperature of the aluminum alloy. Typically aluminum alloys are poured between 650 and 760°C.
Figure 14. Thermo gravimetric analysis of the five sand samples. Curves are based on five different trials.

Figure 15 takes the weight loss measurement from the TGA results at approximately 982°C and compares it to the results from the loss on ignition testing, which was conducted at 982°C. The overall trend in weight loss is similar, with the total weight losses of each sample following the same order in both the LOI testing and TGA testing. The only difference between the two samples is that TGA results have a slightly higher weight loss. The difference can be due to the sampling processes between the two testing methods.
One of the main differences between the two testing conditions that could contribute to this difference is the atmosphere in which the materials were tested. The LOI testing was conducted with an oxidizing atmosphere. The TGA testing occurred in a neutral atmosphere with nitrogen as the cover gas. There is the possibility that iron, which is tied up within the olivine structure, oxidized during the reaction process, allowing an increase in weight from this reaction. This would result in a decrease in weight found in the LOI testing due to the atmosphere.

Outside of a reaction occurring due to the heat and type of atmosphere, another possibility is the amount of sand used for the LOI compared to the TGA testing. The relative amount of surface area used for each of the samples analyzed would be hard to measure. Even though proper splitting techniques were used to prepare the samples, the surface area between the larger LOI sample and smaller TGA sample may have
influenced the overall weight loss. It would be possible that the concentration of fines could have been different between the two types of samples, changing the total amount of weight loss between the two testing methods. It was discovered during the physical property testing that materials with higher fines also had a higher amount of weight loss. A combination of the two theories is also possible.

Utilizing the results from the TGA, a derivative was used to potentially understand when during the heating process a hydrated mineral, if contained within the olivine, was breaking down and releasing a gas. Using the average curve of the five aggregates tested, a first derivative curve was produced for each of the olivine sand samples ($\Delta T/\Delta t$). This evaluation would determine the start of the reaction due a change in slope from the curve being produced during the heating cycle.

The first samples analyzed using this process was LE75, Figure 16(a). The derivative from the thermal decomposition identified a change occurred within the olivine sample. The sample had a major inflection point at a temperature of 685°C (1265°F). Hamilton also had an inflection point at this temperature. The remaining samples from testing, LE80 Figure 16(b), LE105 Figure 16(c), and LE120 Figure 16(d) had an inflection point that was slightly higher than the Hamilton and LE75. This inflection point occurred at 673°C (1243°F). The reaction occurring with the base aggregate was occurring 12°C (54°F) lower than the inflection on LE75 and Hamilton.
Based on the data collected, LE120 was the first sample analyzed utilizing the TGA with the MS. This sample and LE105 was selected based on the highest amount of weight loss, for both TGA and LOI. To understand how much potential water vapor was coming off of the olivine sand, a ramp rate was set at the same setting as the TGA, which was 20 degrees/minute until a final temperature of 1200°C was reached. The sample remained in the equipment, returned to room temperature, and a second test was performed with the exact same sample and the same parameters.
The sample was retested to determine if a dehydroxylation event occurred, weight loss by removal of water from the mineral. The initial test provided a curve that had a total weight loss of 1.30%. This weight loss corresponded to the earlier testing found in Figure 14. The mass spectrometer was programmed to acquire all ions related to moisture. The ion currents that were being analyzed were 2, 16, 17, 18, 19 and 20 amu. Testing was inconclusive and the results did not indicate that there was a presence of water in any form.

DSC Results

Since the equipment utilized was also a DSC, this data was also collected and analyzed. The results from the DSC indicate no major differences between the five samples analyzed. LE105 had a problem with all five DSC results during testing and was omitted from the results. Between the control sample, Hamilton, and the samples tested that had the potential to contain hydrated minerals, all had a similar result on the DSC. The results, shown in Figure 17, indicate an endothermic reaction until around 350°C. After this point there is a small exothermic reaction.
There were also no changes in energy states detected by the DSC in the temperature ranges between 673-685°C. As the mass was decreasing there was a minor energy change. Again, this is the theorized range for serpentine. As stated before, all samples had a similar energy changes and provided no indication of one sample generating more pin holing defects than any other sample.

Casting Trial Results

As discussed in Chapter 3, two castings were produced for each sand system using sodium bentonite as the bonding mechanism. Once cast the samples were cleaned off of excess sand with only the use of water. Images were produced of the cope and drag on the castings. The results from the castings show that each material produced a different number of pinholes, Figure 18. The results from the second castings produced with olivine aggregates can be found in the appendix.

Figure 17. Results from DSC testing.
Figure 18. Photographs of each casting that was analyzed in this study. Both drag (left image) and cope (right image) were captured. (a) Hamilton, (b) LE75, (c) LE80, (d) LE105, (e) LE120.

Casting Evaluations

The results from the qualitative measuring can be found in Table 8. The results revealed a significant difference between the standard olivine, Hamilton, and the remaining olivine samples. The results from the two castings produced from Hamilton averaged 79 pinholes per castings. The next closest casting was LE75, which had 69% more pinholes. LE80 produced 71% more pinholes; LE120 was 74% greater in pinhole
defects. LE105 had the greatest amount of pinhole porosity producing 79% more pinholes than the standard Hamilton aggregate.

Table 8. 
*Results from ranking the average number of pinhole defects on the surface of the aluminum castings that were produced from the five aggregates used in this study.*

<table>
<thead>
<tr>
<th>Sand (Olivine Aggregate)</th>
<th>Average Number of Pinholes/Casting</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamilton</td>
<td>79</td>
<td>1</td>
</tr>
<tr>
<td>LE75</td>
<td>254</td>
<td>2</td>
</tr>
<tr>
<td>LE80</td>
<td>275</td>
<td>3</td>
</tr>
<tr>
<td>LE120</td>
<td>306</td>
<td>4</td>
</tr>
<tr>
<td>LE105</td>
<td>377</td>
<td>5</td>
</tr>
</tbody>
</table>

Results from the visual evaluation using the comparison device showed that surface finishes were also different. The surface didn’t correlate to the pinhole evaluation. The top three ranked in average number of pinholes, Table 8, were in the bottom of the surface finish results, Table 9. LE120 had the best surface finish, but contain the majority of the pin hole defects. This was followed by LE105, LE80, and Hamilton. The casting with the roughest surface finish was LE75. The possibility as to why LE120 and LE105 had a better surface finishes could be due to the samples having a higher GFN, containing higher amounts of fine sand. The sample with the higher GFN, had a higher amount of fines, which increases the surface area on the mold/metal interface. This reduces the overall amount of voids and pockets between sand grains, improving the surface finish, due to the liquid aluminum not filling in these void spaces, resulting in a smoother finish on the aluminum casting.
Table 9.
*Comparison results on surface finish of the casting produced with the various aggregates for this study.*

<table>
<thead>
<tr>
<th>Sand (Olivine Aggregate)</th>
<th>Average C Value</th>
<th>Rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>LE120</td>
<td>C25</td>
<td>1</td>
</tr>
<tr>
<td>LE105</td>
<td>C30</td>
<td>2</td>
</tr>
<tr>
<td>LE80</td>
<td>C35</td>
<td>3</td>
</tr>
<tr>
<td>Hamilton</td>
<td>C40</td>
<td>4</td>
</tr>
<tr>
<td>LE75</td>
<td>C60</td>
<td>5</td>
</tr>
</tbody>
</table>

**Stereoscopic Inspection**

The analysis from the stereoscopic inspection seems to indicate that the majority of the larger pinholes in the castings contained a grain of sand. Under closer inspection the aggregate was surrounded, and some nearly encased, by the aluminum during solidification. Each casting showed the same type of sand grain entrapment. Images were gathered from LE80 Casting #1 for this report with an image of a typical pinhole, shown in Figure 19 and Figure 20.
Figure 19. Close up image of LE80 Casting 1. Note the aggregates that are embedded into the surface of this casting. Magnification: 22.5x.

Figure 20. Image of LE80 Casting 1 with a piece of the Olivine aggregate that appears to almost be encased by the aluminum alloy. Image is representative of the type of pinhole that formed in all cast trials. Magnification: 82x.
Discussion

The results from the study indicate that the foundry standard olivine sand, Hamilton, had different physical characteristics, as compared to the LE olivine samples. A couple of the major differences were pointed out between the LOI and TGA results. Hamilton sand ended up with lower weight losses than the LE samples. The TGA coupled with the MS was unable to confirm the increases in weight loss were associated to the hydrated mineral, serpentine, breaking down and releasing water from the sand.

The derivative produced from the TGA weight loss curved did indicate an inflection point was that was within the ranges of which serpentine was known to breakdown into olivine and water. Literature indicated that serpentine dehydroxylation occurred from 550°C and 800°C. Even though the MS did not indicate water vapor coming from the aggregates, a change in slope was found for all the samples occurring between 673°C and 685°C. With the A356 aluminum alloy, that is unmodified, it is expected that solidification of this alloy will begin around 610°C (1130°F). A356 recalescence temperature is estimated at 568°C (1054°F) (Giese, Ravi, Boss, & Biersner, 2012). Inflection range of the olivine is 75°C (167°F) to 63°C (145°F) above the start of solidification. This inflection could be an indicator as to when a change is occurring in the olivine aggregates, producing the various amounts of pinholes from all olivine aggregates.

The results from the stereoscopic images indicate that the pinhole porosity was not strictly forming from gas generating from the mold. Individual sand grains are
entrapped within the castings. These sand grains don’t appear to be floating on the aluminum, since they are equally distributed between the cope and drag sides of the casting.

It is known that a casting skin is forming on the surface of aluminum casting and molding aggregate. Based on the results found on the image analysis, Figure 19 and Figure 20, it appears that these grains became entrapped within the aluminum surface. It could be that these grains are pushed into the very start of this skin forming, during the “mushy zone” or eutectic rescalence of the A356 alloy. The reasoning behind why the pinholes formed are not gas type holes is due to their shape. Typically gas holes are spherical in shape, whereas the pinholes found on the test casings were rough in shape, many of these defects also contained a grain of olivine sand.

It was also observed that there was a relationship between the weight loss values in LOI testing/TGA testing and the total number of pinholes found in the casting evaluations. Comparing the two results, LE105 and LE120 displayed the largest amount of weight loss in the LOI test. LE105 also had the greatest amount of pinholes, at 377 pinholes/casting, followed closely by LE120 with an average 306 pinholes/casting. LE120 was followed by LE80, with 275 pinholes/casting, and LE75, with 254 pinholes/casting.

The material with minimal weight loss was the Hamilton aggregate and was the casting with a significant drop in the amount of pinholes on the casting surface at 79 pinholes/casting average. Although there is no definitive answer for the increase in LOI,
an explanation could be made for the increase in pinhole defects related to GFN. LE120 and LE105 have a higher concentration of fines. Both aggregates have 4.00-5.00% retained on the pan, Figure 8. These fines increase the amount surface area.

The increase in surface area would require the clay bond to cover more area with the same amount of sand. This study used the same amount of bentonite clay, at 8.00% for testing. This level may not have provided enough bentonite to produce a sufficient level of bond for the high GFN sands. The result would be loose sand falling into the casting cavity during filling and become entrapped during solidification. This reduction in bond could be the main contributor for the olivine samples producing pinhole type defects. The smaller grains are not efficiently coated in bentonite and became free to float around inside the casting cavity.

**Summary**

All samples provided for this study were tested to better understand the formation of pinhole porosity with olivine in aluminum castings. The experiments consisted of a standard foundry sand testing analysis of the sands. This testing was followed by a more quantitative approach using a DSC/TGA that was later coupled with a mass spectrometer.

The results following typical foundry sand testing procedures indicated there were differences in from the control sample of olivine in the amount of weight loss, screen distribution/GFN, and ADV between the five samples tested to potentially contain hydrated minerals. The largest correlation discovered was the GFN of the olivine aggregates, which ended up corresponded to the amount of pinhole porosity on the cast
surface, produced by the olivine sand samples. The smaller the olivine grain became the greater propensity for pinhole defects.

The increase in fineness levels also corresponded to increases in the LOI and acid consumption of the foundry aggregates. The variation in grain sizing from sample to sample was not designed into the original testing parameters, and the results of this was a common clay bond for all samples, utilizing 8.00% bentonite based on sand. This may not have been a proper amount of bond level for the increased surface area of the finer sand systems, leading to the potential for increased pinhole defects due to sand inclusions in the castings from un-bonded sand grains.

The results from the DSC/TGA testing also confirmed testing results from the standard foundry sand testing results. Weight losses measured by the equipment had a relationship that was the same as the LOI results. The mass spectrometer coupled to the DSC/TGA did not indicate the presence of serpentine and the occurrence of dehydroxylation. Chemical compositions, XRF analysis, of the olivine sand samples were consistent with a typical olivine aggregate.
Conclusions

This study was designed to provide preliminary information into understanding how a foundry could predict impurities, such as serpentine, generated pinhole porosity defects on the surface of aluminum castings. The problem was classified into two separate objectives to determine when the impurity would break down and if current foundry testing equipment could be used to predict the formation of pinhole porosity before the casting process was initiated.

The standard foundry testing practices did indicate differences between the five sources olivine aggregate. The loss on ignition results indicated there was a larger amount of weight loss between the standard foundry olivine Hamilton, and the four other olivine samples tested. There were also varying amounts of pinhole porosity on each of the aluminum castings produced with the olivine aggregate.

Thermogravimetric analysis also was comparable to the standard loss on ignition testing used by the foundry industry. There was also statistical repeatability in the amount of weight loss for each sample tested. When the DSC/TGA was coupled with the mass spectrometer there was no detection of dehydroxylation occurring with the olivine aggregates.
The TGA results were inconclusive in determining if serpentine was present within the olivine aggregates. TGA and LOI results pointed to a larger than normal weight loss in the samples of olivine trialed for foundry use, LE products, as compared to the standard foundry olivine sample, Hamilton. It can also be said that the finer sand had increased the amount of surface area, reducing the overall strength characteristics of the sand system and increasing the potential for sand grains to break from the mold prematurely and enter the casting. Potentially causing the majority of the pinhole porosity.

Recommendations for Future Studies

When performing future research for a topic such as hydrated minerals the following recommendations need to be outlined and considered:

1. Maintain samples with grain distributions that are similar. The higher GFN increased the amount of surface area. Current testing utilized samples that had a 55 point variation in GFN. Using the same level of bond would result in the higher GFN not having enough bond to coat all of the sand grains, due to an increase in surface area. It would also reduce the overall mold strength, increasing its susceptibility to casting defects. Utilizing a similar distribution also would eliminate the possibilities of the clay bond contributing to the pinholes when increased levels of bond are used to compensate for the increase in fines.

2. Use x-ray dispersion or Quantitative Evaluation of Minerals by scanning electron microscopy (QemSCAN), a registered trademark owned by FEI Company. Using
either of these analytical methods will provide the researcher information about what minerals are contained within the sample aggregate. X-ray florescence is a good method to determine chemical composition; however more information is needed to understand water bearing minerals. QemSCAN used and SEM equipped with software that determines the chemical composition and the type of mineral each sand grain would be. It is possible that serpentine is not the issue with the olivine sand. Other mineral contaminates, such as chloride minerals, could be contribution to the pin holing issue with this particular aggregate.

3. The exploration of using the mass spectrometer to measure ion currents outside that of water vapor. The hydrogen being released from the serpentine mineral could be combining with organic binder system during the casting process and forming hydrocarbons.

4. Exploration of the solidification process by means of thermal analysis may provide information into how thin cross section, or modulus, of castings are able to develop pinhole porosity on the surface of aluminum castings and the possibility of understanding when.

5. Implementing data gathered from DSC/TGA, and thermal analysis into solidification software to predict when and what variables are required to generate pinhole defects based on the molding aggregate used.
REFERENCES


APPENDIX

SECOND CASTING SET

(figure continues)
Photographs of each casting that was analyzed in this study. Both drag (left image) and cope (right image) were captured. (a) Hamilton, (b) LE75, (c) LE80, (d) LE105, (e) LE120.