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Relationship between the pH of Sodium Hydroxide Solution and 3D Printed Support Resin Dissolution

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***Abstract*— This work explores the relationship between sodium hydroxide solution pH and effectiveness of support model resin dissolution. The weight of 3D printed parts, which were submerged in sodium hydroxide, and the pH of the solution were recorded over time. Though the correlation calculated was high, no true correlation was determined.**

Keywords*— *Additive manufacturing, microfluidics, cleaning, sodium hydroxide

I. Motivation

3D printing, or additive manufacturing, is able to create lightweight parts with complex geometries that are also cost efficient. 3D-printed microfluidic channels are of interest to researchers and commercial manufacturers.

Microfluidics has a wide range of applications, including the fields of biology, chemistry, optics, information technology, and thermal technology. Small amounts of fluids, in the nano- and atto- (10^{-9} and 10^{-18} respectively) liter range, can be manipulated in channels of micrometer or nanometer thicknesses [1]. Because microfluidic experiments require small amounts of samples and reagents, they are low cost alternatives to full-scale equipment and testing [1]. They would also produce less waste in experiments.

Microfluidics allow for experiments of high sensitivity. Large channels of fluids experience turbulent flow, in which fluids mix when they come in contact with each other. The flow in microsystems is laminar; fluids do not mix when they come in contact with each other. Fluids flow in parallel in micro-channels and mixing only occurs as a result of diffusion [1].

Microfluidics has been used in molecular biology to measure individual cell growth [2] and to track DNA and other proteins for analysis. Fuel cells have taken advantage of laminar flow by separating fuel and oxidant to make efficient alkaline fuel cells [3]. These cells could provide cheap and effective power for small electronic applications.

II. Background

Additive manufacturing, more familiarly known as 3D printing, is the process by which a digital model is made layer by layer into a tangible object. These models are created using computer aided drafting (CAD). Microns-thin layers of support and model resin are laid down in different shapes. The use of support material allows for intricate internal geometry, such as microfluidic chambers, which would not be possible with other machining techniques that rely on the removal of material.

The company that manufactures the 3D printer used in this research, Stratasys, suggests the following cleaning procedure; 1. Remove the support material, preferably with the use of an Objet Waterjet, 2. Immerse the part in 1-2% sodium hydroxide solution for 1-2 hours, 3. Rinse the model with running tap water or a second Waterjet wash, 4. For fastest drying, immerse in isopropyl alcohol and allow to rest for a half hour [4].

Rua et. al. [5] investigated the limitations of additive manufacturing for printing microfluidic heat exchanger components. The study focused on understanding both the limitations the printing had with respect to size and looked at how printing orientation (Fig. 1) affected the part and how the small interior channels could be most efficiently cleaned. This printer was capable of making walls as thin as 16 microns; however walls thinner than 32 microns were not cleaned successfully. The horizontal printing orientation was preferred to both vertical and axial since it allowed for the thinnest walls of the part to be constructed out of the largest layers of model resin.

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The cleaning methods explored include the cleaning of microfluidic channels by gravity, and by submerging in solutions at different temperatures. A solution of sodium hydroxide in water was used for cleaning because this is the method recommended by the Objet Eden 250 instructions. The recommended concentration from Objet was 2% but others have found that 7% was needed [6]. Rua et. al. investigated the effect of 7%, 17%, and 27% concentrations and various temperatures on the cleaning process.

The cleaning of microfluidic channels by gravity was done by filling clear polyvinyl chloride tubing with sodium hydroxide dissolved in water at varying concentrations and allowing gravity to clear through the openings. They were placed in beakers with varying concentrations of sodium hydroxide solution, which were brought to different temperatures. Solutions that were kept at room temperature were changed three times, each when the solution had become particularly yellow, a result of the dissolved model support resin. Whether the acid base reaction between the acidic support material and the sodium hydroxide solution had reached completion was not investigated.

III. Introduction

Dissolving model support resin from coupon pieces in sodium hydroxide solution at room temperature was the lengthiest of the cleaning methods explored in the Rua et. al. [5]. Part of what may have contributed to the lengthy cleaning time could have been that the acid base reaction that occurs between the support material and the sodium hydroxide had reached completion before the solution was replaced with new solution. In order to understand this, experiments were designed and conducted to monitor the pH of the solution used to dissolve the model support resin. In addition to recording the pH of the solution periodically, each part soaked in the solution was weighed in order to find the relationship between the amount of time a part was allowed to soak in sodium hydroxide solution and the amount of support material that has been dissolved.

It was hypothesized that the pH of the solution would become neutral at the same time as the rate of support material dissolution approached zero. This effect is believed to be the cause of the slow removal of support material over time using the sodium hydroxide solution method.

IV. Methods

The pH experiments were carried out using two different concentrations of sodium hydroxide solutions – 17% and 27% by mass. Each part was weighed dry on a digital scale and measured at two specific locations using dial calipers. Measurement location A is the part of the neck closest to where it meets the body (Fig. 2). Measurement location B is the part of the body right above the “1” marking (Fig 3). This is part of the coupons’ identifying marking on one side (Fig. 4). The coupons were submerged in 500mL of 17% or 27% sodium hydroxide solution. The pH of the solution, the weight and the measurements at A and B were taken hourly. The pH was taken using Hydrion pH strips and the weight and measurements A and B were taken when the part was still wet, after patting the coupon dry with paper towel. Once all external support material was dissolved, the fin measurement was taken. This measured the amount of material removed from the tube fitting and fin of the coupon (Fig. 5). Side Measure A was taken from the opening near the “1” mark and side Measure B was taken from the opening near the “0.5” mark on the coupon body (Fig. 4, Fig. 6). Side A was the side placed up in the beaker.

The pH was inspected for change in concentration of the solution, and the weight and measurements of amount of support material dissolved were used to track efficiency and speed of cleaning.

V. Results

This experiment was designed to investigate the most efficient cleaning process for 3D-printed parts. Once the sodium hydroxide is neutralized to 7.0, it is no longer basic and will no longer dissolve support material. The change in pH over time and the change in weight of the coupon over time were compared to find the relationship between pH and change in weight. The cleaning time would be minimized by adding more base when the pH of the solution approached 7.0, which was assumed to be the point at which the effectiveness of the solution would decrease. There would have to be a direct correlation between these two variables for the hypothesis of this experiment to be proven true.

The pH of the solution in which the coupons were submerged was monitored over time and recorded as shown in (Fig. 7). The range of the pH strips used in this experiment was from 8.0 to 5.5. The pH reading of the strips changed in increments of 0.2 except between 7.6 and 8.0 where the increment was 0.4. Although some pH levels in this experiment may be recorded as 8.0, they could be higher. The range for a base is from 14.0 – 7.0. The pH of the 17% sodium hydroxide solution dropped to 7.6 over 25 hours of use. This means that the pH of the solution does not change dramatically over a 24-hour period.

The correlation coefficient between the pH levels of the 17% sodium hydroxide solution and the weight loss of support material is 0.849, as shown on (Fig. 8). The correlation coefficient could not be taken for the remainder of parts submerged in 17% sodium hydroxide solution because the pH of this solution did not change in that 5-hour period. For the coupons submerged in 27% sodium hydroxide solution the correlation coefficients are 0.838, 0.818, and 0.824 for coupon A, B, and C, respectively. The data for the 27% sodium hydroxide is found on (Fig. 9).

These correlation coefficients is misleading since very little data was collected and the pH values collected range from 8.0 to 7.6. Due to these limitations, and the fact that the pH measured did not change sufficiently over time, it is not certain that the completion of the acid-base reaction was the contributing variable that led to slow cleaning times in the research performed by Rua et.al. [5].

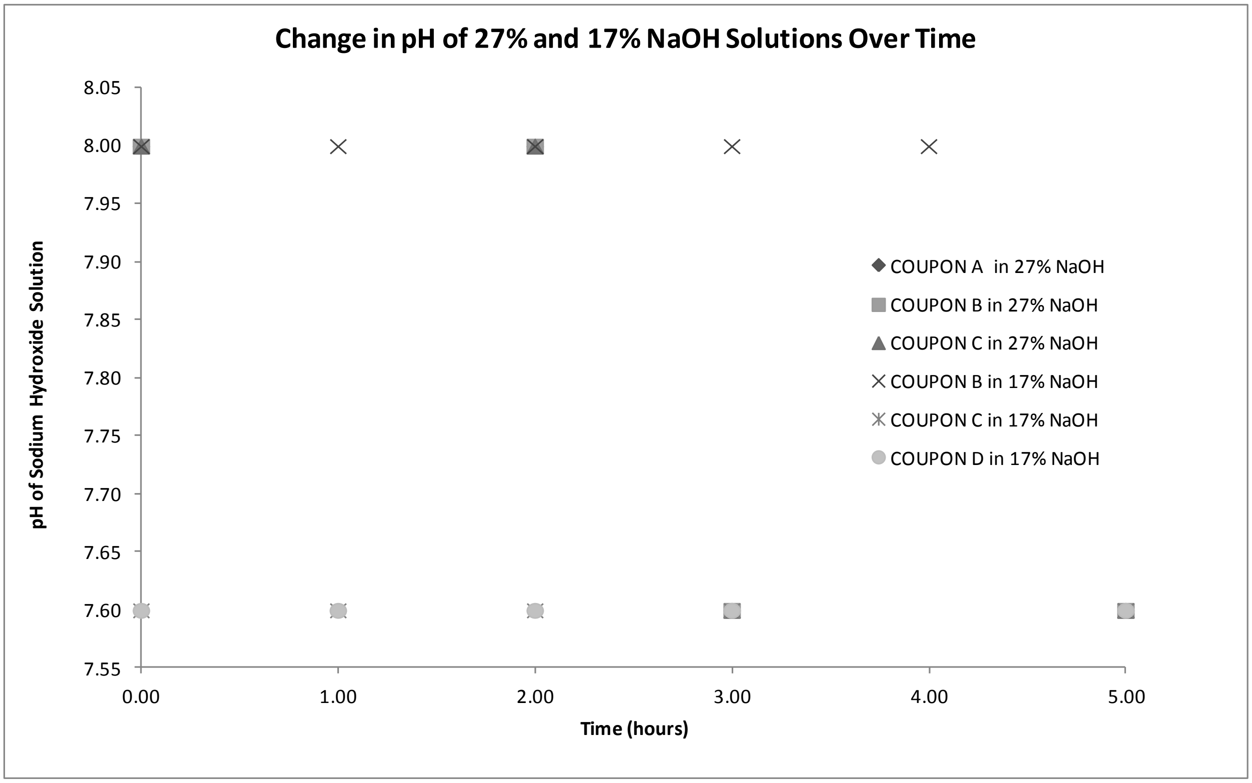

Fig. 7. The change in pH of 27% and 17% sodium hydroxide solutions changed at most from 8.0 to 7.6.

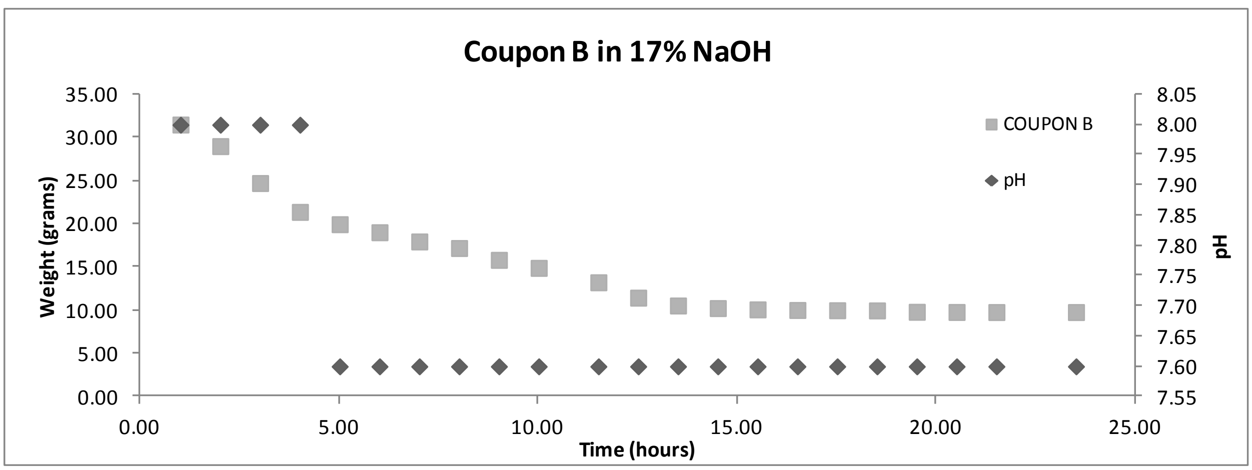

Fig. 8. The weight of coupon B in 17% sodium hydroxide and the pH of the solution were graphed together.

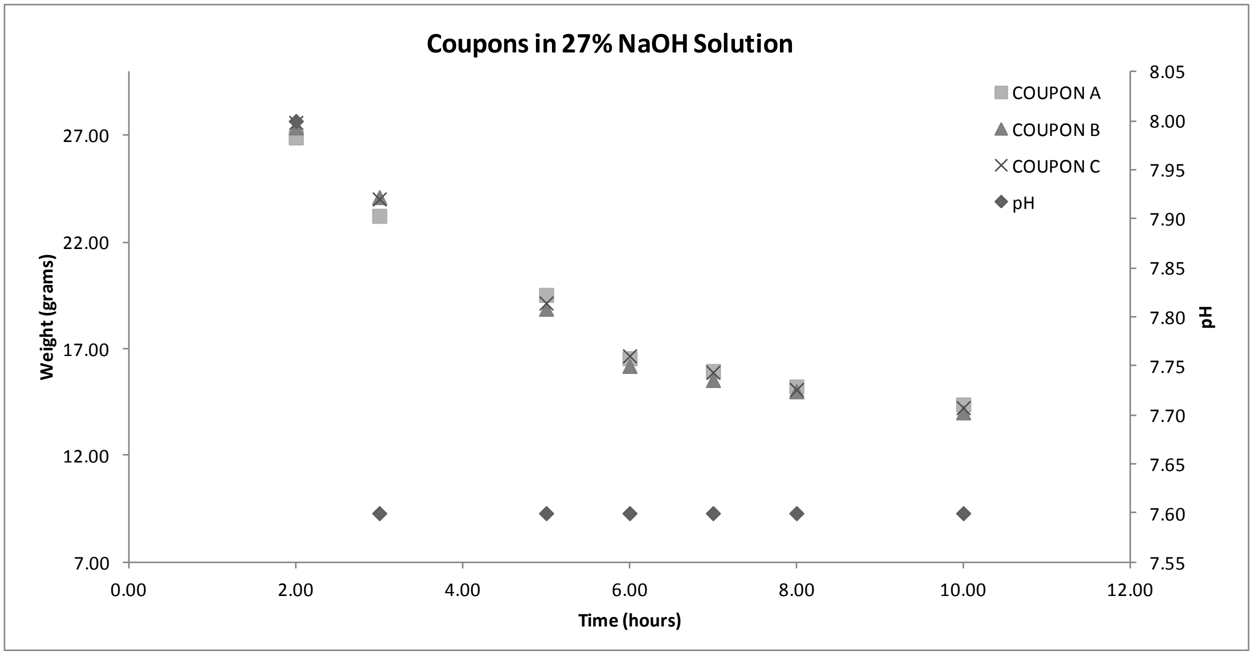

Fig. 9. The change in weight of coupons A, B, and C in 27% sodium hydroxide solution, and the pH of the solution were graphed together.

The initial dry weight of each coupon was not included in charts because the weight of the coupons increases after the coupons' porous support material absorbs some of the solution it is submerged in. The small differences in data between coupons submerged in 17% and 27% sodium hydroxide solution demonstrates the insignificance of the concentration of this solution to the change in weight of the coupon. The data for the weight of coupon B in 17% sodium hydroxide solution over time was sectioned off at the 18 hour mark. It is around this time, according to the data collected from this experiment, and the experiments conducted by Rua et. al.[5] that all of the external support material has been dissolved.

The weight of coupon B in 17% solution is shown on two graphs, one that shows data while external support material is removed, and one that shows data while internal support material is being removed. A trend line has been added to each figure to demonstrate the change in rate at which support material is removed. The first chart (Fig. 10) has a trend line of

$$y = 0.0812x^2 – 2.723x +32.976. \quad (1)$$

If the second chart (Fig. 11) were to use a polynomial-fit line, the trend line would be

$$y = 0.011x^2 - 0.4873x + 15.194 \quad (2)$$

however, this is not accurate enough to predict future values. Its parabolic shape will predict weight gain, which is not possible. Instead a logarithmic trend line is used (Fig. 11)

$$y = -0.0383x + 10.635 \quad (3)$$

This is less accurate in terms of how many data points it crosses, but better represents the general trend of the material loss.

The changes in neck measurements (Fig. 12) were slightly faster for the 27% solution than for the 17% solution. This difference is minor and does not offer a clear advantage to using a higher concentration of sodium hydroxide solution.

The change in body measurements was the fastest measurement to hit the minimum value (Fig. 13). The 17% solution on average took an hour longer to clear the support material down to the body of the coupon than the 27% solution. This does indicate a small advantage to using a higher concentration of sodium hydroxide solution.

The neck and the body are so fast to clean is because they are more exposed than the inner channels. The neck is encased in more support material than the body is, which makes it faster to clean.

The change in fin openening measurements over time can be seen in Fig. 14. Both side A and side B measurements appear to plateau once a certain amount of material has been removed. This is likely due to the lack of accessability into the internal geometry of the coupon. It is difficult for a significant amount of sodium hydroxide solution to enter the tube fitting of the coupon if the solution is not being aggitated or moved somehow.

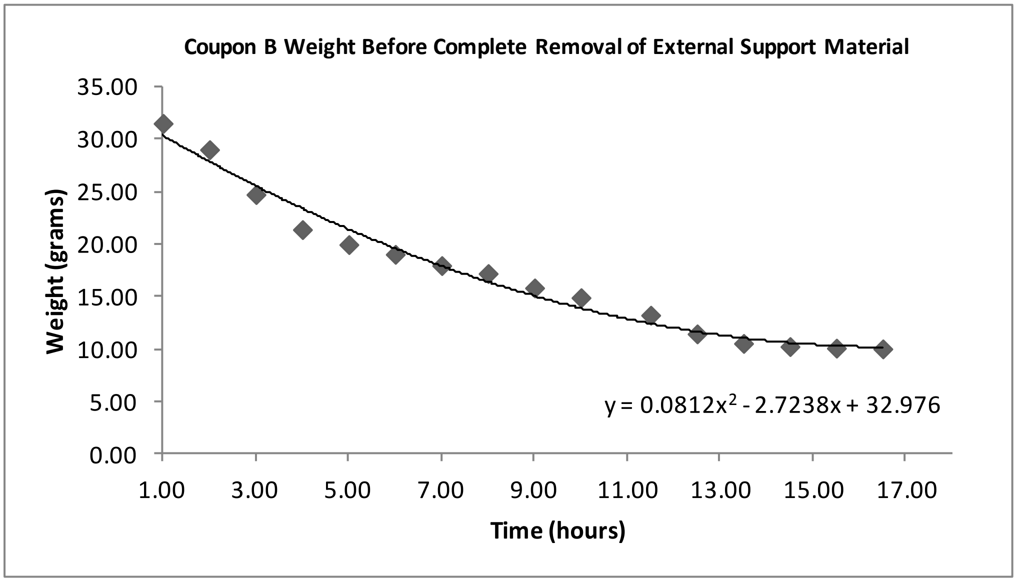

Fig. 10. The data for the weight of coupon B in 17% sodium hydroxide solution over time was sectioned off at at the 18 hour mark; the first section was fit with a polynomial trend line.

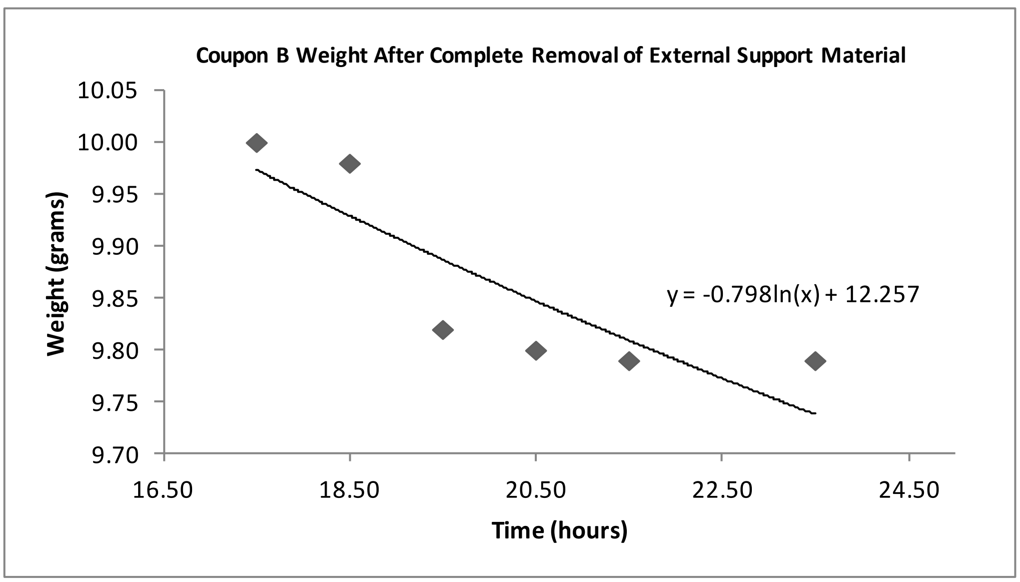

Fig. 11. The second half of the data for the weight of coupon B in 17% sodium hydroxide solition was fit with a logaritmic trend line.

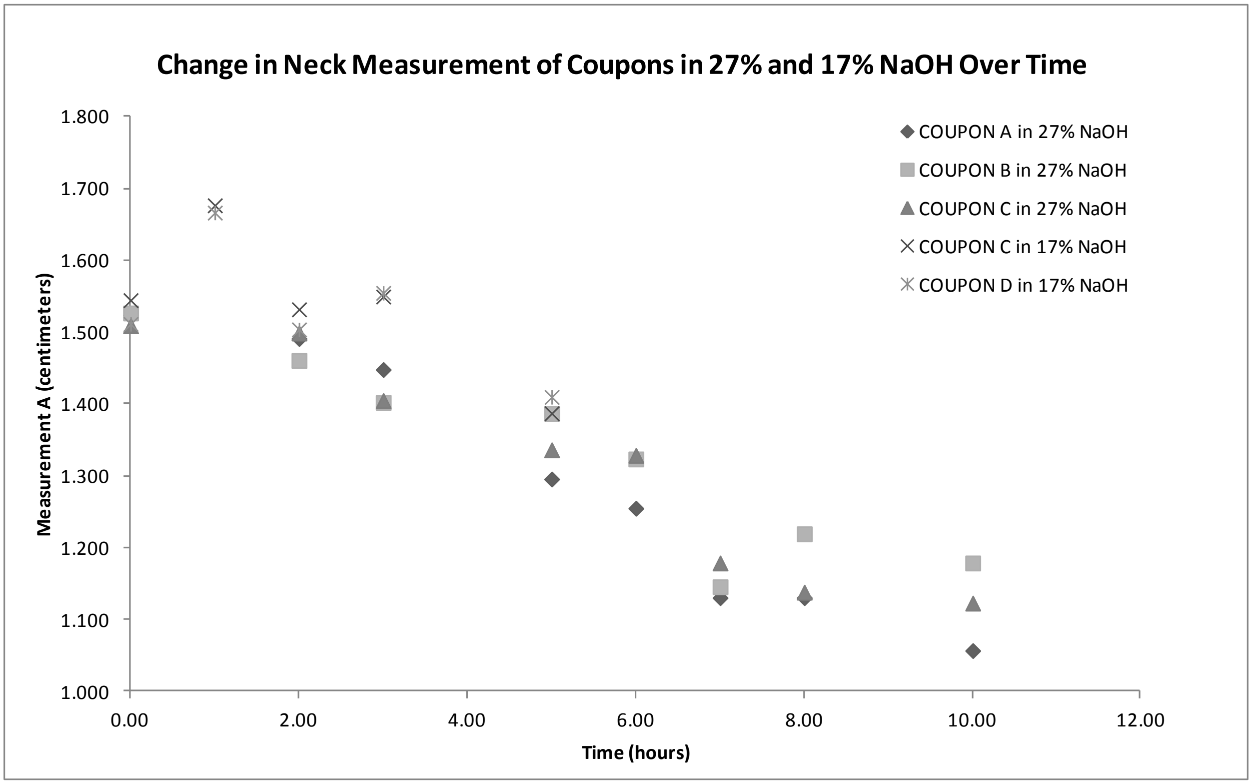

Fig. 12. The change in neck measurements for the 27% and 17% sodium hydroxide solutions were nearly identical.

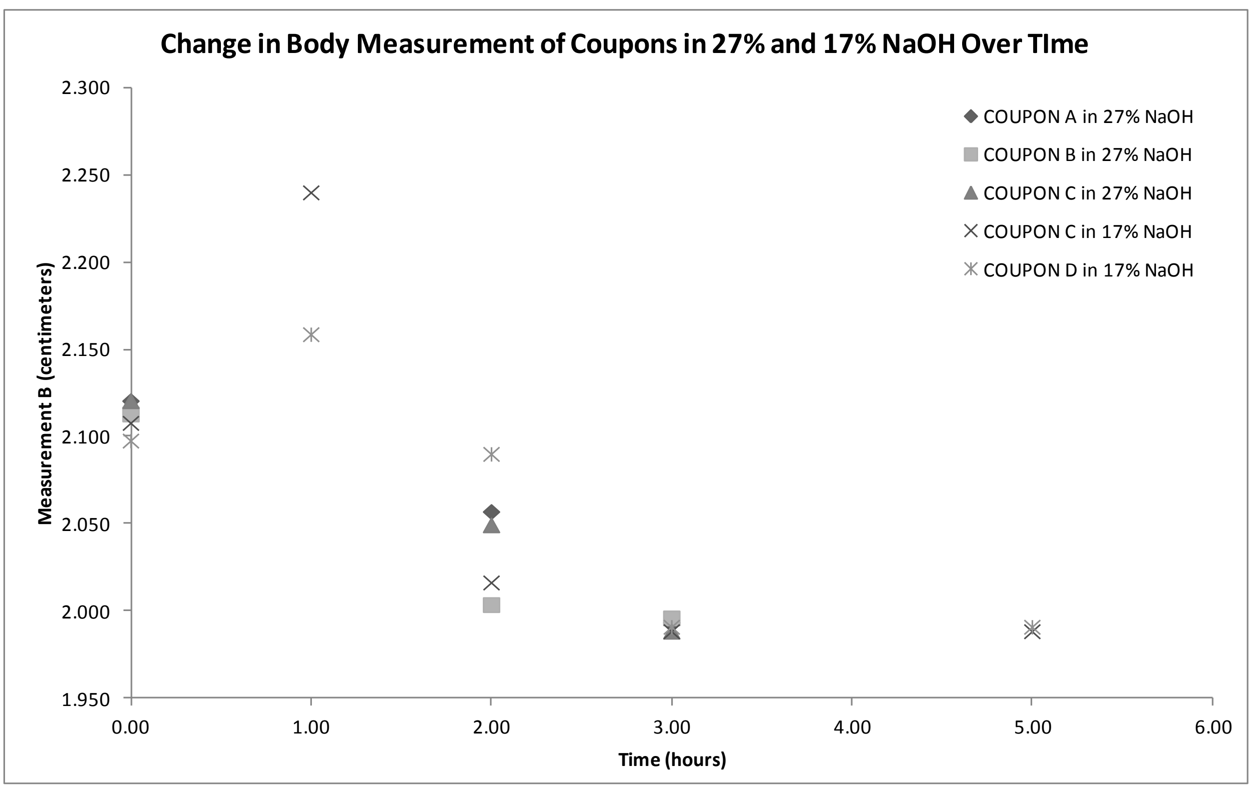

Fig. 13. Support material on the body was cleared an hour faster for the coupons submerged in 27% than those submerged in 17%.

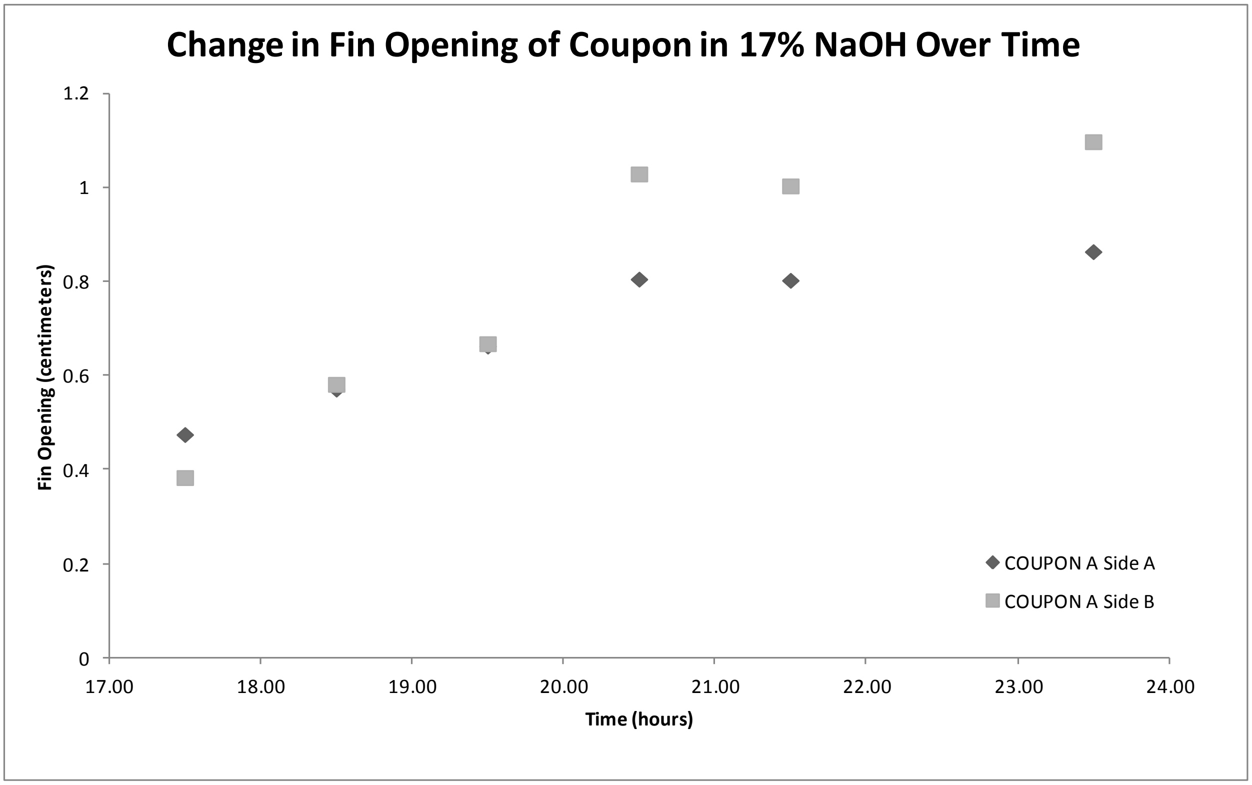

Fig. 14. The change in fin opening measurement appears to plateau after a couple hours in the 17% sodium hydroxide solution.

VI. Discussion and Future Work

This study shows that the sodium hydroxide solutions were not being neutralized over a 24 hour time period. Therefore, that is not the main cause of the long and inefficient cleaning process. It was observed that the concentration did not change over time but that the support material continued to be removed by the solution. The 27% solution removed material slightly faster than the 17% solution did, but there was not much difference between the two. The cleaning process remains slow. This is likely due to the geometry of the coupons tested. The space between the fins and the small channels inside the coupon are not exposed to the solution as much as the outside surfaces are. Fig. 2 shows that the weight of the coupon decreases quickly initially but stagnates over time. This corresponds to the difference in the speed of removal of material from outside the coupon and inside the channels of the coupon. Fig. 3 and Fig. 4 show that material is removed fairly quickly from the coupon. Fig. 5 shows that removal of support material from inside the channels is a slow process. Manual cleaning may be helpful in cleaning but this is not an efficient cleaning method for large-scale manufacturing processes. While the bulk pH did not change, a local pH change my account for the slow cleaning. Further work for improving this process includes designing a system with a pump which constantly applies a pressurized stream of sodium hydroxide will be a quicker method of eroding the support material from small parts of geometry that are not exposed fully to the solution. The pump would constantly mix the bulk and local sodium hydroxide solution, which may change the effectiveness of cleaning. Pump designs that have inserts to allow cleaning of pieces of an array of sizes, and that have different pressures and flows will be examined to optimize fast and efficient cleaning of 3D printed pieces with small geometries and channels.

Reference Figures

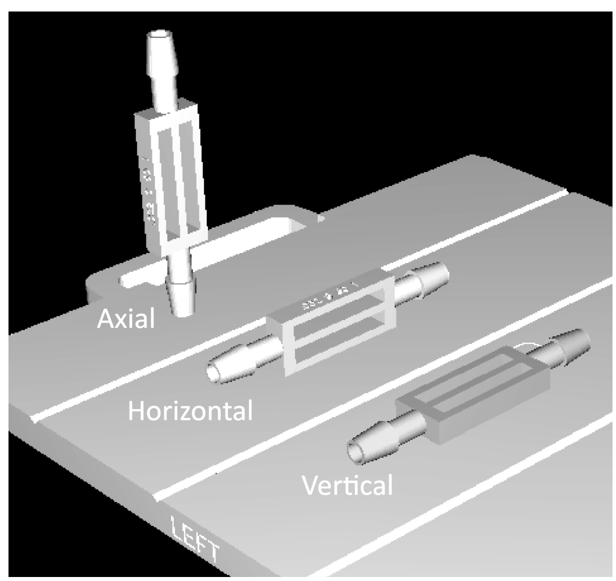

Fig. 1. There were three potential printing orientations: axial, horizontal, and vertical.

Fig. 2. Neck Measurement Technique

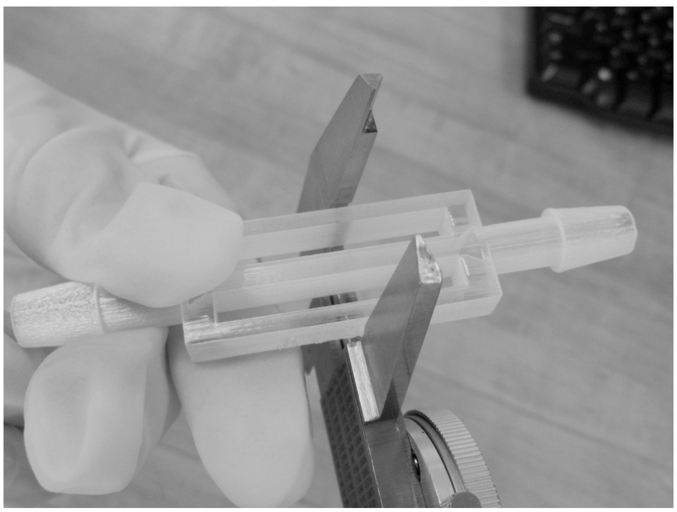

Fig. 3. Body Measurement Technique

Fig. 4. Each coupon has an identifying mark on the side that indicates dimensions.

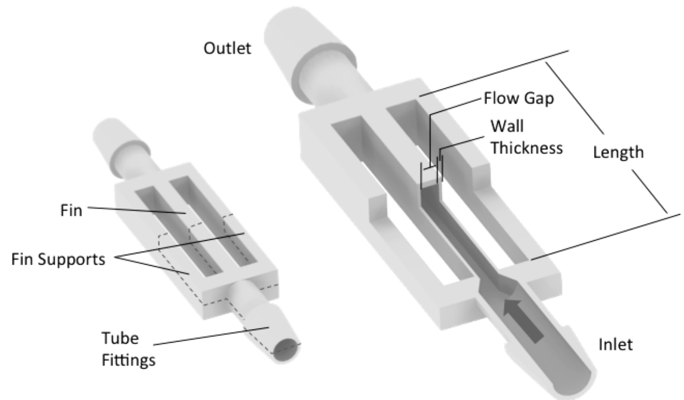

Fig 5. The parts of the coupon can be identified on the graphic above.

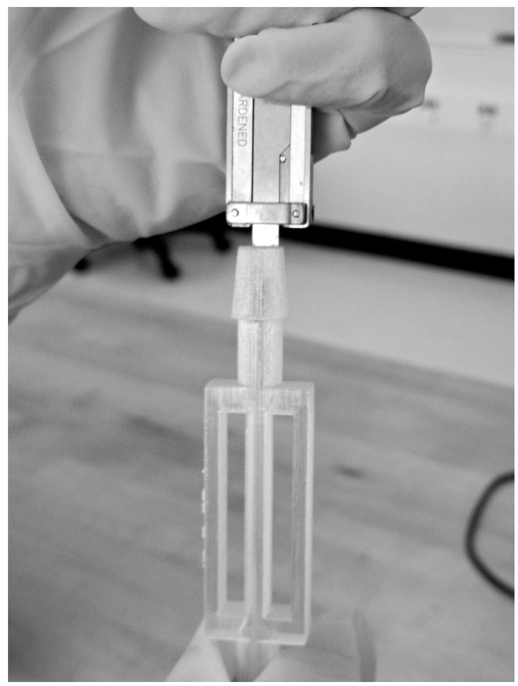

Fig. 6. Fin Measurement Technique – used for sides A and B

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