DEVELOPMENT OF A VISUAL HUMIDITY INDICATOR FOR 3D PRINTING FOR METAL CASTING

A MAJOR QUALIFYING PROJECT REPORT

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Abstract

During metal casting, cores are emplaced in the mold. Cores with high moisture content give rise to porosity in the cast part therefore impairing quality. The project goal was to create a visual humidity indicator to determine moisture content of a 3D printed core. We accomplished this by successfully incorporating phenolphthalein into sand based powder in the printing process. The success of our project will optimize digital manufacturing and metal casting by ensuring high quality cast products and improved productivity.

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Executive Summary

Within the metal casting industry, more advanced technology is being developed to accomplish previously conventional tasks. Viridis3D is a recently established company introducing a means to create sand molds and cores of complex shapes and contours through a process known as 3D printing. Pieces that often took weeks to create could be designed, computer modeled, printed, and finally metal casted in half the time. Viridis3D's additive manufacturing technology can print many molds or cores faster than a CNC machine can be programmed within traditional subtractive manufacturing techniques.

Offering a variety of construction materials of molds and cores, Viridis3D does not perform the task of metal casting, but rather outsources its molds and cores to an off-site foundry. A typical setback that often hinders progress occurs at the foundry. Frequently, the company has encountered circumstances where the mold arrives at the foundry but because of miscommunication or lack of attention, the mold is not casted immediately, sometimes sitting for days or weeks before any action is taken. This causes a problem because in those few days or weeks, moisture from the surrounding environment is absorbed into the mold. Molds that have absorbed some humidity should not be casted as the final casted metal piece will have impurities or irregular surface areas due to the change of phase of water from liquid to gas during a pour. These inaccurately casted pieces then need to be re-casted, causing delays to customers.

The overall goal of this research project is to develop an affordable, practical chemical compound that successfully provides a visual indication of humidity absorption within a 3D printed mold or core to be used to cast a metal part. This developed compound must have the following characteristics: unreactive with Viridis3D's three casting sands, functions as visually distinguishable humidity indicator, reversibility of such humidity indicating functions, and finally easy transition and application to Virids3D's existing 3D printing processes. The three main components of this research address the following concerns: the ability to function as a moisture indicator, the effect of the humidity level on the indicator's function, and the practicality of the scale up of this process to an industrial part.

Five chemical compounds were chosen as potential candidates for the visual humidity indicator. These five indicators went through three experimental phases: preliminary experimentation, in-depth 3D printing experimentation and internal laboratory testing. Preliminary experimentation of the initial five chemical compounds eliminated the practicality and functionality of three of the compounds, yielding two compounds for further experimental analysis. After preliminary testing, these two compounds moved to a more in-depth experimental procedure: application within the 3D printing technology. Finally, internal laboratory testing consisted of humidity testing within controlled humidity environments.

Following the three experimental phases, phenolphthalein was chosen as the humidity indicator. With all of the required characteristics, this compound showed a distinct color change when exposed to 99% relative humidity for the course of one week in the designed humidity environments. To further the project, two concentrations were also compared to see if lowering the concentration could achieve similarly effective results. This was successful, allowing us to recommend to Viridis3D to use a lower concentration. Finally, a production scale mold was made to determine its scalability and usability in the industry. From this demonstration, it was clear that there were some problems printing a large scale mold than a tile. It was also noted that the color change is dimension-dependent. Nevertheless, the color differences between a dry mold and a moist mold were clear and their resulting final cast parts also demonstrated the damaging effect of moisture.

This project was able to successfully develop an indicator that could be incorporated into Viridis3D's technology to further leverage their company value. End users can now look at a mold and be able to visually deduct whether it was safe to pour or not. Finances and resources could be saved by allowing foundry workers with a very simple way to detect moisture in a mold before a casting; which will ultimately lead to the optimization of digital manufacturing and metal casting for Viridis3D by ensuring high quality cast products and improved productivity.

1 Introduction

Within the metal casting industry, more advanced technology is being developed to accomplish previously conventional tasks. Viridis3D is a recently established company introducing a means to create sand molds and cores of complex shapes and contours through a process known as 3D printing. Not only are these shapes unique, but the process of metal casting itself is revolutionized. Pieces that often took weeks to create could be designed, computer modeled, printed, and finally metal casted in half the time. Viridis3D's additive manufacturing technology can print many molds or cores faster than a CNC machine can be programmed within traditional subtractive manufacturing techniques.

Offering a variety of construction materials of molds and cores, Viridis3D does not perform the task of metal casting, but rather outsources its molds and cores to an off-site foundry. Not only is this process time consuming, but any additional complications further delays progress in meeting customer deliverables or internal research and development objectives. A typical setback that often hinders progress occurs at the foundry. Frequently, the company has encountered circumstances where the mold arrives at the foundry but because of miscommunication or lack of attention, the mold is not casted immediately, sometimes sitting for days or weeks before any action is taken. This causes a problem because in those few days or weeks, moisture from the surrounding environment is absorbed into the mold. Molds that have absorbed some humidity should not be casted as the final casted metal piece will have impurities or irregular surface areas due to the change of phase of water from liquid to gas during a pour. These inaccurately casted pieces then need to be re-casted, causing delays.

Past researchers have investigated the potential use of humidity indicators within various industries. From architecture to sports, the idea is by no means novel, but the application to such a specific need has not been explored. Additive manufacturing is slowly making its presence within the metal casting industry, but its novelty remains an advantage. Many chemists have developed humidity indicating dyes using silica gels and various pH indicators by way of complex hydration reactions; however the incorporation of this chemistry into 3D printing cores and molds for metal casting remains unexplored.

The overall goal of this research project is to develop an affordable, practical chemical compound that successfully provides a visual indication of humidity absorption within a 3D printed mold or core to be used to cast a metal part. This developed compound must have the following characteristics: unreactive with Viridis3D's three casting sands, functions as visually distinguishable humidity indicator, reversibility of such humidity indicating functions, and finally easy transition and application to Virids3D's existing 3D printing processes. The three main components of this research address the following concerns: the ability to function as a moisture indicator, the effect of the humidity level on the indicator's function, and the practicality of the scale up of this process to an industrial part. Through various experimental trials with silica gels and various pH indicators, this research project will provide Viridis3D with resources in both time and finances, potentially creating additional business opportunities.

2 Background

Before beginning this project, an extensive review of the prior research on humidity indicators was completed. Other members of academia have discovered various methods to detect humidity within various applications. A brief selection of these methods and applications are described in this section. In addition, this section also includes a brief description of Viridis3D's 3D printing technology.

2.1 Color-Indicating Chemistry

Within the field of research to discover color-changing chemical reactions, many studies have been completed for the past decade. Detection of humidity has become important in many different industries, spurring the recent research. Of the many studies conducted, each study is unique in that the approach to the problem is different. Using different chemical development methods and chemical compounds, the following section details a few methodologies.

2.1.1 Inorganic Polymers

K. Mackenzie experimented with the incorporation of acid-base indicators and inorganic polymers to potentially provide a visual color-change for indicating humidity in materials.[1] These inorganic polymers are x-ray amorphous aluminosilicates with random arrangements of tetrahedral Al-O and Si-O units. Indicators used in this study included the following: thymol blue, bromcresol green, methyl red, bromothymol blue, phenolphthalein, and thymolphthalein. Their organic chemical structures can be seen in Figure 2-1 below.

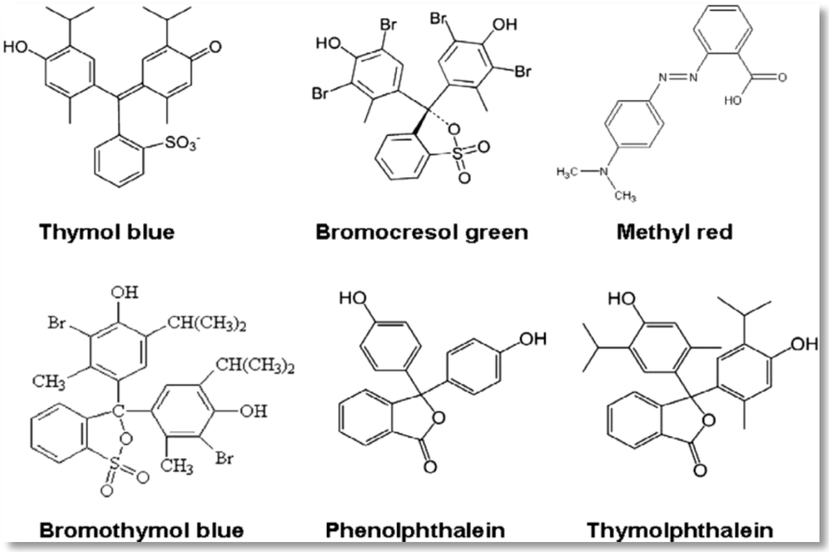


Figure 2-1. Chemical Structures of Indicators Used in Mackenzie's Study[1]

Experimental procedure required that these indicators be mixed thoroughly with the uncured polymer in concentrations up to 0.5 mmol. After the polymer cured at 50°C overnight, the solid samples were then grounded to powder form and characterized by x-ray diffraction. Following this, the powder was dried and then exposed to levels of high humidity. Color change was examined both visually and by UV-spectroscopy between wavelengths of 300-800 nm.

This experiment discovered that the pH of a geopolymer is reversibly dependent on humidity, as demonstrated by the color change in the pH indicator dyes. While there is a promising dye that meets all of the application needs, none of the tested dyes were able to bind firmly with the geopolymer matrix, display a distinct color change in the designated pH range, chemically stable at a high pH, and resistant to bleaching and oxidation under humid conditions.

2.1.2 Humidity Sensitive Ink

Within the past few years, another research team led by Andrew Mills has also developed a reversible relative-humidity indicator ink based on methylene blue and urea. [2] Typical humidity sensors are inorganic salts such as cobalt (II) chloride which changes from anhydrous (blue) to hydrated (pink) at a relative humidity of 40%. However, this team discovered that when methylene blue is contained within a polymer, like hydroxyl ethyl cellulose (HEC), with a large amount of urea, the resulting ink is blue. This blue ink becomes an opaque, thin pink film under ambient conditions (RH = 60% and T = 20) and quickly changes to a clear blue color when exposed to RH values greater than 85% as demonstrated in the photograph below.

Figure 2-2. Photographs of MB/urea/HEC humidity indicator during color change after exposure to 100% relative humidity[2]

This discovery is unusual in such that it yields a sharp evident reversible color change at high relative humidities, whereas this has been a problem in other investigations, specifically the experiment detailed in section 2.1.1. Considering Figure 2-3 below, it is apparent that there is a relative humidity that demonstrates a point of highest absorbance. As the relative humidity continues to increase to 100%, absorbance decreases, indicating that absorbance (or color change) is not at its highest potential at higher humidity levels.

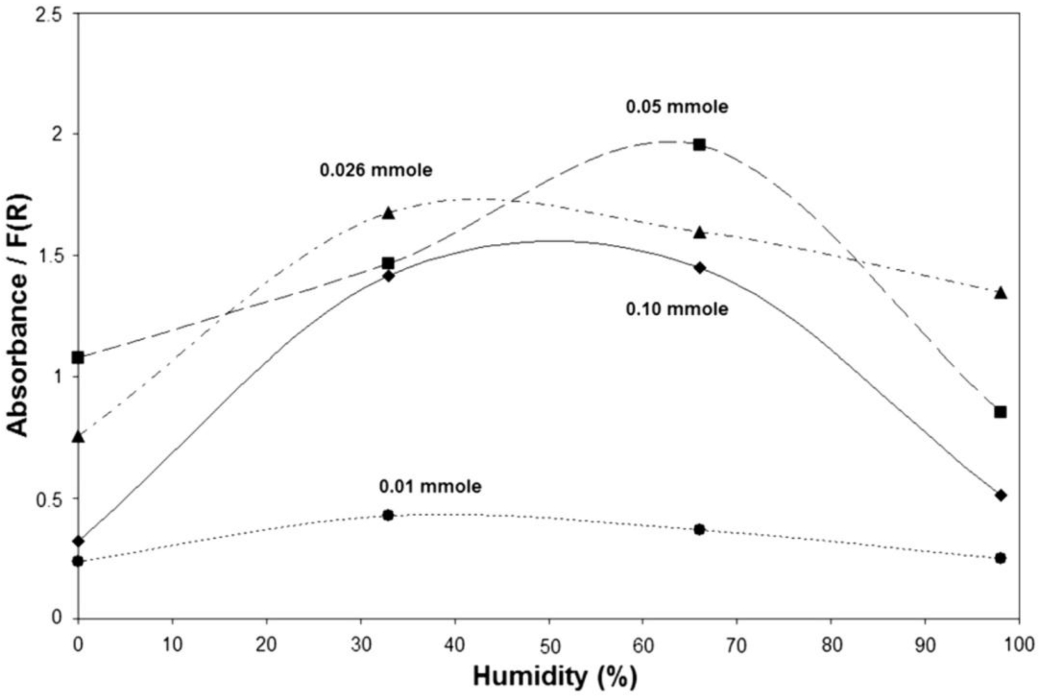


Figure 2-3. Absorbance vs. Relative Humidity Results from Mackenzie's Experiment[2]

The experimental procedures for this humidity sensitive ink required that the sensor was spin coated in an ink made up of methylene blue and urea in an HEC aqueous solution. After the thin film dried, the resulting product is an opaque pink film. Exposure to high relative humidity conditions renders the pink film a clear blue.

Results from this research yielded a relative-humidity indicator that is particularly useful at high RH values. In addition, its reversibility and quick response rate increases its potential to be used in many applications, such as fruit ripening environments. Further research is being done in order to increase the versatility of this indicator at all RH values.

2.1.3 Silica Gel Applications

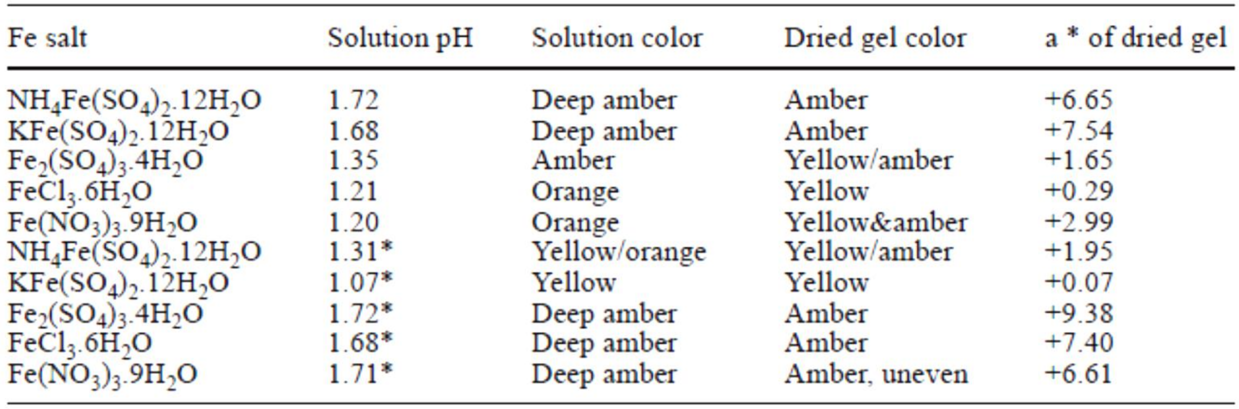
Silica gel has been traditionally used as a desiccant for many years.[3] Its high surface area allows it to absorb water rapidly. Colored silica gel variants change color once the gel is hydrated, typically changing from a deep blue to a light pink. This color change is a result of the co-ordination around the cobalt (II) ion, changing from tetrahedral to octahedral as the gel becomes hydrated. Many researchers have studied silica gels as the basis of their research simply because of its history. The following section details areas of research conducted regarding the use of silica gel.

2.1.3.1 Silica Gel Impregnated with Iron (III) Salts

Within the humidity indicator field, Stephen Moreton investigated the interaction between silica gel and iron (III) salts.[4] Silica gels have been used as desiccants for many years; however it requires the use of a color-indicating change which is typically cobalt chloride. It was most recently discovered as a category 2 carcinogenic. In addition, organic pH indicators have been used; however they are unstable at high temperatures, preventing the possibility of reversibility. Moreton impregnated silica gel by initial exposure to water and then immersion in iron salt solutions, stirring at hourly intervals. This mixture was then spread on trays less than 20 mm deep and dried in a convection oven at 145°C for 16 hours. After such procedures, the gel was characterized by the following factors: iron content, surface area, adsorption capacity, and finally the most important visual characteristic, color. Parts of this gel were exposed to humidified air and the resulting data concluded that as humidity increased, the color of the gel faded.

It was also noted that the pH at which humidity was exposed also influenced experimental observations. All impregnated gels prior to drying were of the same pale yellowish color. However, with varying pH solutions, when the gels dried, they were of different shades of amber. Colors and pH values of the varying impregnated and dried gels are displayed in Table 2-1.

Table 2-1. pH values and colors of 10% solutions of iron salts and resulting impregnated and dried gel colors[4]



Fe salt	Solution pH	Solution color	Dried gel color	a * of dried gel
$NH_4Fe(SO_4)_2.12H_2O$	1.72	Deep amber	Amber	+6.65
$KFe(SO_4)_2.12H_2O$	1.68	Deep amber	Amber	+7.54
$Fe_2(SO_4)_3.4H_2O$	1.35	Amber	Yellow/amber	+1.65
$FeCl_3.6H_2O$	1.21	Orange	Yellow	+0.29
$Fe(NO_3)_3.9H_2O$	1.20	Orange	Yellow&amber	+2.99
$NH_4Fe(SO_4)_2.12H_2O$	1.31*	Yellow/orange	Yellow/amber	+1.95
$KFe(SO_4)_2.12H_2O$	1.07*	Yellow	Yellow	+0.07
$Fe_2(SO_4)_3.4H_2O$	1.72*	Deep amber	Amber	+9.38
$FeCl_3.6H_2O$	1.68*	Deep amber	Amber	+7.40
$Fe(NO_3)_3.9H_2O$	1.71*	Deep amber	Amber, uneven	+6.61

In the event that the salt yields a lighter color, it can be changed to produce a darker color simply by raising its pH. This phenomenon explains why specifically, the ammonium iron (III) salt produced the best results, meaning the darkest amber color with the highest change in color, because it yielded the highest pH of all the salts tested in this experiment.

Moreton proposed the following mechanism at which the hydrolysis of iron (III) salts occurred.

$$[Fe(H_2O)_6]^{3+} \longleftrightarrow [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad (1)$$

$$[Fe(H2O)_5(OH)]^{2+} \longleftrightarrow [Fe(H_2O)_4(OH)_2]^{+} + H^+ \qquad (2)$$

The first mechanism represents an aqueous environment at a low pH. This acidic environment allows the iron(III) salts exist as single cations. Undergoing hydrolysis as pH increases, there are more yellow hydroxyl species. However, when the pH reaches a certain level, the second mechanism is valid. The hydroxy species dimerise and polymerize yielding red polynuclear Fe species.

2.1.3.2 Silica Gel/Porphyrin/$MgCl_2$ Composite

Addressing the carcinogenic concern of cobalt (II) chloride, Fueda Yoshiyuki and his colleagues at the University of Miyazaki defined a need for a cobalt-free humidity indicator.[5] Their methods consisted of preparing the composite with silica gel and porphyrin (PCl_2TPP^+). This was done by adding silica gel into a MeOH solution of PCl_2TPP^+, allowing almost all of the (PCl_2TPP^+) to be adsorbed on the silica gel. After filtration and heating at 130°C overnight, the resulting composite is a purple PCl_2TPP^+/SiO_2 composite. A summary of the preparation scheme is shown in Figure 2-4 below.

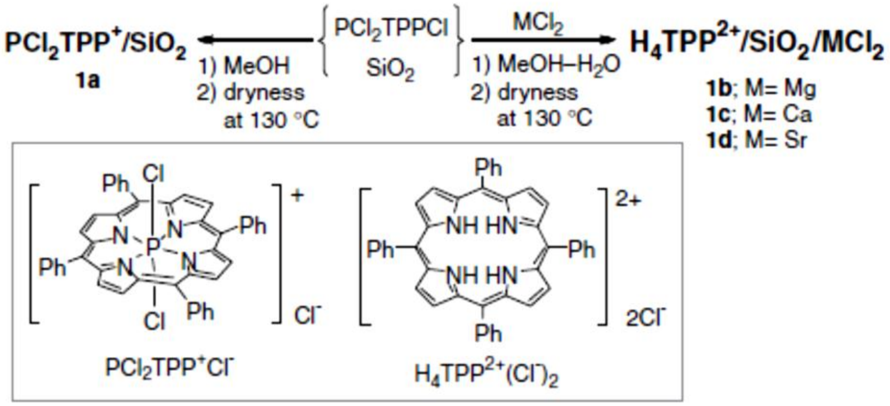


Figure 2-4. Composite synthesis scheme[5]

However, after such experimentation, Yoshiyuki and his team realized that they needed to create acidic environments for these substances. To do this, a porphyrin/MCl_2/SiO_2 composite was prepared in which MCl_2 means an alkaline earth metal chloride. Specifically, the ones used in this experiment were $MgCl_2$, $CaCl_2$, and $SrCl_2$. Again the SiO_2 was mixed with a MeOH solution of PCl_2TPCCl and an aqueous solution of the alkaline earth metal chloride. Filtration and drying occurred after this process to produce a product that is practical to test for specific characteristics. In addition, reversibility was tested by drying the material to see if the material would revert back to its original color. Specifically with the alkaline earth metal Mg, it showed a spectral change of 135 nm between dry and humid conditions within the absorption spectra. It was also sensitive to moisture at even low relative humidity levels without the inclusion of any carcinogenic chemicals. It was concluded that a composite made of silica gel, porphyrin and $MgCl_2$ would be suitable to detect humidity within the test specimens.

2.2 Current Indicator Applications

Humidity indicators have been used in a variety of applications within the past 50 years. From architectural concerns to sports equipment, moisture in the air can cause many issues within various fields. Researchers conducted research in multitudes of manners in an attempt to combat this issue, or at least visually determine when humidity becomes a problem.

2.2.1 Humidity in Architecture

Within the architectural world, humidity can affect the physical structure of historical buildings.[6] These buildings are susceptible to deterioration from environmental sources, such as temperature, light, relative humidity and pollution. In high humidity environments, the degradation of the material due to environmental factors is especially high. Without the proper conservation precautions, protecting these historical, artistic and cultural structures can be difficult. In March of 2007, N. Carmona along with other researchers published a potential solution to problems with humidity. Specifically, their research focused on visual humidity and acidity indicators. Using the pH indicators crystal violet (CV) and chlorophenol red (CR), the research team discovered that when sol-gel systems were created using these two dyes, the systems could detect harmful levels of humidity and acidity in the ambient environment.

Carmona et. al's research considered two environmental factors. The factor of interest is humidity, which is detected using the CV sol-gel system. The sols were applied by dip-coating the material at a drawing rate of 1.35 mm/s. After application, the quality of the coatings was evaluated based on physical defects, optical quality and coating thickness. These sensors were then subjected to varying levels of relative humidity at a constant temperature of 25.5°C. Reversibility was also tested by recording the visible spectrum after immersion for 2 minutes in 1 M of HCl and exposure for 10 minutes to 60% relative humidity.

The absorption spectra were recorded for each sample before and after exposure to humidity. When the solution pH is 2, the CV showed two absorption bands at 425 and 625 nm corresponding to a green hue. At a higher pH of 10, the spectrum exhibited a band peak at 590 nm showing a deep blue color. Results from this research indicated that a comparison could potentially be made between the rate of relative absorption and percent humidity. The research team discovered that the rate of absorption is higher with exposure to a higher percent humidity. This color change is driven by a neutralization-dilution where the water from the humidity dilutes the acid-basic chemical species. The dilution induces pH changes, where color change occurs at very low pH values. When there are small changes in humidity, there is a noticeable color change.

2.2.2 Moisture Indicator in Golf Balls

Robert Winskowicz has a patent that describes the use of multiple moisture indicators incorporated into the production of golf balls.[7] The moisture on a golf ball will yield unpredictable flight patterns, often interfering with game performance. To achieve this, inks or dyes may be micro-encapsulated inside a thin polymer coating in the form of small particles. These micro-capsules vary in size from tens of microns to millimeters and can be integrated with a hard, glassy polymer coating (such as polymethyl methacrylate). This can then be used as a final coating for the ball or the substance can be incorporated into the material that the golf ball is composed of.

There is also another method in which the indicator is dispersed through a controlled release system. The slow dissolution of linear polymer within a solvent results in the release of the encapsulated substance as the coating walls dissolve. In other words, as the coating walls become thinner, the encapsulated compounds become activated. Macro-encapsulation is also possible, in which case the material is slowly released by way of a continuous polymer matrix. This matrix can be shaped into a variety of shapes or forms. Both these methods are similar in the concept of slow diffusion of the material out of a matrix or encapsulated shell but they differ in that micro-encapsulation, the material is found in definite areas on the magnitude of several microns and macro-encapsulation involves the material found in larger areas with a magnitude of centimeters and greater.

2.3 Viridis3D's Technology

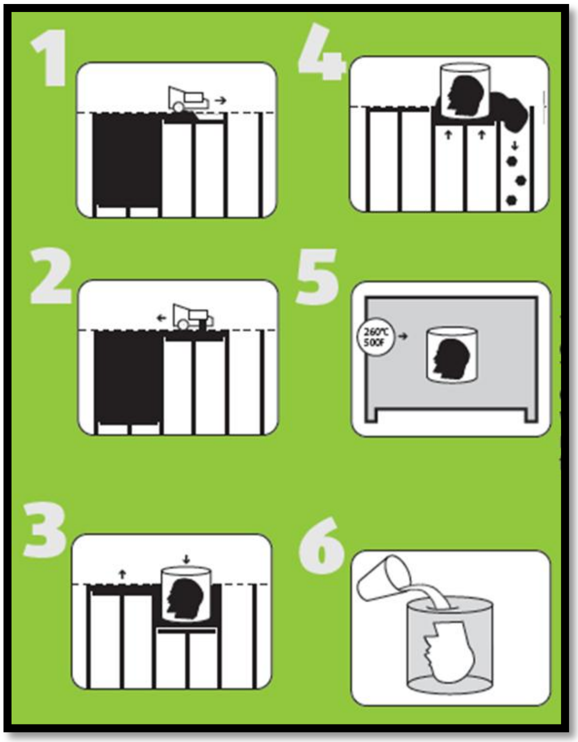


Figure 2-5. Summary of 3D printing process

Three Dimensional Printing (3D printing) is a patented technology invented and developed at Massachusetts Institute of Technology. This technology allows for the production of prototype and end-use parts directly from a computer-aided design (CAD) Model. 3D printing has no geometrical limits, allowing the creation of unique parts of intricate designs and the production of parts made of any material that can be obtained as a powder[8]. The 3D printing process distributes unique binders from ordinary Hewlett Packard (HP) printer print heads onto a bed of powder in order to selectively join powder particles to the specific design of the part. Using a technology that is very similar to 2D ink-jet printing, parts are produced with incredible dimensional accuracy.

3D printing builds its parts in layers; from the CAD model of a desired part, a slicing algorithm draws detailed information for every layer which is then simultaneously printed on adjacent layers of powder in the machine. There are four main components to a 3D printer: the feed box, build box, roller, and print head. The feed box and build box both rest on separate, adjacent pistons, allowing the continuous transfer of powder from the feed box to the build box during a print. The roller and print head are both located on a dolly which runs on a pair of tracks allowing movement in the x direction over the build and feed box. Within the dolly, there is a third rail that allows the print head to freely move in the y direction as well as the x. This can be seen in Figure 2-6 below. This half sphere is cut into cross sections and each layer is printed one a time.

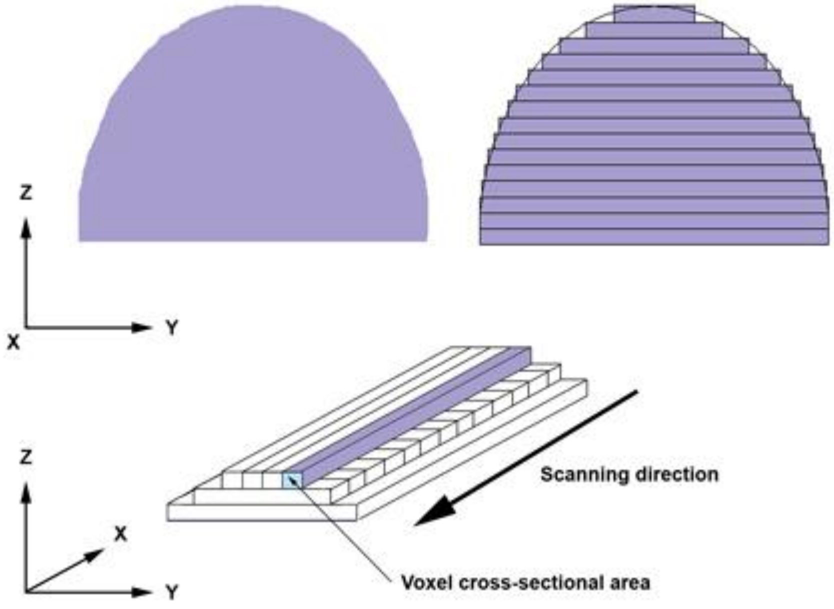


Figure 2-6. Visual of cross-sectioned 3D printed part[9]

Powder is loaded into the feed box of the 3D Printer, the roller then evenly spreads a thin layer of powder onto the build box, and in a fashion very similar to a conventional ink jet printer the print head prints the first cross-sectional layer of the piece onto the powder. The roller then evenly spreads a second layer of powder on top of the first layer in the build box, and the print head prints the second cross-sectional layer of ink. This process repeats until all layers have been printed and the part is complete.

The 3D printing process greatly surpasses conventional powder processing. Unlike traditional methods of powder processing, 3D Printing has no tooling or geometric limitations. 3D Printing also provides the potential for the direct manufacture of structural components with unique microstructures and capabilities, due to its great flexibility in handling a wide range of materials and its unprecedented ability to locally tailor the material composition. 3D printing can greatly enhance product quality by improving the link between design and manufacturing, going directly from CAD to finished part without any unnecessary intermediate steps. This process also lowers product cost by reducing development and tooling costs. Overall, 3D printing can generate final products and engineering solutions faster and cheaper than any other traditional methods, thereby revolutionizing manufacturing through rapid prototyping.

Viridis3D LLC is currently utilizing 3D printing technology to revolutionize the metal casting process by greatly reducing the time to go from CAD design to finished metal part. Viridis3D can produce molds and cores directly from CAD to pour in hours; their fastest CAD to pour time is 7 hours[10]. This process is ideal for making design stage prototypes, low volume production parts, and replacements for the legacy part market. Viridis3D has three sand based powders that they use in order to produce their molds and cores. These sand based powders can be used with ferrous and non-ferrous metals, and pours reaching 2,642 °F (1,450 °C). Pours at these temperatures are capable with no outgassing after proper oven drying of the mold and core. Viridis3D has used their groundbreaking process to successfully cast pieces to be used in pump

3 Methodology

Five chemical compounds were chosen as potential candidates for the visual humidity indicator. These five indicators went through three experimental phases: preliminary experimentation, in-depth 3D printing experimentation and internal laboratory testing. Preliminary experimentation of the initial five chemical compounds eliminated the practicality and functionality of three of the compounds, yielding two compounds for further experimental analysis. After preliminary testing, these two compounds moved to a more in-depth experimental procedure: application within the 3D printing technology. Finally, internal laboratory testing consisted of humidity testing within controlled environments. This section details the experimental procedures and considerations made during the three phases of this research project.

3.1 Phase I: Preliminary Experimentation

After the appropriate literature reviews, five different chemical compounds were selected as the candidates to be incorporated into the 3D printing technology as a visual humidity indicator. These five compounds are: blue-indicating silica gel, orange-indicating silica gel, phenolphthalein, thymolphthalein, and leucomalachite green. These silica gels and pH indicators were chosen based on their previous successes within the humidity color indicating field.

3.1.1 Potential Humidity Indicator Candidate Selection

The blue-indicating and orange-indicating silica gels were chosen as potential candidates because of their past uses as desiccants. When moisture was absorbed into the silica gel beads, there was a reduction or change in the color of the beads. The blue-indicating silica gel changed color from blue to pink as a result of the cobalt chloride hydration. The orange-indicating silica gel changed color from orange to clear, but does not involve cobalt chloride as it was discovered as a less harmful compound due to the carcinogenic effects of cobalt chloride.

Phenolphthalein, thymolphthalein, and leucomalachite green are pH indicators that will change color with pH changes. As shown in Table 3-1, phenolphthalein and thymolphthalein have similar indicating pH ranges from 8.0 to 10.6. Leucomalachite green is not shown in in the table, but its indicating pH range is 0.2 and 1.8.

Table 3-1. Table of Common Acid-Base Indicators

Indicator	pH Range	Acid	Base
Thymol blue	8.0-9.6	yellow	blue
Phenolphthalein	8.0-10.0	colorless	red
α-Naphtholbenzein	9.0-11.0	yellow	blue
Thymolphthalein	9.4-10.6	colorless	blue
Nile blue	10.1-11.1	blue	red

3.1.2 Preliminary Experimentation: Solubility, Color Change and Absorption

In this first phase, the silica gels and pH indicators were evaluated based on its solubility and interactions with two widely used solvents: methanol and water. Tiles made of the processing powder and ink were exposed to these solutions to determine its practicality.

To begin this preliminary experimentation, five independent solutions were made. Since the silica gels were not in powder form, five grams of each the blue indicating and orange indicating silica gels were placed into two separate mortars. These gels were then crushed into a fine powder with a pestle. The five indicators are now in powder form. One gram of each indicator was measured and placed into plastic weigh boats; this was repeated for each solvent, resulting in a total of 10 weigh boats: two weigh boats of each indicator for each solvent. Ten milliliters of methanol was added with a disposable Pasteur pipette to five of these weigh boats, one with each indicator. This was repeated with water. Visual observations were recorded before and after the addition of the solvent. These solutions were then poured over test tiles and observations were then recorded. Exposed test tiles were then baked in a preheated oven at 250°C for 15 minutes. Observations were then made of the baked tiles and compared to previous observations. Based on these observations, the most promising chemical compounds continued to Phase II: incorporation into the 3D printing technology.

3.2 Phase II: Incorporation 3D Printing Technology

There are two components in which the indicators were incorporated into the 3D printing technology: the ink and the powder. Experimental procedures began with the ink due to its economic benefits, but problems arose and procedures then moved to incorporation in the powder.

3.2.1 Incorporation into 3D Printing Ink

Our first attempt to produce a visual humidity indicator for 3D printed molds for metal casting was to incorporate two pH indicators into the printing ink. The two indicators chosen were phenolphthalein and thymolphthalein. These indicators were chosen because they both have color change within a similar pH range (phenolphthalein: 8.0 – 10.0. thymolphthalein: 9.4 – 10.6)[11] that would react with the acidic ink and then theoretically lose color after moisture absorption due to a change in pH.

We attempted mixing each indicator with various concentrations within the ink. In some cases, the concentration was too high and caused the ink to become too viscous to purge[a].

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[a] Purging is the physical discharging of ink from the printing ink head.

Regardless of the concentration, the general procedure for printing test tiles was constant and as follows:

1. Measure desired mass of indicator and ink in order to achieve desired concentration.
2. Add pH indicator to ink in storage tank.
3. Shake solution to dissolve indicator powder.
4. Attach storage tank to the Suckotron[b] to purify and fill ink head with solution.
5. Clean ink lines in printer using an empty syringe
6. Attach filled ink head to printing machine.
7. Fill ink reservoir with solution from storage tank.
8. Run the “purge” command from the computer/printer. This command tests to see if the ink head will discharge ink. Temperature readings from the computer are used as a measurement for ease of discharge (a high temperature is a result from high levels of friction from a more viscous solution).
9. Run “level powder” command from the computer/printer. This command simply levels the amount of powder equally between the feed and print tanks.
10. With the correct Solid Works model loaded – print.
11. After the tiles are printed use hands or shovel to dig tiles out of powder.
12. Bring tiles to the cleaning station and with compressed air remove all loose powder.

This procedure was followed with all various concentrations that are described in this methods.

3.2.2 Incorporating pH indicators into 3D printing powder

An alternative way to incorporate the pH indicators into the 3D printing core was to integrate the indicator powder into the cement powder. Because of the experimentally limited supply of thymolphthalein and greater supply of phenolphthalein only one batch was printed using phenolphthalein. The process for incorporating the pH indicator into the printing powder is as follows:

---

[b] A prototyped instrument used to purge ink head of standard black ink and fill with 3D printing ink.

1. Measure desired mass of pH indicator and powder to achieve the desired percent by mass.
2. Mix both powders into a specially designed paint can. The paint can used to mix the powder has multiple triangular blades that run along the inside of the can to break up clusters of powder.
3. Secure paint can into paint mixing machine.
4. Run paint mixing machine for 20 minutes.
5. Remove paint can from mixing machine and place powder evenly into the empty feed and print tanks on the printer.
6. Run the "leveling" command on the computer/printer distributing powder where necessary until an even field is achieved.
7. Attach ink head (filled with generic printing solution) to printer
8. Run "purge" command.
9. With desired Solid Works model loaded engage the print function.
10. After the tiles are printed use hands or shovel to dig tiles out of powder.
11. Bring tiles to the cleaning station and with compressed air remove all loose powder.

This process was followed with the following percent indicator by mass.

3.3 Phase III: Humidity Testing

After the aforementioned experimentation within the 3D printing technology, the resulting products were tiles containing phenolphthalein and thymolphthalein. These tiles were of various concentrations and the indicator was incorporated within different components of the 3D printed products. The table below indicates the concentrations of the tiles used for testing.

Table 3-2. Testing Tile Concentrations

Indicator	Location of Indicator	Concentration	Quantity
Thymolphthalein	ink	0.05%	12
Thymolphthalein	ink	0.25%	12
Phenolphthalein	ink	0.05%	12
Phenolphthalein	ink	0.2%	12
Phenolphthalein	powder	0.25%	12

3.3.1 Initial Humidity Testing

These test tiles were baked at 200°C in a conventional oven for 30 minutes after curing for three days in a laboratory environment. Their initial and final weights were measured before and after baking. At this point, the tiles should be at their lowest moisture content, at zero percent moisture. Humidity test environments were set-up using 3” x 6” plastic Ziploc bags, one for each tile (see Figure 3-1 below). These bags were each filled with 100 mL of tap water. Test tiles were then suspended inside the bags sitting in plastic weigh dishes on top of the water. Careful precaution was made so that water did not accidentally come in contact with the test tile at all points of this experiment.

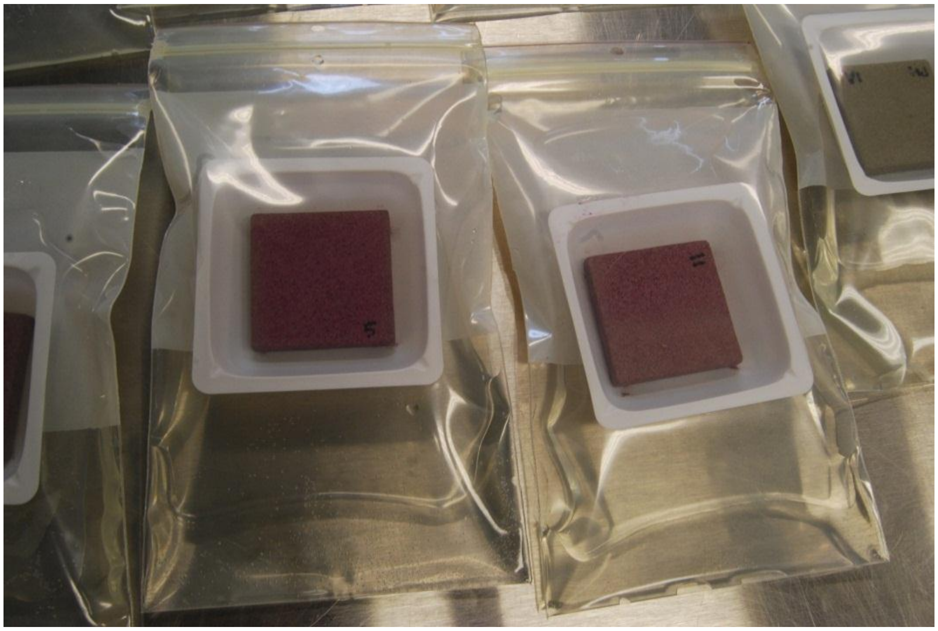

Figure 3-1. Humidity Test Environments

These humidity environments were left out on a laboratory space for two weeks. For the duration of the first week, the tiles were removed from the humidity environments and their weights were measured each day. Color of the tiles was also noted visually. After measurements and observations, the tiles were returned to their humidity environments. At the culmination of the two weeks, the tiles were weighed one final time before baking. After 15 minutes in a conventional oven at 200°C, color change [or lack of color change] was noted. Color change will demonstrate the reversibility of the indicator to indicate humidity after multiple drying cycles. Per many experimental procedures, visual observations were noted at all points of the experiment.

3.3.2 In-Depth Humidity Testing

The initial humidity testing revealed the practicality of the indicator applications within 3D printing. After discovering the effectiveness of each indicator as a visual humidity indicator, further testing was completed to determine if a lower concentration of the indicator would be just as effective as a higher concentration of the phenolphthalein. As such, another set-up similar to the initial humidity testing was prepared.

For this particular section, a total of 96 tiles were printed for experimentation. Of these tiles 48 tiles were of 0.25% concentration by weight phenolphthalein in the powder and 48 of these tiles were 0.10% concentration by weight. Using a set of 12 tiles from each concentration, humidity testing was completed comparing two concentrations. Experimental procedures followed those within the initial humidity testing. However, the only difference is that the tiles cured for a week before baking and testing.

3.4 Data Analysis and Evaluation

After initial experimentation, incorporation into 3D printed tiles and the lab testing of those tiles, data and observations were analyzed using a variety of methods. The color change demonstrated in daily photographs will support results. Initial, intermediate, and final weights were also taken in order to track the water absorption within the tiles.   A compound analysis using both sets of collected data shows that the formula holds great industrial applications.

4 Results

After the completion of Phases I through III, various results in the form of photograph documentation, weight measurements, and other means of characterization were obtained. This section details the resulting entities from these three phases.

4.1 Specimen Characterization

Because it is difficult and impractical to test a potential compound on large scale parts, tiles were used instead to model the reaction the phenolphthalein had on 3D printed parts.

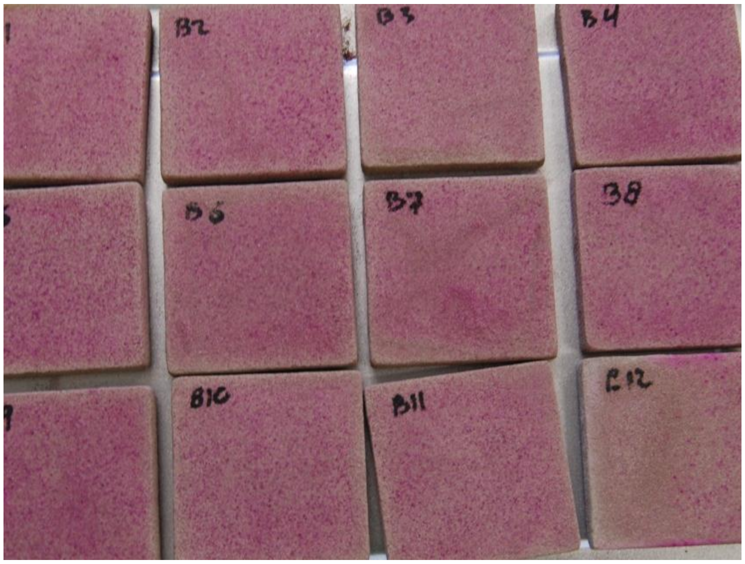

Figure 4-1. 3D Printed Test Tiles

The table below provides the all necessary properties of the tiles used throughout our experiments. Moisture absorption was determined by completely drying out a tile and then saturating the tile with water. Measurements were taken of the dry tile and the water saturated tile. Calculations can be seen in Appendix A. Porosity was determined with additional calculations, which can also be seen in Appendix A. The minimum bake time at 200°C was determined simply by baking a tile and periodically checking the weight of that tile. Once the weight of the tile stabilized, the minimum time yielding this stabilization was recorded.

Table 4-1. 3D Printed Tile Characterization

Dimensions	1.9375 in × 1.9375 in × .3125 in
Volume	1.173 in^3
Maximum Moisture Absorption	35% of its dry weight
Porosity	0.452
Minimum bake time at 200C	20 minutes

4.2 Phase I: Preliminary Results

The first experiment ran was to test a variety of pH indicators and desiccants in order to narrow down and identify the best potential moisture indicators. A successful moisture indicator needed to abide by the following five requirements:

1. Visually unique with humidity absorption
2. Reversible color change with addition and removal of moisture
3. Physically compatible with 3D printing technology
4. Relatively cheap to implement
5. Safe for direct human contact

In total two desiccants (blue indicating silica gel and orange indicating silica gel) and three pH indicators (thymolphthalein, leucomalachite green, and phenolphthalein) were tested. Figure 4-2 shows three of these indicators in powder form.

Figure 4-2. Photograph of Preliminary Testing Phase I

Results from these preliminary tests in observational and photograph form are displayed the following sections.

4.2.1 Desiccants: Silica Gels

Table 4-2 summarizes observations taken during the preliminary testing of the silica gels. In reference to the steps in this table, the steps are as follows:

Step 1- Place the whole desiccant pellets in water and observe reaction.

Step 2- Ground the pellets into a fine powder and add to methanol in order to form a solution; record observations.

Step 3- Apply solution to individual tile; record observations.

Step 4- Dry tiles in industrial oven at 250◦C for 20 minutes and record observations.

Step 5- Apply water to dry tiles; record observations.

Step 6- Let tiles sit in ambient air overnight; record observations the following day.

Table 4-2. Silica Gel Phase 1 Summary

DESICANTS	OBSERVATIONS: *Step 1*	*Step 2*	*Step 3*	*Step 4*	*Step 5*	*Step 6*
Orange Indicating Silica Gel ***$5.94 per 100 grams***	Pellets turned clear from their original orange color. The pellets also began to crack into smaller pieces.	Methanol did not dissolve the powder; orange particles could still be seen in the solution.	Solution showed no color on tile; solid un-dissolved particles in the solution were clear on top of the tile.	Area where the solution was applied is now white, while the solid particles remained clear.	White area on tile is now clear again.	White area on tile reappeared , and there was also a stained area around the white powder.
Blue Indicating Silica Gel ***$6.82 per 100 grams***	Pellets initially emit a pinkish color and turn clear, when reaction is over the pellets are a light pink color.	Some powder turns pink, but most remain blue, not soluble in methanol	Solution on tile is clear, and the un-dissolved particles have a clear pink	The un-dissolved particles regained solid blue color, no solution reaction.	The un-dissolved particles immediately turned clear with a	The un-dissolved particles are white with a pink tint, stained area on the

		tint.	pink tint.	tile around the particles.

4.2.2 pH Indicators

During preliminary testing, Table 4-3 summarizes the visual observations taken during this phase. The steps referenced in the table are as follows:

Step 1- Add PH Indicator to methanol / water, to form solution; record observations.

Step 2- Apply solution to individual tiles; record observations.

Step 3- Dry in an industrial oven at 250◦C for 20 minutes; record observations.

Step 4- Add water to dry tiles; record observations.

Step 5- Leave tiles to sit overnight; and record observations the following day.

Table 4-3. pH Indicators Phase 1 Summary

pH INDICATORS	**OBSERVATIONS: *Step 1***	***Step 2***	***Step 3***	***Step 4***	***Step 5***
Thymolphthalein ***$273.00 per 100 grams***	No noticeable changes, powder does not fully dissolve.	White area on the tile with blue/ purple dots slowly forming.	White powder visible with specs of blue.	Dark blue ring forms around some still visible white powder.	Most of the area is white with a dark blue stained perimeter.
Leucomalachite Green ***$400.00 per 100 grams***	Not dissolving at all in water, the powder turned pasty white.	Un-dissolved white powder on top of tile.	White powder remains same color.	No color change.	No color change.
Phenolphthalein ***$26.90 per 100 grams***	Fully dissolved, water turned a milky white color.	Spot on the tile turned a bright purple/pink.	Amorphous color change from bright pink to dark purple.	Instantly turns clear, and then as the water soaks in dark purple returns.	White with streaks of pink and pink stains around the perimeter.

4.2.3 Phase I Summary

Through these preliminary tests we were able to identify two pH indicators that fit the criteria for a potential moisture indicator: phenolphthalein and thymolphthalein. From visual observations, these two indicators showed promising results due to their reaction with the tiles (Figure 4-3).

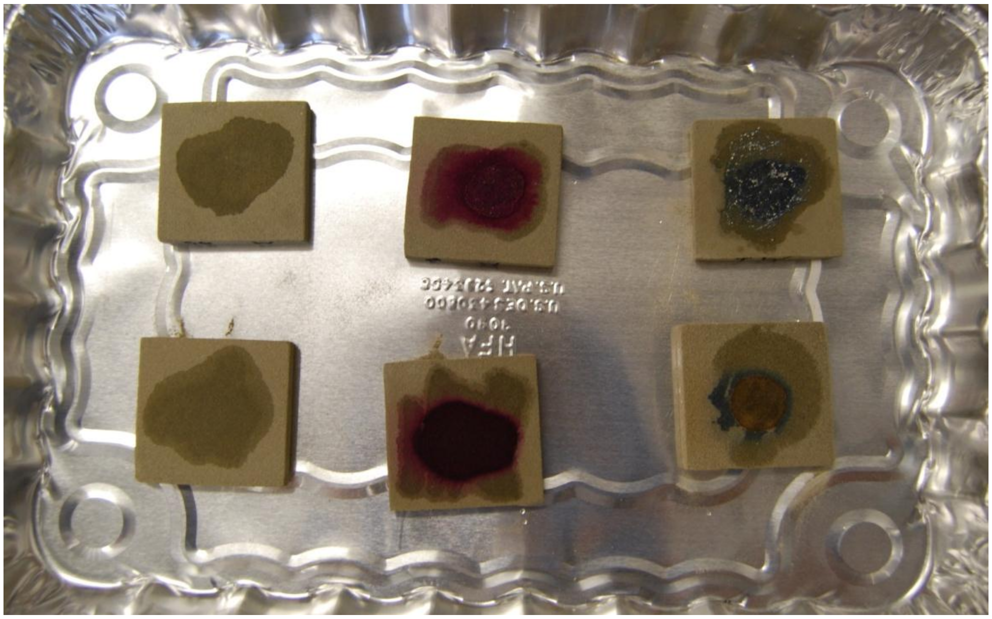

Figure 4-3. Tile Interactions with Blue Silica Gel powder (left), Phenolphthalein (center) and Thymolphthalein (right) after application of water

Both of these indicators were safe for direct human contact, visibly unique with moisture absorption, and both had a color change with the addition of moisture. When comparing the cost of both indicators, it was clear that thymolphthalein was more than 10 times the cost of phenolphthalein. Although both these indicators moved on to Phase II, this cost was considered during the next phase.

4.3 Phase II: Incorporation into 3D Printing Technology

Phase II consisted of the indicator incorporation into the 3D printing technology. There were two main methods in which this occurred, through the ink and through the powder. This results section details the observations and resulting decisions.

4.3.1 Incorporation into the 3D Printing Ink

The first method of approach was incorporation through the ink. Since it was the most economical solution, this seemed to be a good starting point. This section describes the various results of experimental procedures of both the phenolphthalein and thymolphthalein.

4.3.1.1 0.25 weight% Phenolphthalein (2 g indicator + 800 g ink)

This was a reasonably high concentration to attempt to incorporate into the ink solution. After mixing the solution, un-dissolved indicator was visible and after filling the ink reservoir settlement could be seen in the storage tank meaning that the solution was oversaturated. Oversaturation of the solution would not allow the printer head to print the ink properly without being clogged by the solid indicator particles. The next procedure was to reduce the concentration and begin again.

4.3.1.2 0.05 weight% Phenolphthalein (0.36 g indicator + 730 g ink)

The concentration was reduced significantly to see if any concentration of the phenolphthalein could be printed through the ink. This solution mixed well and the solution was moderately clear. After purging the ink head of its current solution and filling it with the 0.05% concentration, the "purge" command was run on the printer ("Hugo"). The ink head would not discharge successfully so the ink head was repurged. After purifying the ink head two times, the "purge" command was run again. The ink discharged successfully at an average temperature of 80℃. This temperature was higher than the ideal printing temperature but still functional (printer head purging temperatures nearing 90˚C is too high to operate). Since the ink discharged, a full set of tiles were printed at a concentration of 0.05 weight% phenolphthalein.

4.3.1.3 0.20 weight% Phenolphthalein (1.85 g indicator + 931 g ink)

After mixing this solution of an increased amount of phenolphthalein, it was apparent that the solution was nearing a saturation point. The solution was cloudy, but no settlement was visible so the procedure was continued using the "Hugo" printer. The ink head was able to complete the "purge" command however when it began printing tiles it was obvious that the concentration was too high because the ink printed in streaks. The process was stopped and rubbing alcohol was added to the solution in an attempt to lower the viscosity. The print was resumed however quality was still poor. The print was stopped short of completion and the result was only seven tiles at 0.2 weight% phenolphthalein.

4.3.1.4 0.05 weight% Thymolphthalein (0.2 g indicator + 400 g ink)

After experimenting with phenolphthalein, ink solutions were mixed with another indicator, thymolphthalein. This solution of 0.05 weight% was relatively clear after mixing; purification of the ink head using the prototype instrument was completed without problems. This concentration of ink was applied to a second printer "Glenn." The rest of the procedure was completed without resistance. The printing temperature was relatively high at an average of 80℃ but still not overheating. The print was cut short due to time restrictions. The result of this print was 12 tiles at 0.05% thymolphthalein.

4.3.1.5 0.25 weight% Thymolphthalein (2.0 g indicator + 820 g ink)

This solution had a concentration five times greater than the previous so it was expected to be oversaturated however the solution was reasonably clear so the experimental procedure was continued. The printer "Glenn" failed the first "purge" command but after cleaning the ink lines again the ink head was able to discharge. The printing process was of good quality until the start of the third set when the print started getting streaky. The print was stopped and the result was 12 tiles at 0.25% thymolphthalein concentration.

4.3.1.6 Ink Incorporation Summary

Contrary to our hypothesis, the acidic ink did not react or show color change when either pH indicator was introduced to the solution. When the mixed solution made contact with the print powder there was also no visible color change. In addition, there were problems with the print head when the indicators were introduced to the ink. The applications for these solutions looked bleak.

4.3.2 Incorporation into the Powder

From experimentation with the ink, the next logical effort was incorporation into the powder. The solubility issues that caused problems with the ink would not exist if the indicator were to be incorporated into the powder.

4.3.2.1 0.25% Phenolphthalein by weight (5 g indicator + 2 kg printing powder)

After the indicator was incorporated into the powder in this print the printer was able to print smoothly through the “purge” command and the entirety of the print process. As the printing process began the pH indicator present in the powder instantly reacted with the acidic ink producing a dark purple/pink color. Due to time restrictions the print was cut short and the result was 12 tiles at 0.25% phenolphthalein by weight. These tiles seemed most promising as they were colored at their most moist state, right after they were printed.

4.4 Phase III: Humidity Testing

This section details the visual observations and moisture absorption of the test specimens in both parts of the humidity testing: initial humidity testing and a concentration comparison.

4.4.1 Initial Humidity Testing

Following the trial and error procedures during phases I and II, phase III followed more structured methods. This yielded the following results for the initial humidity testing of a set of 12 tiles with a 0.25 weight% phenolphthalein.

4.4.1.1 Color Change

First and foremost, there was a significant relationship between tile color and moisture absorption. It was noted that after baking the tiles at the start of the procedure, the tiles changed from a dull gray pink color to a bright pink color, as shown in Figure 4-4.

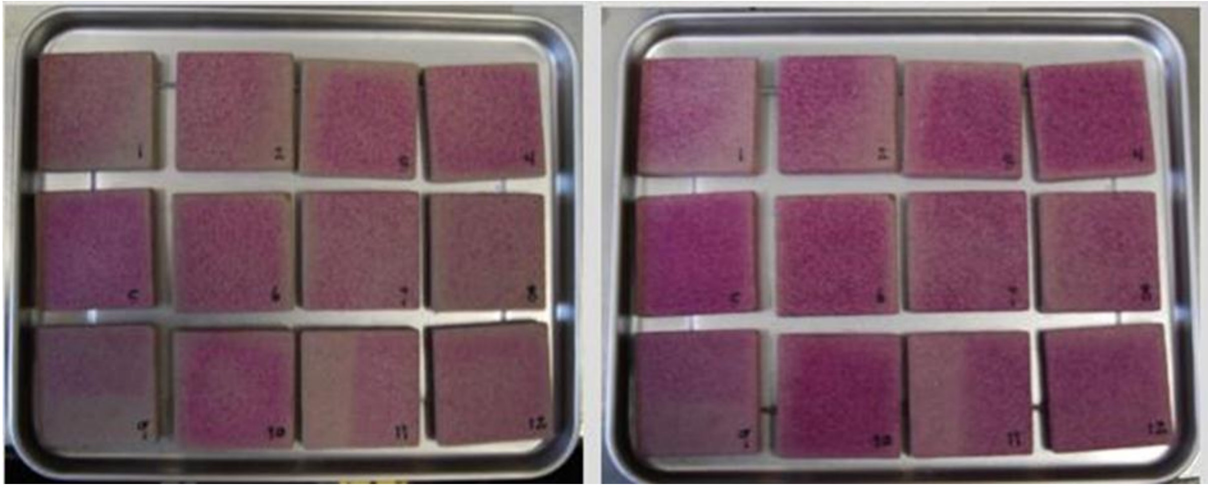

Figure 4-4. Pre-baked tiles (left) and post-baked tiles (right)

Pre-baked tiles are at their highest peak in moisture. This can be explained by the liquid ink that is used to print these tiles. After being baked in a toaster oven at 200°C, the color changed drastically to a bright pink color. It is also important to note the apparent heterogeneous state of the tiles. There are areas of concentrated coloring. This was explained by the stacking of the tiles during curing (after printing but before baking). The areas that are more concentrated are where the tiles overlapped.

After a week in the humidity environments, the tiles lost their intense pink color and became grayer in color. The color change after a week of being in a humid environment can be seen in Figure 4-5 below. The photograph on the left (Day 1) shows the tiles after the first bake before the initial mass recording and center photograph is of the tiles after being exposed to the humidity environments for a week.

Figure 4-5. Tiles of 0.25 weight% phenolphthalein on day one (left) and after one week (right)

As shown, the tiles lost their intense pink color and in some cases the tiles lost their color entirely. For example, the two pinkest tiles before exposure to moisture are tiles 5 and 12. After one week and after absorbing moisture, the tiles have turned an almost complete gray in color. Overall, the images show a change in color of the tiles, drastic enough to be incorporated into a mold and used to determine if it has absorbed large amount moisture.

Reversibility was demonstrated in this experiment by then baking the tiles on Day 7. The result is shown in the photograph labeled Day 7 after Bake. As predicted, the color returned to its original bright pink color after being baked dry. Notice that the same gray and pink pattern that the tiles exhibited on Day 1 is then regained after baking on Day 7.

4.4.1.2 Moisture Absorption

In addition to the daily photographs, the weights of each were also taken. The following graph was generated using the mass recordings collected over the period of the experiment. Figure 4-6 below shows the steady increase in mass each tile experience while being in the humidity environments. The left axis represents the mass (in grams) of each tile and the x axis denotes the day each mass measurement was taken. From this graph, it is clear that the tiles gained moisture throughout the week. The slopes of the lines in the graph show that there is a significant increase in weight between the first two days. At an average weight gain of 0.405 grams, the increase between the second and third day almost halves to 0.226 grams on average. As the week progresses, the average amount that the tile absorbs decreases slightly each day, ranging between 0.178 grams to 0.135 grams. This can be explained simply because as the tile absorbs moisture each day, the difference in concentrations of water decreases, decreasing the flux of water.

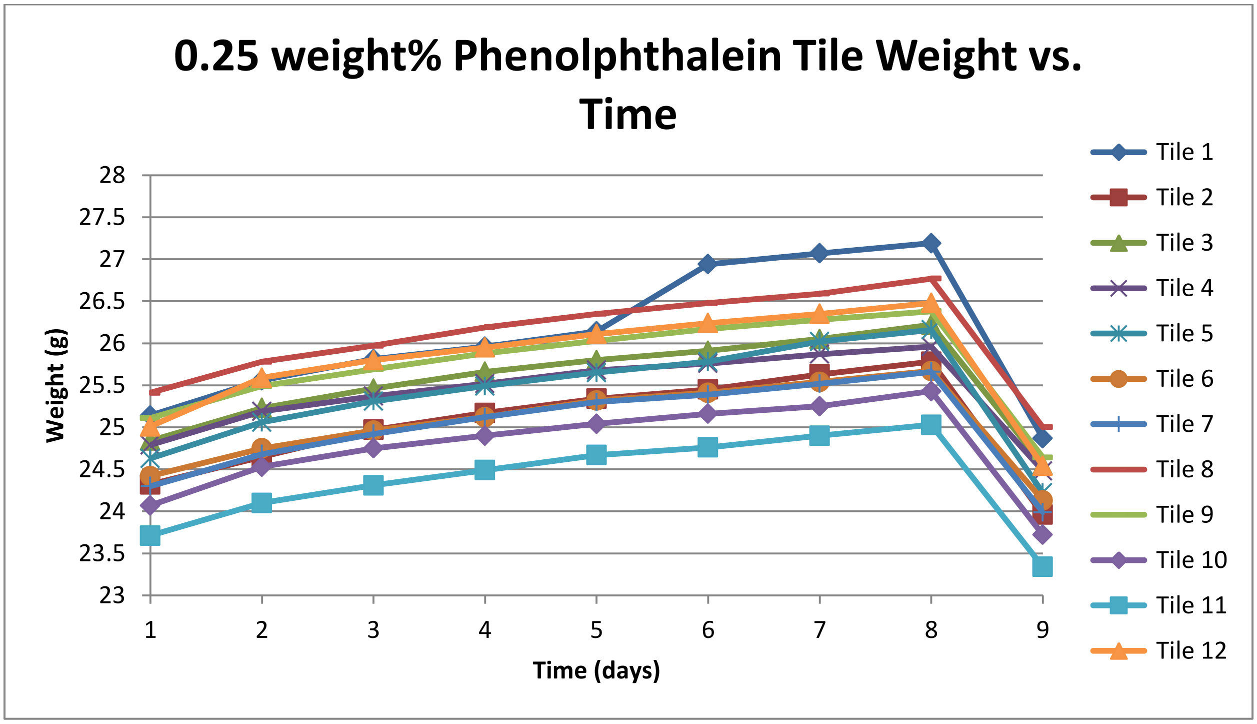

Figure 4-6. Moisture Absorption of 0.25 weight% Phenolphthalein Tiles Exposed to Moisture Environments

The graph also shows some anomalies. The data points for Tile 1 seem to be inconsistent with the other data points at Day 6. There is a large increase in weight gain of the tile from 26.14 grams to 26.94 grams, yielding an increase of 0.80 grams. This is much higher than the average for that day at 0.168 grams. By observations, this can be explained simply by experimental error; water was accidentally spilled onto the tile during one of the daily weight measurements. The final data point in this graph indicates the weight at the conclusion of the experiment after the tiles were baked dry. Because their weights at this point were not equal to the initial weights taken on day 1, it is safe to assume that the tiles were not completely dry at the beginning of this experiment, potentially affecting the results in this section,

Figure 4-7 below displays the same data in percent mass increase between days over the duration of the experiment. As described in an earlier section, the tiles initially gain almost 2% in weight between the first two days. However, as the time continues, the weight gain is almost steady at 0.80%. The same anomaly seen in Figure 4-6 is seen in Figure 4-7, with the large spike in Tile 1 between days 5 and 6 due to the addition of water to the tile by experimental error.

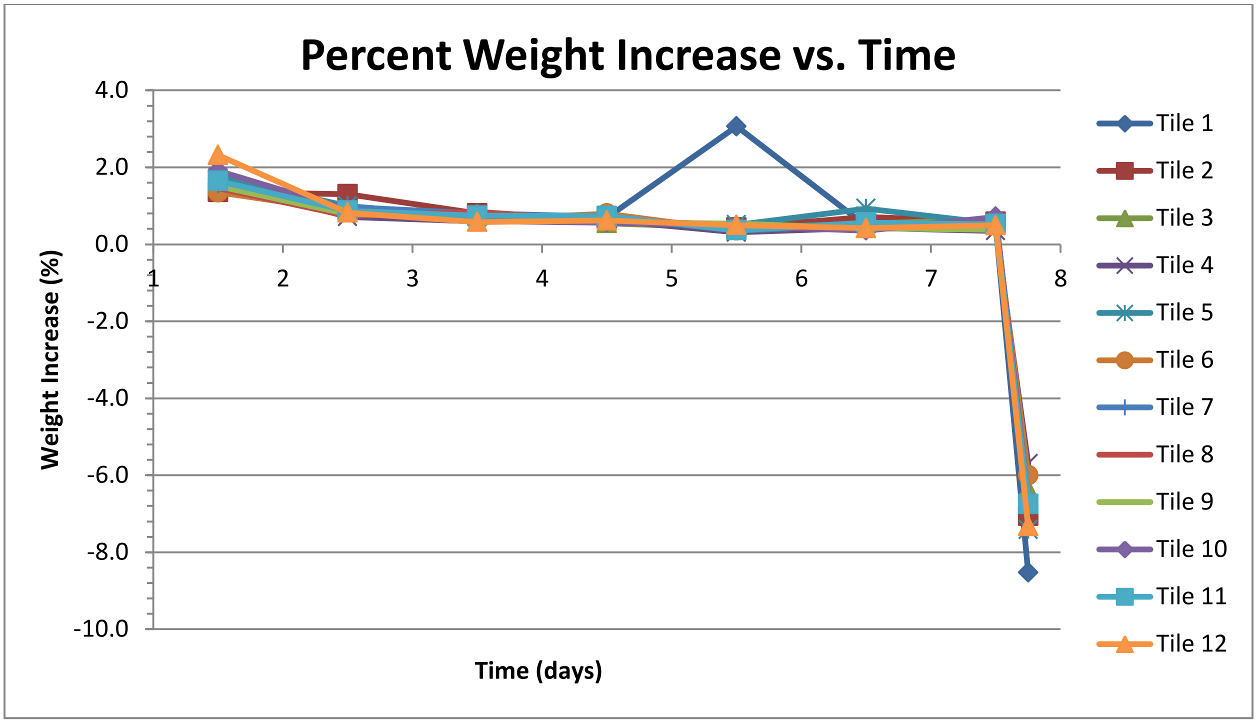

Figure 4-7. Percent Weight Increase over One Week

The large decrease in weight following the recording between days 7 and 8 is accounted for by the bake. After baking, the tiles lost an average of 6.8% mass from the last day of measurements. The interactions between the water molecules and the tile are characterized by the diffusion model in Section 4.5.

4.4.2 In-Depth Humidity Testing – Concentration Comparison

Initial testing of the 0.25 weight% phenolphthalein incorporated into the powder demonstrated the practicality of its use as a visual humidity indicator. To further investigate its potential in the 3D printing industry, a lower concentration of phenolphthalein was compared to the original 0.25 weight%. A lower concentration could result in lower implementation costs for the industry. After completing methods similar to the initial humidity testing, the results are detailed in this section.

4.4.2.1 Color Change

As expected, color change was observed in both concentrations after exposure to 99% relative humidity for the duration of one week. However, contrary to initial hypothesis, the tiles of lower concentration (0.10%) showed a more drastic color change over the duration of the experiment than the 0.25% concentration.

Between the two concentrations, the color changes after the initial bake were of the same pink shade. Just as in the initial humidity testing, the pinkness of the tile increased significantly from a dull gray pink to a bright pink shade after baking in a 200°C oven. These tiles are shown in Figure 4-8 in the first column labeled Day 1.

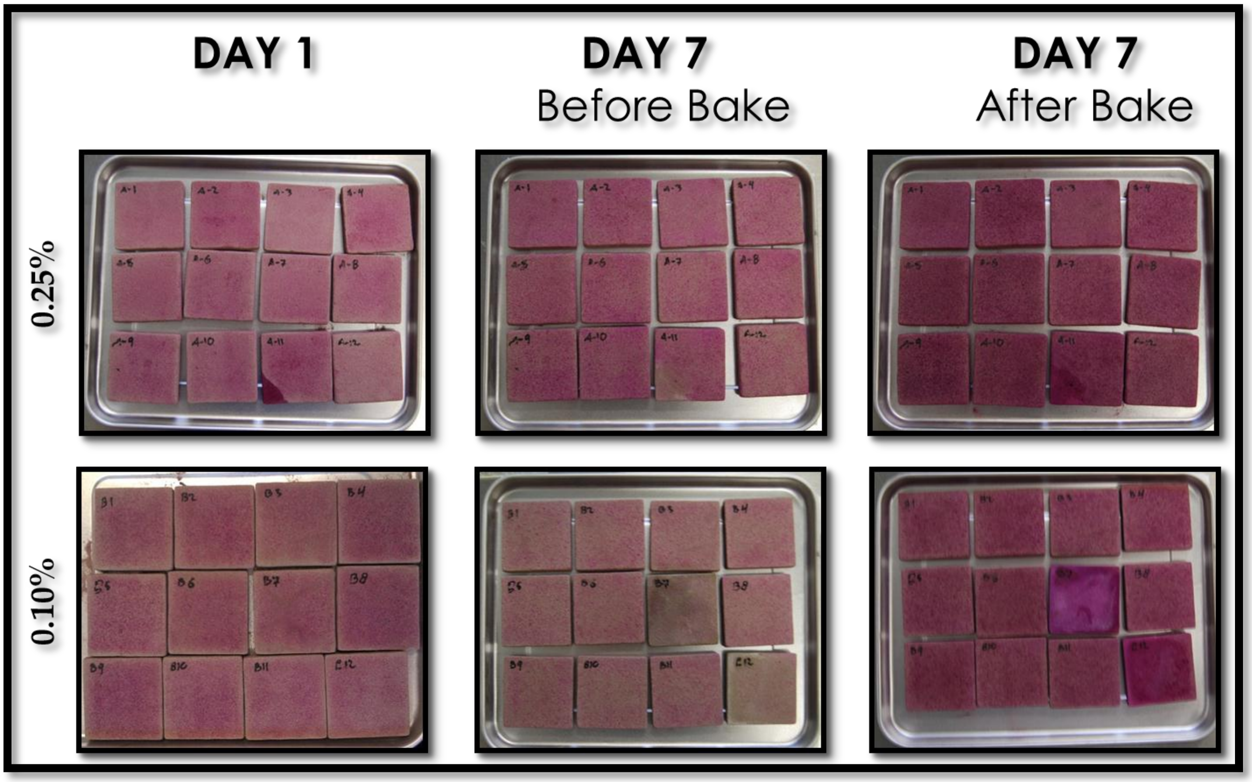

Figure 4-8. Photograph of Tiles for In-Depth Humidity Testing

The tiles then changed to a more dull pink color after exposure to the moisture environments. This same change was observed with the initial humidity testing with the 0.25

weight% phenolphthalein. When comparing the two concentrations, the 0.10 weight% phenolphthalein demonstrated a higher change in color between Day 1 and Day 7, indicating that a lower concentration is more beneficial to the industry in two ways: effectiveness and finances. The 0.10 weight% phenolphthalein became grayer and is cheaper to implement into the 3D printing process because less phenolphthalein is required per unit of powder.

However, it is important to note that the color change between Day 1 and Day 7 before the bake was much less in this run than in the initial humidity testing for the same 0.25 weight% phenolphthalein. This could be explained by the number of days the tiles were allowed to cure before they were baked. Typically, after a piece is printed from the 3D printing machine, the piece is left to cure for a few days before it is baked dry and then cast into a final metal piece. It was clear that the cure time for these molds affected the color change because the tiles for this concentration comparison were cured for a full week compared to the two days in the initial humidity testing. The difference in days of curing affected the amount of color change observed between the first day of the week and the last day of the week.

The last part of experimental procedure was to determine its reversibility. As already seen in the initial humidity testing, it was expected that these tiles also demonstrated a reversibility property. Photographs before and after the bake on day 7 of each concentration can be seen in Figure 4-7. The top row shows the 0.25 weight% tiles after a week in humidity environments and then after the moisture is baked out; the bottom row shows the same but with the 0.10 weight% tiles. Distinct color changes can be seen in both cases however the color change appears more dramatic with the 0.1 weight% tiles. From this result, the lower concentration of phenolphthalein by weight clearly produces a wider range of color change in tiles, which would be more beneficial in visually determining the amount of moisture a tile has absorbed at a given time.

4.4.2.2 Moisture Absorption

Similar to the initial humidity testing, moisture absorption for these tiles of two concentrations showed the same trend. Over the course of a week, the weights of the tiles were recorded and their averages on each day are shown in Figure 4-9 below. This graph demonstrates the same trends as shown in the Initial Humidity Testing, with an initial weight increase per day then leveling off to a steady weight increase during days 3 through 8. Finally, the tile loses all the moisture it gained over the course of a week after the tile is baked out (noted as day 9 on the graph).

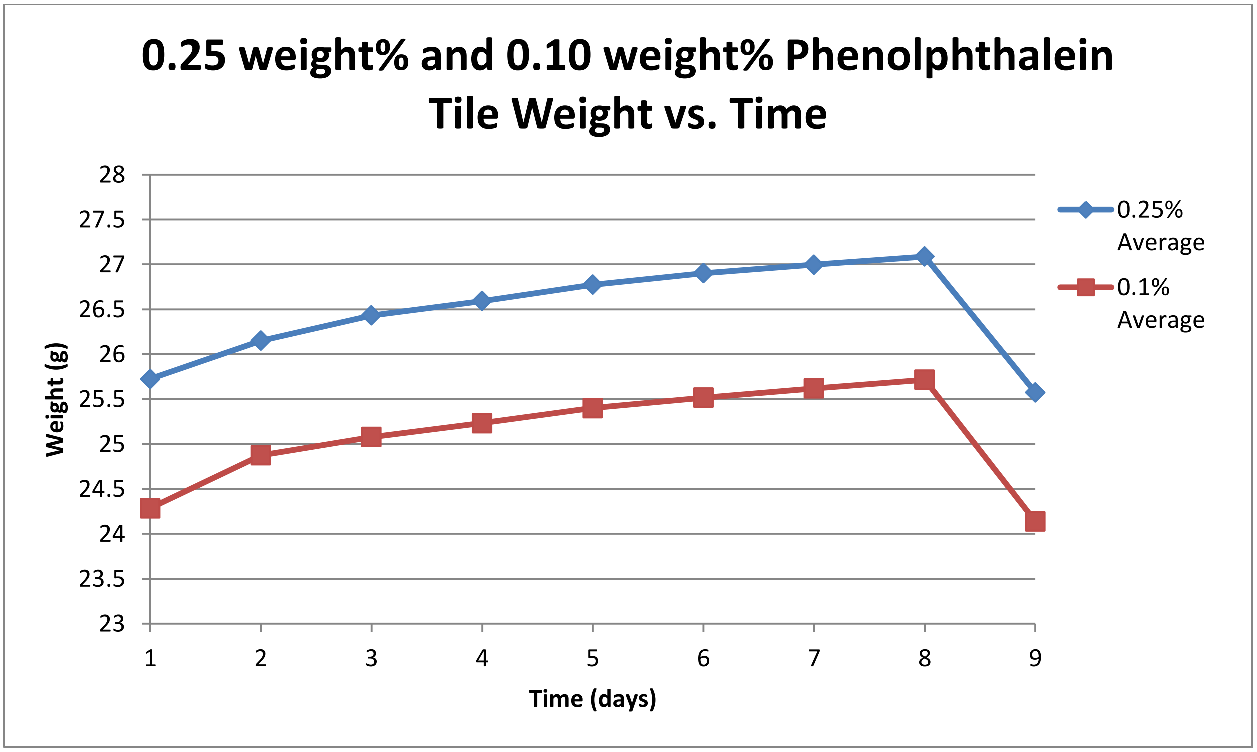

Figure 4-9.Moisture Absorption of 0.25 and 0.10 weight% Phenolphthalein Tiles Exposed to Moisture Environments

From this graph, it is evident that there is no difference in moisture absorption between the two concentrations, meaning that there is no relationship between concentration and moisture absorption.

4.5 Chemical Mechanism

After discovering the validity of using phenolphthalein as a color moisture indicator, it is important to consider the mechanism by which this occurs. It is known that phenolphthalein changes from its white powder form to a bright pink color when exposed to liquid water, but this is not the case when the phenolphthalein interacts with the ceramic powder and is exposed to water vapor in gaseous form. This section details the mechanism by which diffusion occurs, potentially explaining the interaction phenolphthalein has with water vapor.

4.5.1 Diffusion Models

Within the experimental environments, diffusion of water is the main factor contributing to color change within the test tiles. With increasing absorption of water vapor from the environment into the test tile, the phenolphthalein loses its pigment, making the tile appear grayer.

This diffusion can be characterized by various models of mass transfer, more specifically – diffusion. The water vapor in these environments moves by way of molecular diffusion, in which the motion is attributed to the random motion of the vapor molecules into the porous tile. Composed of many sand particles, the tile can be considered a porous solid. The water vapor molecules diffuse into the tile through the vacant spaces made by the sand particles, as shown in Figure 4-10 below. The smaller blue spheres represent water vapor molecules while the matrix of larger gray spheres represent the porous tile at a molecular scale.

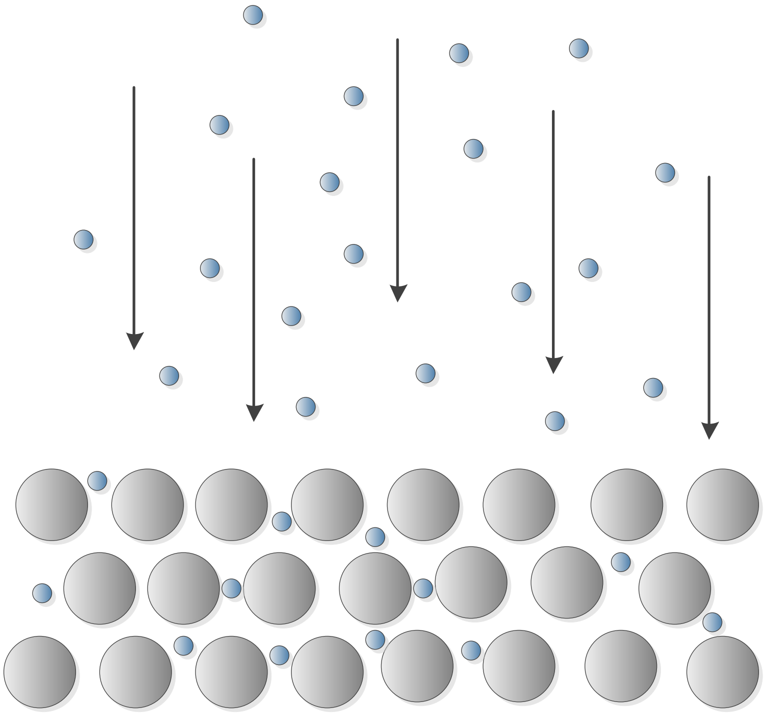

Figure 4-10. Visual Representation of Tile and Moisture

This diffusion can be modeled mathematically with theoretical expressions. The flux (J), or movement of molecules per unit time, is generically defined as:

$$J = -D\frac{\partial c}{\partial x}$$

where D is defined as the diffusion coefficient and $\frac{\partial c}{\partial x}$ is the concentration gradient. In order for diffusion to occur, there must be a sufficient concentration gradient for the molecules to flow through. Since the concentration of water molecules outside the tile is significantly higher than the concentration inside the tile (assuming that the tile is dry at initial measurements), there will be a movement of molecules from higher concentration to lower concentration, explaining the water absorption mechanism. In addition, the diffusion coefficient can be represented by the following expression:

$$D_{KA} = \frac{d'\sqrt{\frac{8RT}{\pi MA}}}{3}$$

where R is the gas constant, T is temperature, M is the mass, A is the area and d’ is the average pore diameter. This expression is only valid when the size of the pore approaches the mean free path of a moving molecule.

4.5.2 Interactions with Phenolphthalein

After understanding the mechanism of diffusion, the color change of the phenolphthalein from bright pink to colorless can be explained. Because the phenolphthalein becomes colorless after exposure to humidity (H_2O), the tile appears more gray, simply because gray is the color of a tile without the dye indicator. To understand the mechanism of color change, it is important to understand the chemistry at a molecular level. Figure 4-11 shows the phenolphthalein molecule when it is dry and pink in color.

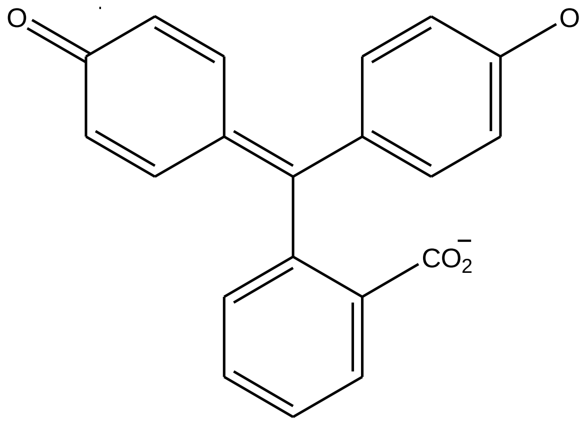

Figure 4-11. Form 1: Phenolphthalein's Chemical Structure in a Dry Tile, Colored Form

After exposure to water molecules, the phenolphthalein can take on one of two forms, both resulting in a colorless state.

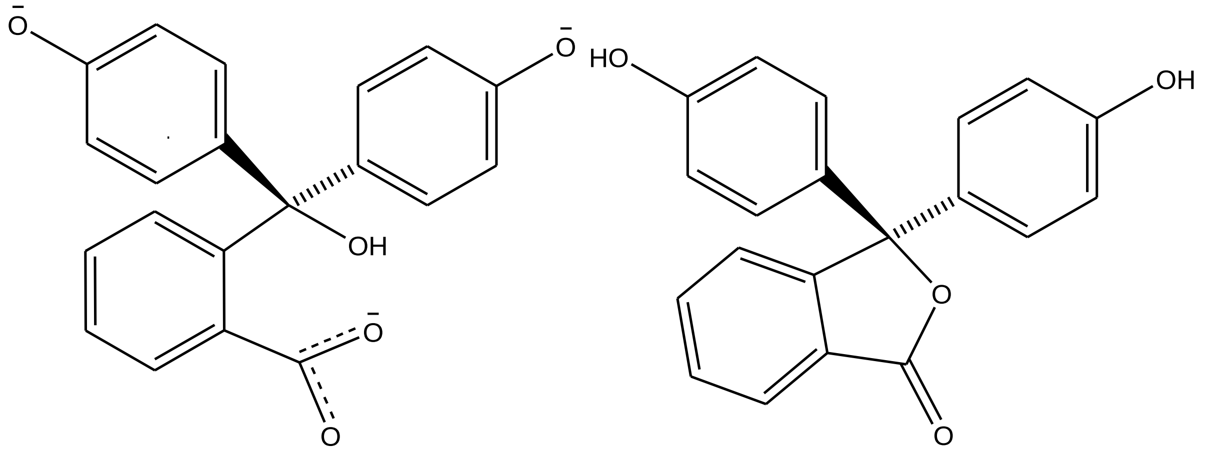

Figure 4-12. Phenolphthalein's Chemical Structure in a Moist Tile, Colorless State: Form 2 (left) and Form 3(right)

These two forms are possible because the water is amphoteric, meaning it can act as both an acid and a base. When the water molecule splits, it splits into a hydroxide ion (OH^-) and a hydron cation (H^+), reacting with Form 1 to yield forms 2 and 3. These two forms yield a color change of pink to colorless, indicating that the tile has absorbed moisture.

4.6 Production Scale-Up

To conclude the project, full size molds were printed using the phenolphthalein formula in order to test the industrial application of the formula. The goal of this demonstration was to first prove that moisture present in a printed mold would indeed negatively affect the quality of the final piece, and secondly prove that the applied formula could accurately indicate the moisture and therefore predict the quality of the final piece.

To perform this demonstration, three molds of identical chemical composition were printed using the same phenolphthalein formula of 0.10% phenolphthalein concentration. The molds were then treated differently to achieve the desired moisture levels. These molds can be seen in Figure 4-13. Mold 1 was baked immediately after printing (general practice in the 3D printed industry) and baked again prior to the metal pour to rid the mold of any moisture.

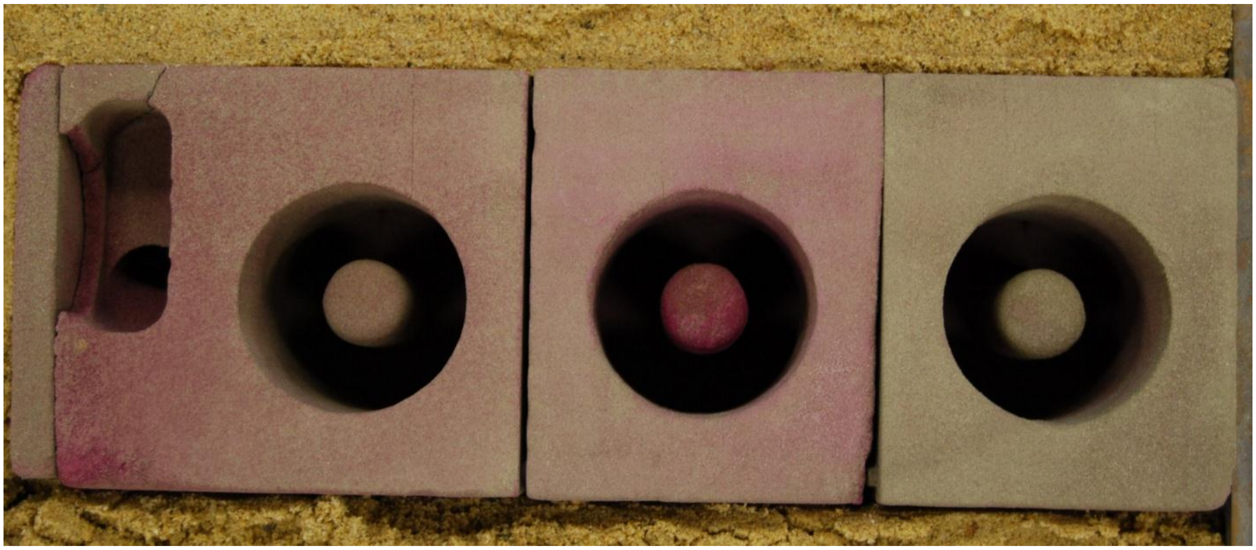

Figure 4-13. Scale-up Molds 1, 2 &3 from left to right

Mold 2 was also baked immediately after printing but was then re-humidified. To re-humidify the mold, it was placed in an oven at 125^o Celsius above an open container of water for 24 hours. In this environment, the water would evaporate from the container and be quickly absorbed by the mold. This mold was again exposed to moisture an hour prior to the metal pour to ensure the presence of moisture. Lastly, mold 3 was the control of the experiment and therefore no treatment was applied to this mold. This mold remained "green" in ceramic terminology and the mold was not baked or treated in any way after printing. The weights during the treatment of these molds can be seen in Table 4-4 below. A graph has also been generated using this data in Figure 4-14. Note that the higher weight of Mold 1 is due to the extra weight of the mold from the additional part in the mold used to pour the aluminum into the molds.

Table 4-4. Summary of Scale-Up Molds

Mold	Characteristic	Weight Change
1	Dry	-16.8%
2	Moist	2.4%
3	Green	0%

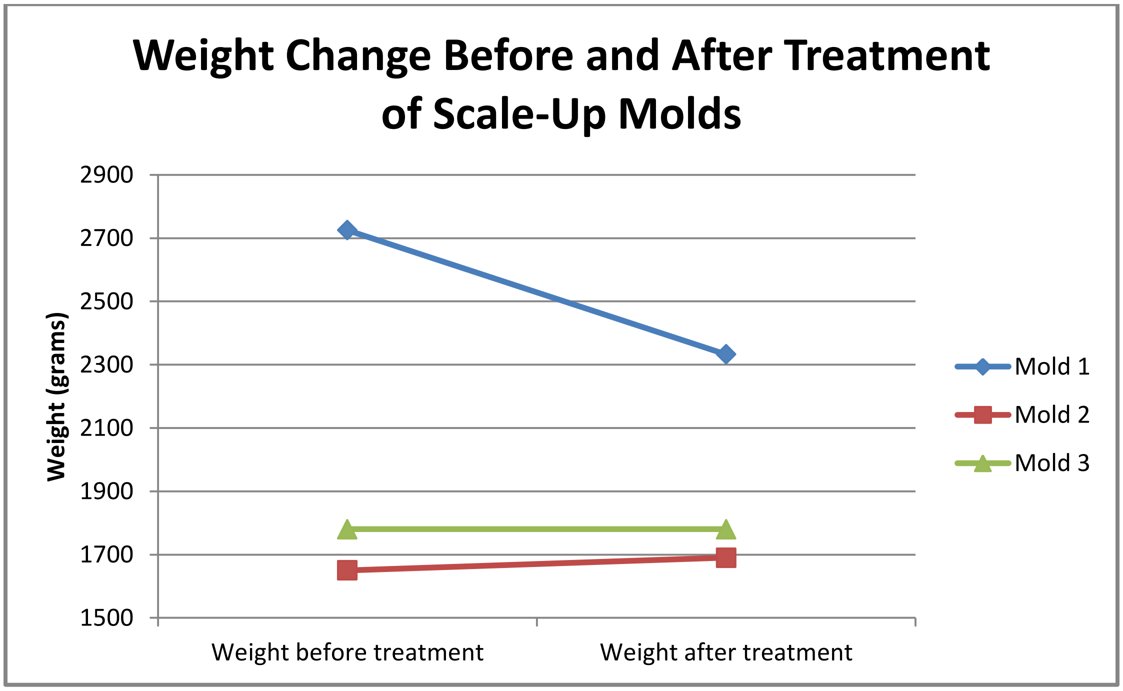

Figure 4-14. Scale-Up Mold Weight Change

As a result of these treatments and the data provided above, it is apparent that mold 1 had very little to no moisture, mold 2 contained an amount of moisture, and our control mold, mold 3 contained a considerate amount of moisture. The colors of the molds were then observed to see if the correct moisture level was being indicated. As seen in the image below (Figure 4-15), mold 1 did in fact show signs of no moisture (indicated by the pink color) while mold 2 indicated a high level of moisture. Let it be known that mold 3 had the same color properties of mold 2. However, this color identification was not shown throughout the mold. From this scale up, it is clear that the coloring of the mold is directional, dependent on the direction that the mold was printed. Because the test tiles used in our methods were all printed with the largest surface area facing upwards, we were not able to determine this dependence on direction until this scale up. The surfaces shown in this figure were in the direction that the mold was printed. Other surfaces of this mold did not indicate moisture as clearly.

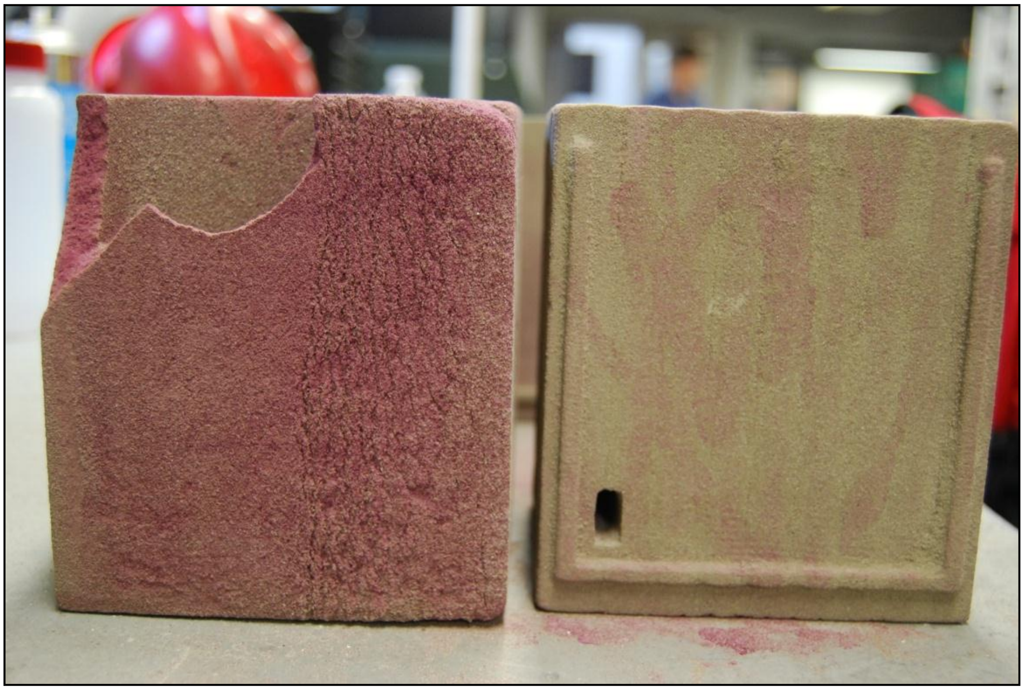

Figure 4-15: Images of mold 1 (left) and mold 2 (right) before casting

With the desired moisture levels reached, the next step was to execute the metal pour. The pour was done using molten aluminum heated to 800^{o} C and poured at 750^{o} C. The molds were designed so that the molten metal would flow through a channel connecting all three molds therefore causing the metal to fill in the molds from bottom to top in a uniform matter, reducing the effect of turbulence. This process would control the amount of out-gassing allowing us to better observe the effects of moisture alone on out-gassing.

Figure 4-16: Aluminum metal pour using the three treated molds

As seen in the image above, molds 2 and 3 show higher levels of out-gassing compared to that of mold 1. To be sure of the level of quality due to the presence of moisture, the casts were cut open to visually measure the porous properties of each cast. As seen below molds 2 and 3 are of a much lower quality compared to mold 1. Mold 1 has virtually no pours in the main body of the cast and the cylindrical pore is very defined and clean. Molds 2 and 3 on the other hand show large pours in the body of the cast and the cylindrical pores in both cases are very uneven and would certainly not meet industrially quality standards.

Figure 4-17: Final Cast parts. From left to right cast 1, 2 and 3.

From this scale up, it was observed from this experiment that the formula did accurately predict the moisture content in the molds and therefore predicted the quality of the final pieces.

5 Recommendations

Experimentation yielded a practical moisture indicator to be used to detect moisture change in test tiles, but this project would not be useful unless it would be able to be adapted into the industry. The scale-up procedure demonstrated the practicality of this indicator; this section details the application of this indicator in the metal casting industry as well as potential areas of research.

5.1 Application in Industry

For use in the metal casting industry, we recommend that all molds printed with the phenolphthalein indicator to be accompanied by a color card with instructions as follows: DO NOT POUR IF: the color of the mold does not match the color of this card. If the color of the mold does not match the color of this card please dry at 200◦C until it does so.

Figure 5-1. Future Applications Color Matching Card

This process will ensure that foundry workers bake out all moisture in the mold and core prior to casting. This will in turn lead to higher quality castings and optimize productivity in the industry.

5.2 Future Research

There are two recommendations to be made for future research of a visual humidity indicator:

1. The possibility of lower concentrations of phenolphthalein into the molds.
2. The use of thymolphthalein as a visual humidity indicator for 3D printed molds

We were able to lower the concentration of phenolphthalein in Viridis' sand based powder down to 0.10% by weight and still had a very significant color change. Due to time constraints, we were not able to research lower concentrations, but feel strongly that lower concentrations of phenolphthalein can be used while still getting the same vibrant color change. There are two benefits to lowering the concentration of phenolphthalein in the powder. The first and most obvious is for economic reasons; the less phenolphthalein used, the more money saved. The second reason is that the lower the concentration of foreign particles in the 3D printing process, the better the printed parts and the more efficient the process.

Thymolphthalein was very promising in the preliminary experiments; it turned a dark blue in the presence of moisture and would turn clear when dried out. The sole reason phenolphthalein was chosen as the indicator was because thymolphthalein was 10 times the cost of phenolphthalein. Further research needs to be done into using thymolphthalein because if it has a much better color change in the presence of moisture than phenolphthalein, then it might be worth using, despite its high initial cost.

6 Conclusions

The culmination of the project resulted in an affordable, practical chemical compound that successfully indicates the presence of moisture within a 3D printed mold. This was accomplished through the incorporation of phenolphthalein into Viridis3D's sand based powder during the printing process. The phenolphthalein provided the mold with a dark purple color when dried, and an opaque gray color when saturated. This color change was reversible, allowing the mold to continuously indicate the presence of moisture through multiple cycles of drying and readmitting moisture. This compound will indisputably enhance productivity and ensure a high caliber of quality casts on a more frequent occurrence. The visible color change will provide foundry workers with a quick and effortless method to determine the moisture level (content) in a mold. This will eliminate outgassing in metal casts due to the presence of moisture. Ultimately the introduction of the chemical compound into the metal casting industry will lead to the optimization of digital manufacturing and metal casting for Viridis3D by ensuring high quality cast products and improved productivity. Such improved products and productivity will further allow Viridis3D to allocate its financial and human resources to other areas, ultimately providing a competitive advantage and leverage the business to a higher achieving entity.

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8 Appendix A: Tile Property Detailed Calculations

Determination of the Minimum Time to Bake out All Moisture at 200C

In order to determine the minimum time needed to bake out all moisture in a 3D printed tile at 200°C, we had to run a minor experiment. We took one tile straight from printing, and weighed it. We then placed it into an oven at 200°C and removed it every 15 minutes to take weight measurements. The results are in the table below:

Table 8-1. Detailed Results of Time Determination

TIME	Mass of Tile 1	Mass of Tile 2	Mass of Tile 3
0 Minutes	24.85 g	21.46 g	22.36 g
15 Minutes	24.26 g	20.98 g	21.78 g
30 Minutes	24.19 g	20.94 g	21.73 g
45 Minutes	24.21 g	20.95 g	21.73 g

Because there was no decrease in mass from 30 to 45 minutes, we can conclude that the tile was fully dry after 30 minutes of baking.

Maximum Moisture Absorption Calculation

Each tile was dried at 200°C for 30 minutes, and the dry mass was taken. The dry tile was then fully submerged in water for two minutes, at which point it was fully saturated. The tile was then removed from the water and weighed to get the fully saturated mass. The following equation was used to calculate the maximum moisture absorption:

$$\%\, mass\ gain = \frac{M_s - M_d}{M_d} * 100$$

M_s = Fully saturated mass

M_d = Dry mass

The average mass gain in all of the tiles was 35%. This meant that the 3D printed tiles were capable of absorbing a maximum of 35% their dry weight in water.

Porosity Calculation

The porosity was calculated using the following equations:

$$\Phi = \frac{V_v}{V_t}$$

$$V_t = L * W * H$$

$$V_v = \frac{(M_s - M_d)}{\rho}$$

Φ = Porosity

V_v = Volume of void space

V_t = Total Volume

L = Length of the tile = .0492 m

W = Width of the tile =.0492 m

H = Height of the tile = .00793 m

M_s = Fully saturated mass = .03321 kg

M_d = Dry mass = .02453 kg

ρ = density of water = 1000 kg/m3

By subtracting the mass of the dry tile from the mass of the fully saturated tile, we can get the total mass of the water in the fully saturated tile. By dividing the mass of the water by the density of water, we get the total volume of the water in the tile when fully saturated. This volume is equal to the total volume of void space when the tile is dry. The total volume of the tile is calculated by multiplying the length by width by height. We now divided the volume of the void space by the total volume of the tile to get a porosity of 0.452.

9 Appendix B: Detailed Data Tables for Humidity Testing

Initial Humidity testing of Phenolphthalein formula (0.25 weight%)

Table 9-1. Mass Recordings of Tiles 1 Through 12 Over a Week

Tile	1	2	3	4	5	6	7	8	9	10	11	12
7-Feb	25.14	24.32	24.84	24.79	24.63	24.42	24.3	25.41	25.11	24.07	23.71	25.01
8-Feb	25.56	24.65	25.23	25.19	25.06	24.75	24.68	25.78	25.49	24.53	24.1	25.59
9-Feb	25.81	24.97	25.46	25.37	25.31	24.96	24.92	25.97	25.69	24.75	24.31	25.8
10-Feb	25.96	25.17	25.66	25.52	25.49	25.12	25.12	26.19	25.88	24.9	24.49	25.95
11-Feb	26.14	25.34	25.8	25.68	25.65	25.32	25.3	26.35	26.03	25.04	24.67	26.11
12-Feb	26.94	25.45	25.91	25.76	25.78	25.41	25.39	26.48	26.17	25.16	24.76	26.24
13-Feb	27.07	25.63	26.05	25.87	26.02	25.54	25.52	26.59	26.28	25.25	24.9	26.35
14-Feb	27.19	25.78	26.22	25.96	26.16	25.67	25.66	26.77	26.38	25.43	25.03	26.48
14-Feb Bake	24.87	23.96	24.55	24.48	24.22	24.13	23.99	25.00	24.64	23.72	23.34	24.54

Table 9-2. Percent Mass Increase of Tiles 1 through 12 Over a Week

Tile	1	2	3	4	5	6	7	8	9	10	11	12
8-Feb	1.64	1.34	1.55	1.59	1.72	1.33	1.54	1.44	1.49	1.88	1.62	2.27
9-Feb	0.97	1.28	0.90	0.71	0.99	0.84	0.96	0.73	0.78	0.89	0.86	0.81
10-Feb	0.58	0.79	0.78	0.59	0.71	0.64	0.80	0.84	0.73	0.60	0.73	0.58
11-Feb	0.69	0.67	0.54	0.62	0.62	0.79	0.71	0.61	0.58	0.56	0.73	0.61
12-Feb	2.97	0.43	0.42	0.31	0.50	0.35	0.35	0.49	0.53	0.48	0.36	0.50
13-Feb	0.48	0.70	0.54	0.43	0.92	0.51	0.51	0.41	0.42	0.36	0.56	0.42
14-Feb	0.44	0.58	0.65	0.35	0.54	0.51	0.55	0.67	0.38	0.71	0.52	0.49
14-Feb Bake	- 9.33	- 7.60	- 6.80	- 6.05	- 8.01	- 6.38	- 6.96	- 7.08	- 7.06	- 7.21	- 7.24	- 7.91

Humidity Testing Comparing Concentrations

Table 9-3. Mass Recordings of Tiles A1 Through A12 and B1 Through B12 Over the Course of a Week

Tile	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	**A8**	**A9**	**A10**	**A11**	**A12**
12-Mar	24.6	24.7	25.2	25.3	25.8	26.1	25.8	25.4	26.4	27.0	26.2	26.2
13-Mar	25.0	25.0	25.6	25.5	26.2	26.5	26.1	25.8	26.7	27.5	27.2	26.7
14-Mar	25.2	25.3	25.9	25.9	26.5	26.8	26.5	26.0	27.1	27.7	27.4	27.0
15-Mar	25.5	25.4	26.1	26.0	26.6	27.0	26.6	26.2	27.3	27.9	27.5	27.1
16-Mar	25.6	25.7	26.2	26.3	26.8	27.2	26.8	26.3	27.4	28.1	27.7	27.3
17-Mar	25.7	25.8	26.3	26.4	26.9	27.3	26.9	26.5	27.6	28.2	27.8	27.4
18-Mar	25.9	25.9	26.4	26.5	27.0	27.4	27.0	26.5	27.7	28.3	27.9	27.5
19-Mar	25.9	26.0	26.5	26.6	27.1	27.5	27.1	26.6	27.8	28.4	28.0	27.6
19-Mar BAKE	*24.5*	*24.5*	*25.2*	*25.1*	*25.6*	*25.9*	*25.7*	*25.3*	*26.3*	*26.6*	*26.1*	*26.1*
	B1	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**	**B10**	**B11**	**B12**
12-Mar	24.2	23.9	24.6	24.5	24.6	24.2	24.2	24.1	24.5	23.9	24.2	24.5
13-Mar	24.6	24.3	24.9	24.9	24.9	24.5	24.6	24.7	24.9	24.3	25.6	26.1
14-Mar	24.9	24.6	25.3	25.2	25.3	24.9	24.9	24.9	25.2	24.5	24.8	26.2
15-Mar	25.1	24.7	25.5	25.3	25.4	25.0	25.1	25.1	25.4	24.6	25.0	26.4
16-Mar	25.4	24.9	25.6	25.4	25.6	25.2	28.4	25.2	25.5	24.8	25.2	26.6
17-Mar	25.6	25.0	25.7	25.6	25.7	25.3	28.4	25.3	25.6	25.0	25.3	26.7
18-Mar	25.6	25.1	25.8	25.7	25.8	25.4	28.4	25.5	25.8	25.1	25.4	26.8
19-Mar	25.7	25.2	25.9	25.8	25.9	25.5	28.5	25.5	25.9	25.2	25.5	26.9
19-Mar BAKE	*24.1*	*23.8*	*24.4*	*24.3*	*24.5*	*24.1*	*24.3*	*24.0*	*24.3*	*23.7*	*24.0*	*24.5*

Note: Mass recordings is in grams and 0.25% is denoted by A and 0.10% is denoted by B

Table 9-4. Average weights (grams) of 0.25% and 0.10% phenolphthalein tiles.

Date	**0.25% AVG**	**0.10% AVG**
12-Mar	25.73	24.29
13-Mar	26.15	24.87
14-Mar	26.43	25.08
15-Mar	26.59	25.23
16-Mar	26.78	25.40
17-Mar	26.90	25.52
18-Mar	27.00	25.62
19-Mar	27.09	25.72
BAKE	25.58	24.14

Table 9-5. Percent Mass Increase of Tiles A1 through A12 and B1 Through B12 Over a Week

Tile	**A1**	**A2**	**A3**	**A4**	**A5**	**A6**	**A7**	**A9**	**A10**	**A11**	**A12**
12-Mar	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13-Mar	1.24	4.05	3.97	3.95	3.88	3.83	3.88	3.80	3.70	3.81	3.81
14-Mar	1.03	1.15	1.04	1.24	1.02	1.23	1.29	1.33	0.97	0.58	0.96
15-Mar	0.98	0.63	0.65	0.58	0.49	0.59	0.64	0.55	0.57	0.44	0.48
16-Mar	0.59	0.90	0.50	0.99	0.60	0.88	0.67	0.69	0.61	0.51	0.62
17-Mar	0.43	0.47	0.42	0.34	0.45	0.44	0.48	0.54	0.50	0.61	0.62
18-Mar	0.58	0.39	0.42	0.57	0.30	0.29	0.30	0.36	0.25	0.25	0.25
19-Mar	0.15	0.31	0.30	0.23	0.30	0.40	0.44	0.40	0.35	0.29	0.47
BAKE	*-5.3*	*-5.5*	*-5.2*	*-5.5*	*-5.3*	*-5.8*	*-5.3*	*-5.6*	*-6.1*	*-6.9*	*-5.7*
	B1	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B9**	**B10**	**B11**	**B12**
12-Mar	0	0	0	0	0	0	0	0	0	0	0
13-Mar	1.71	1.44	1.21	1.77	1.28	1.22	1.63	1.53	1.61	5.28	6.43
14-Mar	1.32	1.42	1.74	1.11	1.38	1.37	1.28	1.27	0.86	-2.94	0.38
15-Mar	0.80	0.40	0.71	0.55	0.55	0.52	0.76	0.67	0.69	0.72	0.53
16-Mar	1.06	0.60	0.43	0.51	0.63	0.71	11.74	0.51	0.81	0.71	0.64
17-Mar	0.70	0.28	0.39	0.47	0.47	0.51	-0.14	0.51	0.44	0.43	0.45
18-Mar	0.08	0.44	0.35	0.39	0.46	0.39	0.14	0.50	0.52	0.39	0.37
19-Mar	0.27	0.36	0.35	0.39	0.42	0.35	0.07	0.54	0.48	0.27	0.34
BAKE	*-6.1*	*-5.4*	*-5.8*	*-5.5*	*-5.7*	*-5.6*	*-14.7*	*-6.1*	*-6.1*	*-5.9*	*-8.9*

Note: Mass recordings is in grams and 0.25% is denoted by A and 0.10% is denoted by B

Table 9-6. Average percent mass increase (%) of 0.25% and 0.10% phenolphthalein tiles

Date	**0.25% AVG**	**0.10% AVG**
12-Mar	0.00	0.00
13-Mar	3.66	2.34
14-Mar	1.07	0.81
15-Mar	0.60	0.61
16-Mar	0.68	0.66
17-Mar	0.48	0.46
18-Mar	0.35	0.40
19-Mar	0.33	0.37
BAKE	-5.58	-6.11