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FOR

STUD.TECHN. ØYSTEIN HEDEN KÅLÅS

PATTERNLESS DIRECT MOULDING OF SAND CASTINGS

Direkteforming i sandstøping uten fysisk modell

THE NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

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Abstract

The goal of this project was to investigate and test methods of direct moulding for use in ferrous sand casting. Directly printing sand-cast for high temperature materials like steel and cast iron is currently not commercially available. This is an attractive technology because of the dramatically reduced cost and lead-time for a new product to be introduced into the market. Significant background research had to be done in this project to cover the existing technology, and thus get a better understanding of the various methods of rapid prototyping. In particular it was essential to find what research had been done in three-dimensional printing of moulds, both for low and high temperature metals.

To find the best-suited material mixture the research started with a recipe found in a Z Corporation patent about casting materials for three-dimensional printing. This sand and fluid mixture are designed to be used with high temperature molten metal. The recipe was both small- and full-scale tested, however slight changes were made to the original recipe due to material availability and time constraints. After testing the material mixture full-scale in the 3D-printer, it was apparent that the material mixture from the recipe in the patent was not strong enough for a useful casting material, and indeed not even strong enough to be removed from the printing area.

The next step was to test different combinations of reagents to find the recipe that would make a stronger material mixture. The solution was to increase the cementing ingredients in the mixture (MgO and monocalcium phosphate) and reduce the amount of filler material (zircon sand and limestone). From further research, an article was found that had studied the optimal MgO to phosphate and cement to filler-material mol-ratio. After converting this to weight-ratio a new material mixture recipe was developed and small-scale tested. It was clear that the new mixture had significantly higher strength. The additional step of heating the final product in an oven was also investigated, but did not increase the final strength of the product. The new material mixture was then tested full-scale on the 3D-printer. The desired strength was obtained after changing the

printing settings, however the final product had a very poor surface quality. This did not change, even when changing the layer height or reducing the solvent in the fluid. Due to time constraints a third recipe was not developed, but the reasons for the uneven surface are discussed. The grain size of the PMMA, the filler material to cement ratio and the limited printing parameters were concluded to be the most likely reason for the poor surface finish. Since this type of material is not yet in the market, it is suggested that the surface finish could also be one of the restricting factors in Z Corporation marketing this product.

Sammendrag (Norwegian)

Målet med dette prosjektet er å undersøke og teste metoder for direkte-printing av sandformer som kan brukes for støping av høytemperatur metaller. Materialer for printing av sandformer for høytemperatur mataller som stål og støpejern er for tiden ikke kommersielt tilgjengelig. Dette er en attraktiv tekologi siden det kan redusere kostnadene og tiden fra et nytt produkt er utviklet til masseproduksjon kan startes. Omfattende bakgrunnsundersøkelser ble gjennomført for å få en bedre forståelse av hurtig prototyping, og de forskjellige etablerte metodene for dette. Det var også nødvendig å innhente informasjon om hva som her blitt gjort innen 3D-printing av sandformer for både høy- og lavtemperatur metaller.

For å finne et brukbart materiale startet arbeidet med en oppskrift fra et Z Corporation patent om støpematerialer brukt for 3D-printing. Sand- og væskeoppskriftene fra dette patentet er ment for bruk med høytemperatur metaller. Oppskriften ble testet på liten skala, men med noen forandringer på grunn av begrensinger i tilgjengelighet av materialer og tid. Etter å ha testet sand- og væskeblandingen i full skala på 3D printeren viste det seg at sluttproduktet ikke hadde nok stryke til å kunne brukes for støping, det var ikke en gang strekt nok til at det kunne tas ut fra printerområdet uten at det ble skadet.

Neste steg i testingen var å undersøke forskjellige kombinasjoner av reaktantene for å finne en oppskrift som gav et sterkere materiale. Løsningen var å øke de styrkende ingrediensene i sanden (MgO og monokalsium fosfat) og redusere fyllmaterialene (zirkon sand og kalkstein). Etter videre litteratur søk ble det optimale MgO/fosfatforholdet funnet, en ny oppskrift ble utviklet og videre småskala testing ble utført. Den nye oppskriften resulterte i et mye sterkere materiale. Varmebehandling av materialblandingen ble også testet, men resulterte ikke i noen betydelig økning i styrken av materialet. Den nye oppskriften ble også fullskala testet på 3D-printeren. En ønsket styrke ble oppnådd etter at printerinnstillingene var justert, men det endelige produktet

hadde meget dårlig overflatekvalitet. Overflaten ble ikke bedre ved å øke lag høyden eller ved å bruke en væske med mindre løsemiddel. På grunne av tidsbegrensninger ble ikke en tredje oppskrift utviklet, men grunnene til den ujevne overflaten er diskutert. Det er konkludert med at kornstørrelsen til PMMA, fyllmaterial til sement forholdet og begrensninger i mulige printerinnstillinger er de mest sannsynlige grunnene til den ujevne overflaten. Den dårlige overflatekvaliteten kan være en av årsakene til at Z Corporation foreløpig ikke har satt materialene til kommersiell produksjon.

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Abbreviations

3D – Three-Dimensional

AUT – Auckland University of Technology

CAD – Computer Aided Design

CNC – Computer Numerical Control

DCP – Direct Croning Process

Dpi – Dots per inch

MgO – Magnesium Oxide

MSDS – Material Safety Data Sheet

NTNU – Norwegian University of Science and Technology

NZ – New Zealand

PMMA – Poly(methyl methacrylate)

RP – Rapid Prototyping

SLS – Selective Laser Sintering

TDP – Three Dimensional Printing

UoA – University of Auckland

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1 Introduction

1.1 Approach

The goal of this project is to investigate different methods of patternless moulding of sand casting that should be usable for ferrous metals. Different material combinations for mould fabrication are looked at. The concept of rapid prototyping will be reviewed and both the advantages and disadvantages of patternless moulding will be considered to find and investigate material mixtures that can be used for sand casting of ferrous metals.

1.2 Background

Rapid Prototyping (RP) is developing quickly and has gone from being a tool for fast product development, to becoming a tool for fast product manufacturing. The early stages of product development is still the most important part of RP and by using methods such as Three Dimensional Printing (TDP), Selective Laser Sintering (SLS), Computer Numerical Control (CNC) machining and others, the cost and lead time for a new product to be introduced into the market will be dramatically reduced [1].

Patternless moulding is a RP process where the steps of creating an actual pattern of wood, urethane, etc. are skipped and the desired shape is printed into a sand mould. It is a very flexible method because the shape is stored as a Computer Aided Design (CAD)-file and then converted to a printing language. Changes to the product can be made quickly and efficiently with the use of CAD, without compromising the accuracy or quality of the product. Changes can be made close to deadlines and milestones without causing critical delays in the project. Time to market for low volume and prototype products is therefore at least cut in half [2].

The advantages of patternless moulding are:

- Turnaround time is much less than for new pattern development.
- No pattern storage, maintenance, or tracking.

- Cost-effective solution for R&D projects.
- Quick modifications for shrink factors related to different alloys being poured into the same mould design.
- No tooling wear or repair.

The initial materials and chemicals investigated in this thesis are found in the Z Corporations patent *Three Dimensional Printing Material System and Method* [3]. This material has not been commercialised yet, so this project will mainly focus on investigating if this composition is suitable for sand casting of high temperature molten materials, and to clarify any material property reasons why this material might not be suitable for commercialisation. By investigating the material mixture on both small- and full-scale, the properties of the composition will become clarified. Since there is no existing material that can be used for printing three-dimensional moulds for high temperature materials on the marked, hopefully this project can help to develop such materials. The target is thus to make working sand casts that can be used to produce prototypes, "engineer-to-sell" products and low quantity/luxury products much faster and cheaper than existing prototyping methods.

1.3 Theory

1.3.1 Three Dimensional Printing

Z Corporation is an American company and one of the most important producers of three-dimensional printers and printing materials. Their printers can have a resolution of 600 dpi, a layer thickness from 0.089 to 0.2 mm and a maximum vertical build speed of 28 mm/hour. The biggest build size is 254 x 381 x 203 mm [4]. See Figure 1 for a picture of the printer.

The principle of the Z Corporation printers is a TDP technique that uses an ink-jet printing head to deliver a liquid binder to a layer of a powdered material. The powder material is delivered to the surface by a counter-roller, which lays a new layer after the printing head has delivered the binder to a pre-determined pattern on the cross section. The pattern is generated by a CAD-file. The binder infiltrates the porosity in the powder material and hardens to bond the material. The hardened binder also bonds each layer to the previous one. This process is repeated for each cross-layer until the final article is formed [3], see Figure 2 for a schematic overview.

Figure 1. The ZPrinter® 310 Plus [4].

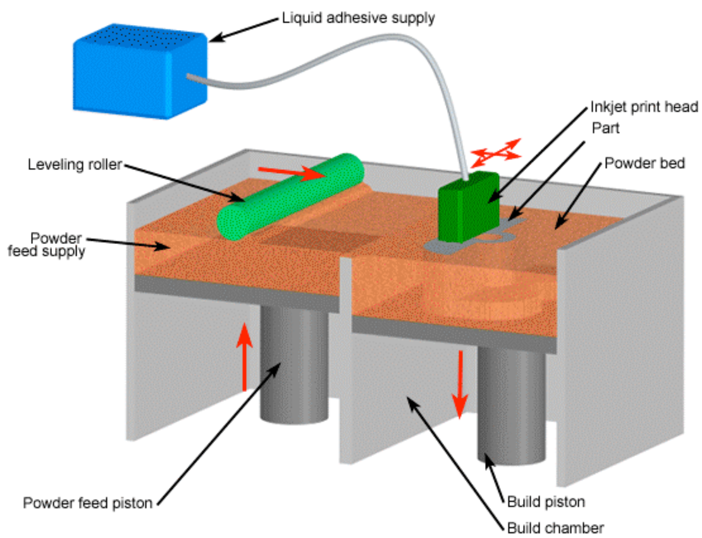

Figure 2. Schematic overview of how TPD works [5].

The Z Corporation patent "*Composition For Three-Dimensional Printing Of Solid Object"* [6] gives a general view of what the particulate formulation and fluid should contain. The particulate formulation should contain a filler material and also in most cases an adhesive component. The material can also include a fibrous component to add strength and printing aids to reduce edge curling and other forms of distortions. The activating fluid should include an additional adhesive and/or a solvent for activating the adhesive. It can also contain printing aids as a humectant to retard evaporation of the solvent from the printed material and prevent clogging of the print head, a flowrate enhancer to alter the hydrodynamic properties and wetting characteristics to maximize the volume of fluid delivered by the print head and a dye which is proposed to provide contrast between activated and unactivated powder. The fluid activates the adhesive in the particulate formulation, adhesively bonding the material together to form a solid final article [6].

1.3.2 Other methods for rapidly making sand moulds

The Direct Croning Process (DCP) uses a SLS process with polymer-coated sand. SLS uses a laser to melt the polymers and make the sand stick together, see Figure 3. This process requires a lot of energy. The mould is fragile when the supporting sand is removed hence the mould needs to be post cured to be used with high temperature alloys like steel and grey cast iron. This process is therefore slower and more expensive than TDP [7].

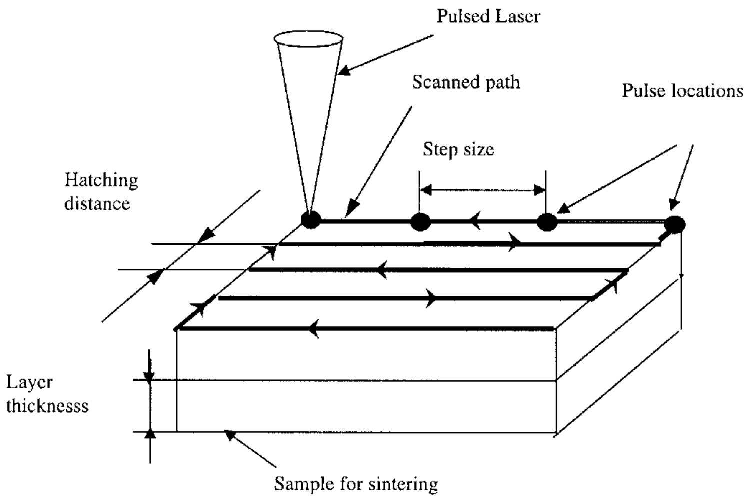

Figure 3. A schematic diagram showing the process parameters of DCP [8].

The ConiferRob® technique produces a mould directly from a CAD model, but it differs from the DCP in that it machines the mould directly from a block of moulding sand, see Figure 4. This process has to make the mould in two halves, hence it cannot have integrated cores. This process is much faster than traditional mould making, but due to the preparation time needed for preparing instruments before starting the process, it is slower and need more work hours and attention than TDP [9].

Figure 4. The ConiferRob® technique in progress [9].

1.3.3 Sand casting

Of all cast products, sand casting produces the most tonnage. This method is advantageous because of its design possibilities and cheap production cost when larger quantities are made. There are many different ways of making the sand stick; the most commonly used approach is a fine grade of sand (smaller than 150 μm) mixed with clay and other adhesives. Chemical binders, oils and carbon dioxide can also be used to make the sand more adhesive [10.1].

In this research, the no-bake mould method has the most resemblance and relevance to the physical effects occurring in TDP. No-bake moulding involves mixing of two or more chemicals with sand to form a filled mould that cures or air-hardens within few minutes at room temperature. One of the chemicals must be a catalyst or hardener to make the resin binder undergo a chemical reaction, binding the grains to bind together and thus cure the mould. Variables such as temperature, reaction rate between the chemicals and humidity, affect the work time and strip time. Work time is the period during which the sand mixture can be used to produce a satisfactory mould and strip time is the time after mixing when the pattern can be removed [10.2].

There are several important material properties to a sand mould that have to be considered when making a mould material, the most important properties with relevance to this projects are:

- *Permeability* is the ability of the mould material to allow steam to pass through the walls. It is measured with an apparatus that measure the volume of air that passes through a test specimen per minute under a standard pressure. Good permeability is important cause it allows trapped gas to escape. Trapped gas can decrease the surface and material quality [10.3].
- *Compressive strength* is the maximum strength that the mould material can hold without a predefined amount of deformation when subjected to compression. High compressive strength is important to withstand the

pressure exerted when the high temperature material is poured into the sand mould [10.4].

- *Refractoriness* is the ability of the moulding sand to withstand high temperatures without fusing or breaking down. Sand used for casting steel must therefore be more refractory than for materials with lower melting temperature. Naturally bonded sand contains appreciable amounts of fluxing agents that lower the fusion point of the sand. There are different methods of testing refractoriness. The instruments for testing it are very costly, but it can also be tested by a so called step pattern method where molten brass or bronze is poured over a test mould with different thickness (i.e. in a step pattern, see Figure 5). If the surface layer of the mould peels on one of the steps after the cast is removed the thickness of the mould has to be larger than the thickness where it peeled [10.5].

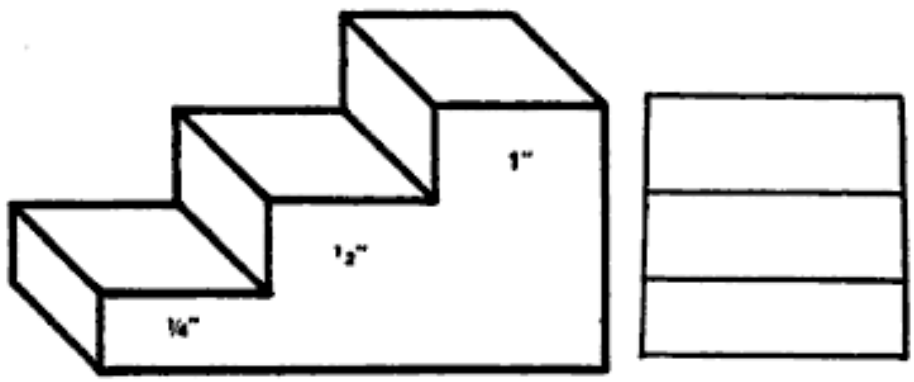

Figure 5. The step pattern method, the molten material will be poured over the steps [10.5].

1.4 Method

In this report sand is used when referring to the particulate formulation. Fluid is used when referring to the fluid mixture that is added to the sand to activate the adhesive factors. Material mixture is used when referring to the resulting material when the sand and fluid are mixed. Final product is used for the resulting product when printing an object on the 3D-printer from a CAD-file.

To print a mould there are different properties that have to be considered, some of these are, but not limited to:

- When mixing the sand and the fluid the final product should have as little shape distortion from the original shape as possible.
- The sand must have a fine size grade to able the counter-roller to make thin and even layers.
- The fluid must not damage the ink-jet printing system, i.e. the fluid should not be acidic (pH should be between 4,9 and 10,3), not contain a sufficient amount of solvent to dissolve the polymer components, and cannot contain particles that crystallize in the nozzle [11].
- The final product must withstand temperatures up to 2000 K. The mould cannot contain any material that will burn when subjected to the high temperature of the molten metal, since this will make the sand mould unusable and potentially dangerous.
- The final composition must have a high compressive strength and permeability. This is explained further in the theory section of this dissertation.

1.4.1 Fluid and sand mixture composition

From the patent “Composition For Three-Dimensional Printing Of Solid Objects” [6] the sand mixture has to consist of an adhesive and some kind of filler and/or fibres. Printing aids can also be added. The fluid has to consist of a solvent and/or a water-soluble adhesive, but a humectant, flowrate enhancer and dye can also be added to improve the properties of the final composition [6].

From the Z Corporation patent "Three Dimensional Printing Material System and Method" [3] there are two sand mixtures and one fluid mixture (see Table 1 and 2) that are said to work with high temperature molten metals like brass, cast iron and steel. This approach was investigated in this thesis by various experiments to determine if the final composition can be used for the said purpose.

Table 1. Overview of the ingredients and their purpose in the sand mixtures as described in the Z Corporation patent [3].

Purpose	**Sand mixture 1**	**Sand mixture 2**
Filler material	Zircon	Olivine
Cement (Adhesive)	Magnesium oxide and monocalcium phosphate	Magnesium oxide and monocalcium phosphate
Forming stronger bonds (Adhesive)	Octacrylamide/acrylate/ butylaminoethyl methacrylate copolymer	Octacrylamide/acrylate/ butylaminoethyl methacrylate copolymer
Flow of power during spreading and printing (Aids)	Zinc oxide, limestone and ethylene glycol octyl/decyl diester	Ethylene glycol octyl/decyl diester and sorbitan trioleate
Fine powder additive (Aids)	Zinc oxide	Zinc oxide and fused silica

Table 2. Overview of the ingredients and their purpose in the fluid as described in the Z Corporation patent [3].

Purpose	**Fluid mixture**
Activating the adhesive (Solvent)	Water
Dissolving the copolymer (Solvent)	2-amino-2-methyl-1-propanol
Facilitate wetting of the fluid in the powder (Flowrate Enhancer)	Isopropanol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate

2 Testing

2.1 Preparation

2.1.1 Materials needed

For reasons of testing and time constraints, this project only will investigate "Sand mixture 1" (see Table 1) since this has the least amount of materials. The materials and chemicals needed for the sand and fluid are listed below.

Sand: Zircon, magnesium oxide, monocalcium phosphate (anhydrate), octacrylamide/acrylate/butylaminoethyl methacrylate copolymer
zinc oxide, limestone (calcium carbonate) and ethylene glycol octyl/decyl diester.

Fluid: Water, 2-amino-2-methyl-1-propanol, isopropanol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate.

2.1.2 Equipment and facilities needed

The equipment needed for testing the material mixture is listed below.

- Lab coat
- Safety glasses
- Neoprene gloves
- Dust mask
- Plastic containers
- Glass bottles
- Mixing equipment
- Syringe
- Scale

The plastic containers, glass bottles and mixing equipment are used for mixing the sand and fluid. The syringe is used to spread the fluid in a way that closely resembles the amount and speed the ink-jet nozzle would have disposed the fluid.

The facilities needed for testing the material mixture are listed below.

- Storing facilities
- Fume cabinet

The laboratory used for the small-scale testing was in the Chemistry department level 2 at UoA. The laboratory has fume cabinets, storing facilities and the required safety equipment available for use.

2.1.3 Safety

Some of the materials are toxic and inhalation can be dangerous hence the need for dust mask and a fume cabinet. Many of the materials are also irritating to skin and damaging to eyes hence the need for lab coat, safety glasses and gloves. Since some of the materials are considered hazardous the equipment has to be cleaned properly after use. The materials also have to be disposed according to the regulations given in the MSDS after the testing is finished. A safe, chilled and ventilated storage facility is important to keep the materials secure and prevent them from opposing a threat to people working in close proximity. Arranging the infrastructure so the test can be performed safely is also important. Material safety data sheet can be found in appendix A.

2.2 Small-scale testing

2.2.1 Materials

The weight proportions of the different chemicals and materials was tested in the same ratio as given in the patent, but with zirconium oxide instead of zircon sand because of long delivery time on the zircon, PMMA instead of octacrylamide/acrylate/butylaminoethyl methacrylate copolymer, because of availability, and ethylene glycol octyl/decyl diester was not included because it would not affect the composition in small-scale testing. The quantity is very low and its purpose is in aiding the printing, thus its absence will not have any effect on a small-scale test. The material experiment table can be found in appendix B. The weight ratios for the first small-scale testing were as shown in Table 3 below.

Table 3. The initial sand and fluid weight ratio.

Ingredients sand	**Weight (%)**
Zirconium oxide	83.90
Magnesium oxide	1.28
Monocalcium phosphate, anhydrate	0.72
PMMA	2,5
Zinc oxide	1.50
Limestone	10.00
Ingredients fluid	
Water	86.50
Isopropanol	10.00
2,4,7,9-tetramethyl-5-decyne-4,7,-diol ethoxylate	1.00
2-amino-2-methyl-1-propanol	2.50

2.2.2 Approach

For the small-scale testing 25 grams of sand material and 10 grams of fluid will be enough to check the initial qualities of the material mixture. The scale used for the tests has an accuracy of 0.01g. Each of the materials were measured separately and then poured into a larger container where it could be evenly mixed. The fluid ingredients were mixed together in a measuring cylinder, and a pipette was used to measure the amount accurately. All of the chemicals were poured into an airtight glass bottle and then shaken to mix the fluid composition.

For testing the material mixture the fluid was put in a syringe and then rapidly sprayed onto the sand, to mimic the movement of the printer ink-jet head. The sand then had to settle for 45-60 minutes and the results were observed. If the material mixture had any clear signs of distortion or did not have enough strength, it is not suitable for three-dimensional printing. The results were documented during the testing by taking notes, timing observations and taking pictures.

2.2.3 First small-scale test trial

For the first test the ingredients were as close to the patent recipe as possible, from the materials available at the time. The recipe used for the test trial are listed in Table 4 and 5:

Table 4. The sand ingredients.

Sand ingredients	Weight (%)	Weight (gram)
Zirconium Oxide	83.98	20.98
Magnesium oxide	1.28	0.32
Monocalcium phosphate, anhydrate	0.72	0.18
PMMA	2.50	0.63
Zinc oxide	1.50	0.38
Limestone	10.00	2.50
Total	100	25.00

Table 5. The fluid ingredients.

Fluid ingredients	Weight (%)	Weight (gram)
Water	86.50	8.65
2-amino-2-methyl-1-propanol	2.50	0.25
Isopropanol	10.00	1.00
2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate	1.00	0.10
Total	10.00	2.50

After mixing the sand it was put on a Petri dish and the fluid was spread on it. The result was hard to observe because it was difficult to get a thick layer and an even surface before applying the fluid, see Figure 6. The solution to this was to fill the sand in a small lid to the rim and even out the surface (see Figure 6 and 7), which gave clearer results.

Figure 6. The material mixture on a petri dish.

Figure 7. The material mixture in a lid.

The material mixture was also tested with parts of the lid covered to get an even split between the fluid covered part and the dry part, to test for any shape distortion. The results were unclear, but the surface seemed to get small dimples and the fluid spreading was slightly uneven. This was most likely because the syringe gives bigger droplets and more volume per unit time unit, resulting in a more random distribution of the fluid. The strength of the material mixture was not satisfactory, it had little to no adhesive strength.

2.2.4 Investigating the polymer cement

As the polymer had to be been changed, the next step was to see if PMMA would dissolve in the 2-amino-2-methyl-1-propanol solvent, since this was supposed to dissolve the octacrylamide/acrylate/butylaminoethyl methacrylate copolymer. After mixing just PMMA and the solvent it was apparent that the polymer was not dissolving. This could be due to the polymer not being the same as in the patent, or because of larger grain size of the PMMA at about 0.7-1mm.

The polymers failure to dissolve could be one of the reasons why the material mixture was mechanically weak. To find the answer to this problem, milling the pellets to get a smaller grain size and finding a different solvent to dissolve the new polymer was investigated. After consultation with Professor Allan Easteal he suggested that the solvent should be changed to carbon tetrachloride.

The machine used for milling the PMMA was a Mortar Grinder RM 200, the fastest method for milling small amounts of material. The material is placed in a mortar like bowl on top of the machine. Then a heavy and hard metal pestle (about 5 cm in diameter) is placed on top of the material, see Figure 8. When the lid is locked on the machine, it can be started and the pestle will start turning, making the material roll and skip around under the pestle, steadily crushing it into a fine powder. The machine has a time and amplitude setting, in this test the amplitude was set to 100 min^{-1} and the timer to 15 minutes. Only about 1 gram of material can be milled at a time.

Figure 8. The mechanism of the Retsch RM 200 Mortar Grinder [12].

2.2.5 Second small-scale test trial

For the second round of small-scale testing, the first step was to see if finer grain PMMA dissolves in carbon tetrachloride. It seem that this had some effect on the polymer, without completely dissolving it, at least not in a reasonable time. The next small-scale test was done following the same procedure and same recipe, except for replacing the 2-amino-2-methyl-1-propanol with carbon tetrachloride in the fluid mixture. This did not have any observable effect on the strength of the material mixture.

The next step was to increase the amount of polymer in the sand mixture and otherwise proceed in the same way. This was done because the grain size of the PMMA still was larger than the 75 µm described in the patent, and larger grains will have a poorer distribution in the sand, decreasing the strength of the mixture. The polymer is one of the strengthening ingredients in the sand through being dissolved and creating polymer cement. By adding more polymer the strength of the material increases, giving the mixture a better chance to sustain shape and mechanical integrity. However these changes did not seem to have any major effect on the material mixture and it was still too weak to be used for moulding.

2.2.6 Changing the solvent

An article on dissolving PMMA [13] was found when investigating reasons for the poor strength of the material mixture. In this document, "Solubility of Polymethyl Methacrylate in Organic Solvents" [13], the dissolution rate of PMMA has been documented in several different solvents. Because the fluid should be environmentally and user friendly, the fluid mixture cannot contain highly toxic ingredients, it is important that the solvent is not threatening to the environment and can be disposed of in an environmentally friendly way. The chemicals from the article were discussed with Professor Allan Easteal to find the best suited solvent that would make the sand-fluid mixture strong enough to sand-cast high temperature metals and that also is relatively nonhazardous. Professor Easteal recommended ethyl acetate (see Table 6) because of its environmentally and user-friendly properties, even though it dissolves PMMA slightly slower than trichloroethylene, which had the fastest rate (see Table 6).

Table 6. Degree Q of PMMA dissolution in organic solvents at 30°C [13].

Solvent	**Q, wt %, at indicated time, min**							
	10	**20**	**30**	**40**	**50**	**60**	**90**	**120**
Benzene	10.4	18.9	25.2	29.2	34.7	38.6	49.9	68.5
Toluene	5.2	11.8	15.5	18.7	21.4	23.1	29.7	40.0
o-Xylene	3.1	4.9	6.1	7.3	8.7	9.2	11.3	15.5
m-Xylene	11.8	13.5	14.6	16.7	17.8	19.5	26.2	27.3
Trichloromethane	0.3	1.1	1.2	1.4	1.8	2.0	3.4	4.0
Trichloroethylene	35.8	65.7	88.4	96.0	100	100	100	100
1,4-Dioxane	5.3	10.6	14.4	17.2	19.7	21.6	27.2	37.9
Cyclohexanone	13.6	24.6	31.7	45.2	53.1	65.0	73.2	77.3
Acetophenone	8.0	14.0	18.1	21.0	23.1	25.8	31.9	45.6
Ethyl acetate	19.7	36.6	48.1	56.7	64.3	71.9	89.5	100
Pentyl acetate	2.2	3.2	4.5	4.8	5.4	6.1	7.2	8.5
Dimethylformamide	6.7	18.7	26.1	33.4	38.7	45.8	61.8	84.7

The ability of ethyl acetate to dissolve PMMA was tested in an isolated environment and without sand particles. A small amount of PMMA was put in a small glass bottle and ethyl acetate was filled up to completely cover the polymers. The lid was sealed and it was set to dissolve for 2 hours at a room temperature of 22 deg C. In addition the degree of dissolving was documented after 60 and 90 minutes. After only 60 minutes it looked like most of the polymer was dissolved and after 90 minutes it was completely dissolved. After two hours the polymer had become a viscous gel instead of the hard polymer pellets. This reaction happened relatively fast, and it is likely that this solvent can be used for dissolving the PMMA, and hence increases the adhesive qualities of the material mixture.

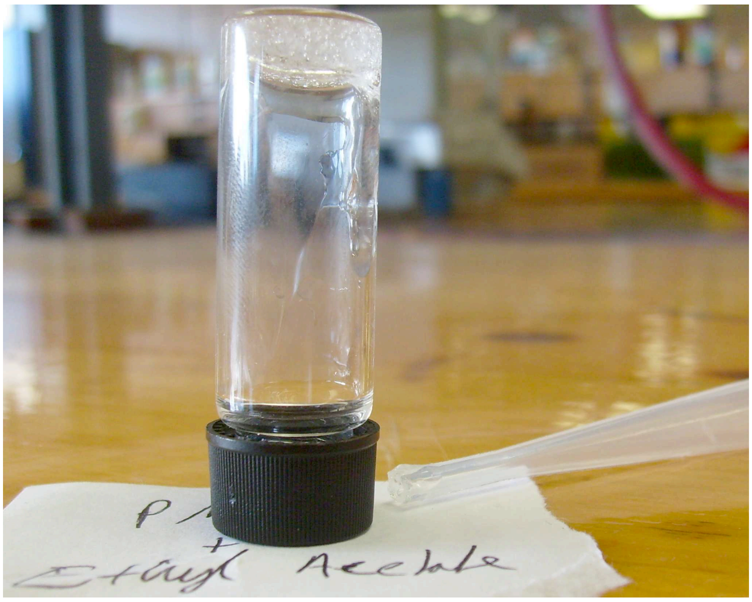

Figure 9. Dissolved PMMA, the PMMA pellets have dissolved into a slow flowing gel.

2.2.6 Third small-scale test trial

The third round of testing included the zircon and ethyl acetate as the only components changed from the previous small-scale testing and the same standard procedure as described in section 2.2.2. Zircon was replaced with zirconium oxide and ethyl acetate with carbon tetrachloride. In this round of testing the material mixture still did not seem to have any observable shape distortion, but the strength of the material was still too weak. The material held together, but not strong enough to safely transport the mould out of the printer and remove the unwanted sand without the final product breaking.

2.2.7 Concentration of ethyl acetate

From investigating the material mixture it was clear that the polymer still was not adequately dissolved. This could be because polymer and solvent was changed from the original recipe in the patent and hence just 2.5 % of the solvent was not enough to dissolve the PMMA. To find the critical amount of solvent in the fluid to dissolve the polymer the ethyl acetate water ratio was tested with 2.5, 5, 10, 25, 50 and 100 % ethyl acetate. PMMA was put in a bottle and enough ethyl acetate/water mixture was added to cover the grains. It was set for 2 hours in 22 deg C room temperature to see how much solvent was needed to dissolve the polymer. From the test 2.5 and 5 % concentration did not dissolve the PMMA, with 10 % the polymers was partially dissolved and had somewhat started to glue together and with 25 % it was almost completely dissolved. At 50 % the mixture had completely dissolved and become a thick viscous fluid. So in this regard 25 % would be enough to dissolve the fine mesh PMMA. This can be seen in Figure 9.

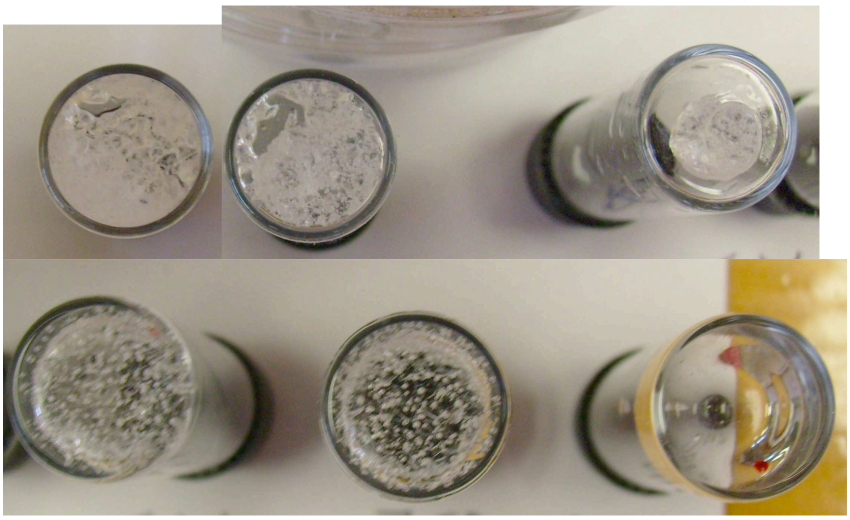

Figure 10. PMMA dissolved in various concentration of ethyl acetate, from top left 2.5, 5 and 10 % and second row from left 25, 50 and 100 %.

2.2.8 Grain size of the PMMA

Another problem with big PMMA grains is that they will have an uneven distribution in the sand mixture, compared to finer grains. Instead of having many small polymer grains in-between the zircon sand particles, the polymer particles will be dispersed as big grains with relatively large distances between them. This will affect the accuracy and the uniformity of strength of the material mixture. Therefore in the new mixture the amount of polymer was increased from 2.5 % to 10 % to make sure there was a good enough distribution of polymer to hold the sand together uniformly. To make up for the increase in polymer the amount of zircon sand was decreased.

2.2.9 Fourth small-scale test trial

For the next test the composition was changed to 25 % ethyl acetate, replaced with water, and 10 % PMMA. With these changes in the composition the sand became slightly stronger, but still not nearly good enough for moulding. A lot for the polymer PMMA was clearly not dissolved. Hence fluid composition with 30 %, 40 % and 50 % ethyl acetate was tested. Neither of these tests made the material mixture stronger in any notable way. Trying with just ethyl acetate did however make the material mixture much stronger, but it seemed like this fluid mixture decreased the surface quality. The reason for this is that the solubility of ethyl acetate in water is 1 ml/10 ml at 25 deg C [14], hence most of the ethyl acetate will not dissolve in the water and it will instead float on top of the fluid mixture. This is not desirable since when the fluid is in the printer, at a percentage of ethyl acetate over 10 %, this will float on top in the binder bottle and not be distributed onto the sand. However having just 10 % solvent in the fluid is desirable because it will be of less risk to the environment, equipment or the operators.

2.3 Full-scale testing

2.3.1 Preparation

Because of the inconclusive results from the previous small-scale testing, the next step was to try the material and fluid in full-scale, to see if printing of the fluid would have any effect on the material mixture and to get a better understanding of the printing qualities of the material. The sand and fluid was tested on a Z Corporation Zprinter 310 plus. When using a syringe and scaled-down test there are many factors that will affect the mixture. The material mixture from the small-scale testing could be weaker than full-scale testing because of difference in fluid deposition. From the small-scale testing it was also difficult to conclude if there was any shape distortion. After consultation with the staff at the Centre for Rapid Product Development at AUT, the sand and fluid recipes were accepted to be used in the printer. The 10 % ethyl acetate fluid composition was considered not to be a threat to damage the instruments and jets, or to dissolve the binder bottle or tubes that were carrying the fluid.

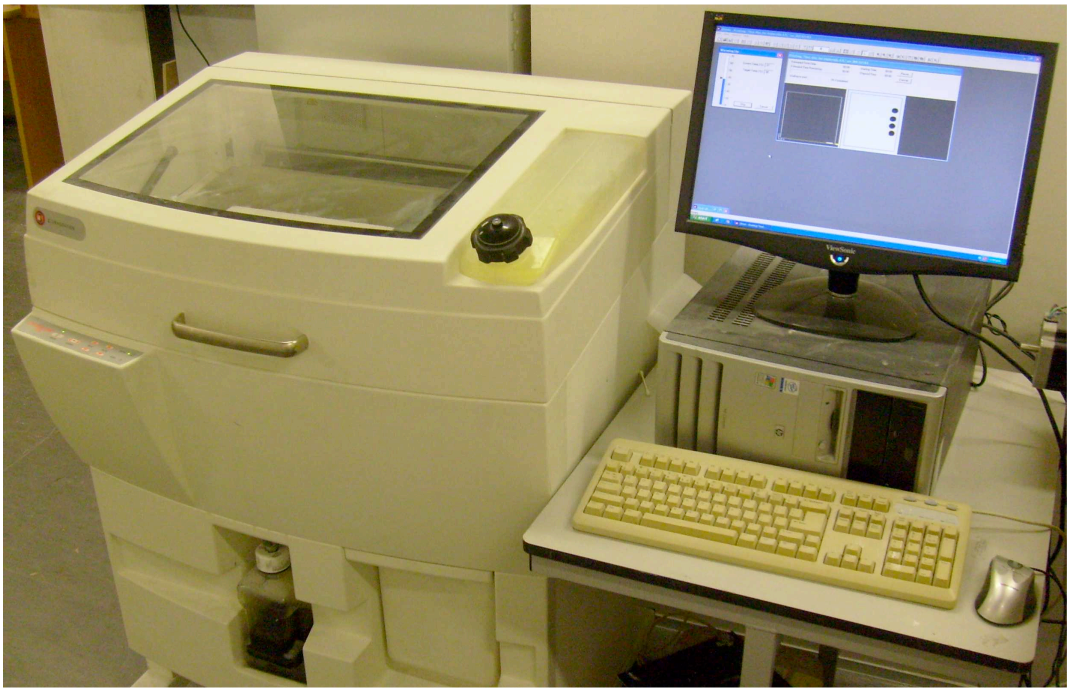

Figure 11. The 310 plus printer and the computer used for the full-scale testing.

The amount of sand needed to fill the 200x200mm sand container to a height of at least 60mm, is 2400 cm^2. The bulk density of zircon sand is 2.7 g/cm^2 [15]. Zircon is the material that has the highest density and weight percentage of the sand mixture. To make a safe estimate of the sand needed we assume that the sand only contains zircon. The amount of sand needed is therefore 2400 cm^2 * 2.7 g/cm^2 = 6480 grams of sand, rounded up to 7 kg for the full-scale recipe. The amount of fluid needed is about 1000 ml ~ 1 kg. This results in the full-scale recipes in Table 7 and 8.

Table 7. Full-scale recipe for the sand.

Ingredients sand	Weight (%)	Weight (grams)
Zircon	80.00	5600.00
Magnesium oxide	1.28	89.60
Monocalcium phosphate, anhydrate	0.72	50.40
Poly(methyl methacrylate)	6,40	448.00
Zinc oxide	1.50	105.00
Limestone	10.00	700.00
Ethylene glycol	0.10	7.00
Total		7000.00

Table 8. Full-scale recipe for the fluid.

Ingredients fluid	Weight (%)	Weight (grams)
Water	79.00	790.00
Isopropanol	10.00	100.00
2,4,7,9-tetramethyl-5-decyne-4,7,-diol ethoxylate	1.00	10.00
Ethyl acetate	10.00	100.00
Total		1000.00

For the full-scale recipe 6.4 % of PMMA was chosen because grain size still was larger than the 75 µm that was recommended in the patent. So to be sure that the distribution of the polymer would be the same if the PMMA had a finer mesh size the weight percent was increased from 2.5 to 6.4 %. Since a larger amount of PMMA was needed for the full-scale testing a Retsch DR 100 hopper was used with a Retsch SM 2000 cutting mill for milling the PMMA, see Figure 12. The pellet size was cylindrical with a diameter of 2 mm and a height of 3 mm. The filter mesh size was 0.5 mm, the minimum mesh size for this machine. However most of the milled PMMA will have a smaller grain size since it has to fall through the holes in the filter, the material having a typical grain size of 200-300 µm. In this machine, about 1 kg can be milled at the same time, but the process was

Figure 12. Retsch SM 2000 cutting mill [16].

relatively slow, taking about 4 hours to mill 1 kg. Other than the change in PMMA and the polymer solvent the recipe was almost identical to the one described in the patent.

2.3.2 Printing

After mixing the material for full-scale testing some of the ingredients in the sand that were older had started to clump together. Sieving the sand and crushing the remaining clumps fixed this. Then the printer had to be cleaned and the sand had to be changed. The fluid also had to be changed and the remaining fluid in system had to be bled out. The next step was to make a fine layer of the sand to prepare for the printing, see Figure 13. A rectangular cube was used as the test object. The printer settings had to be configured before printing could proceed.

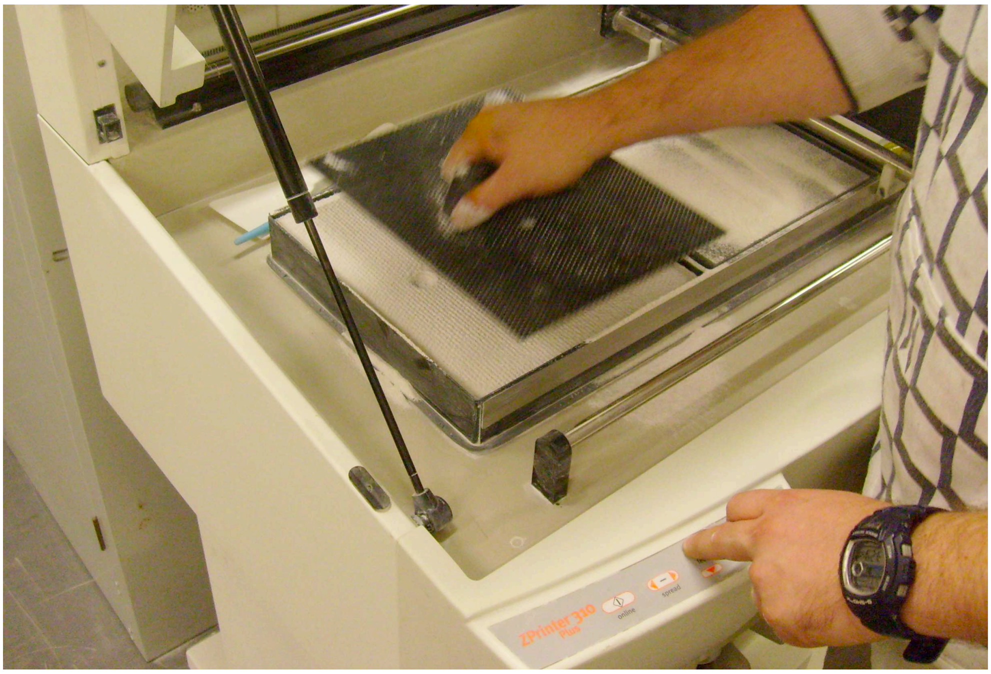

Figure 13. Spreading of the sand in the printer.

For the first test the Zcast 510 material settings were used, for the second test the Zp® 150 material was used and in the last test the same material settings were used, but with overnight drying. The spreading of the sand layers went seemingly without any problems, the spreading of the fluid was good and the final product did not seem to have any significant distortion, but the strength of the material and surface quality were not satisfactory, see Table 9. The surface quality rating is relative, the final product should have 4 or more (out of 5) to have a surface even enough to be used in casting.

Table 9. The results from the first full-scale testing trial.

Test	**Temperature (deg C)**	**Drying time (hours)**	**Saturation (% of full)**	**Strength**	**Surface Finish (1-5)**	**Distortion**
1	22	1	60	not acceptable	2	Some
2	38	2	100	not acceptable	2	Some
3	38	20	100	not acceptable	2	Some

2.4 Changing the recipe

2.4.1 Investigating

Since ethyl acetate only dissolves about 10 % in water adding of other solvents were investigated. By testing the 2-amino-2-methyl-1-propanol solvent from the patent mixed with just PMMA it was observed that it was dissolving the polymer, but at a much slower rate than ethyl acetate. However testing 2-amino-2-methyl-1-propanol is miscible in water meaning that all of it will mix in the fluid [17]. In the next test the same sand composition as used in the full-scale printing was tested, but with fluid compositions: just water, the normal composition (see Table 8), just ethyl acetate and the normal composition with 2.5, 5 and 10 % 2-amino-2-methyl-1-propanol added replacing some of the water. None of these compositions gave any notable increase in strength from the full-scale testing, except for the 100 % ethyl acetate which resulted in a fairly hard material mixture.

Investigated next was using the MgO/monocalcium phosphate cement as the main strengthening ingredient. By reading trough the patent "*Composition For Three-Dimensional Printing Of Solid Objects*" [6] and consulting with professor Jim Metson it seemed like the reason for the poor strength to the recipe from the patent [3] was that the adhesive materials to filler ratio were very small compared to what is described in the Composition patent [6]. From this patent it states that the filler composition usually is from 0-80 %, the adhesive from 10-50 % and the reinforcing component 0-20 %. Even though recipes are not limited to this, it was remarkable how it differs from the recipe found for the Zcast material. The filler in this composition was the zircon sand which was at 83.9 % in the original recipe, the adhesive material which was the MgO and calcium phosphate was combined only 2 % and the reinforcing material which was the polymer was only 2.5 %. Hence the strength of the material mixture was weak because of the small amount of adhesive and strengthening materials. The example composition from the *Composition* patent gives an adhesive weight percent of 30 %, filler 50 % and reinforcing 10 %. Using this information a new sand composition was developed, see Table 10.

Table 10. The new sand recipe.

Sand ingredients	Weight (%)
Zircon	57.00
Magnesium oxide	19.20
Monocalcium phosphate	10.80
PMMA	6.40
Zinc oxide	1.50
Limestone	5.00
Ethylene glycol	0.10

2.4.2 Small-scale testing trial with the new recipe

For the initial tests, the magnesium oxide and monocalcium phosphate amounts were increased and the zircon and limestone content were decreased. The new sand was tested with 0 %, 2.5 % and 10 % 2-amino-2-methyl-1-propanol added to the normal fluid composition, 100 % water and 100 % ethyl acetate, see Figure 14. The test with 100 % ethyl acetate as the fluid did have a decrease in strength, however the 100 % water, 0 %, 2.5% and 10 % mixtures all showed similar and significantly improved strength compared to the previous testing. The mixture was however still not strong enough to be used in casting.

Figure 14. The set-up for the test of the new sand with the different fluid compositions, from the top 100 % water, 0 %, 2.5 %, 10 % 2-amino-2-methyl-1-propanol and 100 % ethyl acetate.

2.4.3 Investigating heating the material mixture in an oven

In the cast material patent [3] it is written under the recipe for "Particulate Formulation II" that the monocalcium phosphate/magnesium oxide makes the initial bond and then the mixture can be moved to a drying oven so the polymer can strengthen to further improve its strength. This is not written under the "Particulate Formulation I" used for this report, but both of these sand recipes are made for high temperature casting. "Particulate Formulation II" has olivine sand as filler material, but otherwise these mixtures are very similar, hence the heating process could be used for both mixtures, even if only specified in one of the recipes. For the heating test 0 %, 2.5 % and 10 % 2-amino-2-methyl-1-propanol material mixtures were tested. For the first test the mixture was put in a drying oven at 85 deg C for 2 hours, however a change in the strength could not be detected. Since the hardness/strength testing so far have been by feel of the material, using hardness/strength machines would give a more accurate indicator of small changes in the material, however the material was still too weak and brittle to be used in the machines available at the UoA. In the next test the material mixture was tested at 110 deg C for 2 hours, this did not observably increase the strength either. When testing the material mixtures at 150 deg C however, the material became weaker. After consulting Professor Allan Easteal about strengthening PMMA by heating, he commented that PMMA does not strengthen by heat-treatment because the polymer does not have any cross-linking. Since the PMMA has glass transition temperature at 110 deg C he said that the only way heat treatment could increase the strength would be to heat it at a temperature below the glass transition temperature for a few hours to make the remaining solvent in the material mixture better dissolve the polymer.

2.4.4 Further investigating the magnesium oxide/phosphate cement.

When investigating the magnesium oxide/phosphate cement, an article was found that had reported on the properties of the cement [18]. From the article the optimum mol-ratio between the phosphate (PO_4) and the magnesium oxide (MgO) is 1 to 4 and the mol-ratio between the cement and filler material is 1 to 1. Monocalcium phosphate anhydrate has the composition $Ca(H_2PO_4)_2$ and a mol weight of 234.05 g [19] and magnesium oxide has the composition of MgO and a mol weight of 40.30 g [20]. 3 mol of monocalcium phosphate contains 2 mol of phosphate. This means that when using 3 mol of monocalcium phosphate, 8 mol of magnesium oxide is needed:

$$3:8 \rightarrow 3 \cdot 234.05 : 8 \cdot 40.3044$$
$$702.15 : 322.44$$
$$702.15 + 322.44 = 1024.59$$
$$Ca(H_2PO_4)_2 = \frac{702.15}{1024.59} = 0.685$$
$$MgO = 1 - 0.685 = 0.315$$

This leads to a weight ratio of monocalcium phosphate anhydrate and magnesium oxide of 68.5 %:31.5 %. 3 mol of monocalcium phosphate and 8 mol MgO is needed to make 10 mol cement, the weight of 10 mol cement is 1024.59 gram. Zircon sand has a mol weight of 183.1 g [21]. Since the ratio of sand to cement is 1 to 1 the weight needed to make 10 mol zircon sand is 183.1*10=1831 gram. The zircon sand to cement weight ratio is:

$$Zircon = \frac{1831}{(1831 + 1024.59)} = 0.643$$
$$Cement = 1 - 0.643 = 0.357$$

Assuming that the limestone and zinc oxide has sand-like factors, the zinc ratio is held at 1.5 % and the limestone is decreased to 5 %, since its purpose is to have small particles to enhance the printing. For the next round of small-scale testing the zircon weight percentage was set to 57.2 %. The MgO/phosphate cement was increased to a combined 30.7 %, where 9.7 % was MgO and 21 % was monocalcium phosphate. The polymer has an adhesive factor and will be considered as a cementing ingredient. Hence PMMA was set to 5 % because of the increase in adhesive material. The ethylene glycol level was not changed. Table 11 shows the new sand recipe.

Table 11. Sand recipe with modified MgO/phosphate cement ratio.

Sand ingredients	**Weight (%)**
Zircon	57.20
Magnesium oxide	9.83
Monocalcium phosphate, anhydrate	21.37
PMMA	5.00
Zinc oxide	1.50
Limestone	5.00
Ethylene glycol	0.10

2.4.5 Second small-scale testing trial with the improved recipe

When small-scale testing the new material mixture, it was notably stronger than the previous compositions (see Figure 15) and considered satisfactory enough to be tested on the 3D-printer. For the full-scale test more monocalcium phosphate had to be ordered, but since the anhydrate version was much more expensive and had a longer ordering time the monohydrate version was ordered. The material was dried in an oven for 20 hours at 80 deg C to remove most of the water hence making it more similar to monocalcium phosphate, anhydrate. Monocalcium phosphate, monohydrate has a melting temperature at 109 deg C [22] so the temperature had to be significantly lower than that, not to risk decomposition of the material.

Figure 15. Picture from small-scale test with the improved material mixture to the left and from the small-scale testing with the first recipe (see Table 4 and 5) to the right.

2.5 Full-scale testing with the new recipe

To find how much material was needed for the full-scale testing the sand used for the small-scale testing was measured in a measuring tube and weighted to find its bulk density. 10.168 gram of the material resulted in 11ml or 11cm^3, this gives a density of 10.18g/11cm^3=0.925g/cm^3. Since 2400cm^3 of sand is needed the mixture should be at least 0.925g/cm3 * 2400cm^3 = 2221 gram, this was increased to 4000 gram. The materials were blended full-scale with the same preparations as the first full-scale test. The ingredients and weights are listed in Table 12. In addition to this formulation, a very small amount of food colouring was added to the fluid to observe the printing and spreading more accurately.

Table 12. Sand recipe for second full-scale testing trial.

Sand ingredients	**Weight (%)**	**Weight (grams)**
Zircon	57.20	2308
Magnesium oxide	9.83	388
Monocalcium phosphate, monohydrate	21.37	840
PMMA	5.00	200
Zinc oxide	1.50	60
Limestone	5.00	200
Ethylene glycol	0.10	4
Total		4000

For the first test the Zp® 150 material settings were used and for the second test a custom setting was created (see Table 13) with the Zp® 150 material as a reference material. In the third test a new custom material was used with the Zcast 510 material as a reference material and in the fourth test the same custom material settings were used but with increased layer thickness and the solvent content of the fluid reduced to 2.5 %. See Table 13 for more details. For all the tests the material dried for 2 hours.

For these tests three discs and one cylinder were printed as the test shape, see Figure 16. The spreading of the sand layers went seemingly without any problems and the spreading of the fluid was good (see Figure 17). The shape of the final product did not seem to have much distortion and the strength of the material was much better. The strength of the final product was best in the second test with thin layer thickness and full saturation settings. However the surface finish was not good on any of the tests.

Table 13. The results from second full-scale testing trial.

Test	**Temperature (deg C)**	**Layer Thickness (mm)**	**Saturation (% of full)**	**Strength**	**Surface Finish (1-5)**	**Distortion**
1	38	0.100	60	not acceptable	1	Little
2	24	0.100	100	acceptable	1	Little
3	24	0.175	100	not acceptable	1	Little
4	24	0.200	100	not acceptable	1	Little

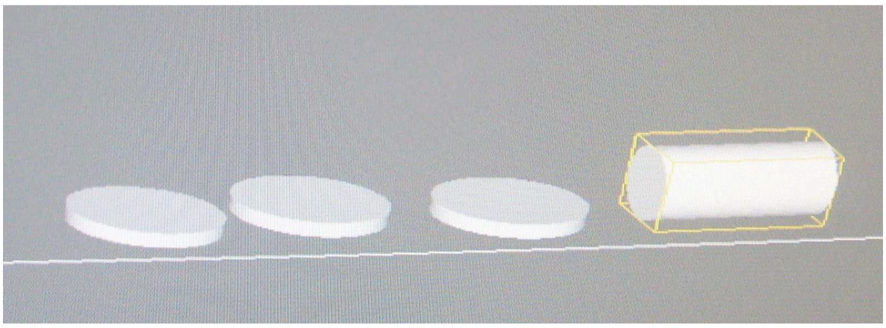

Figure 16. The test shapes used for the second full-scale printing.

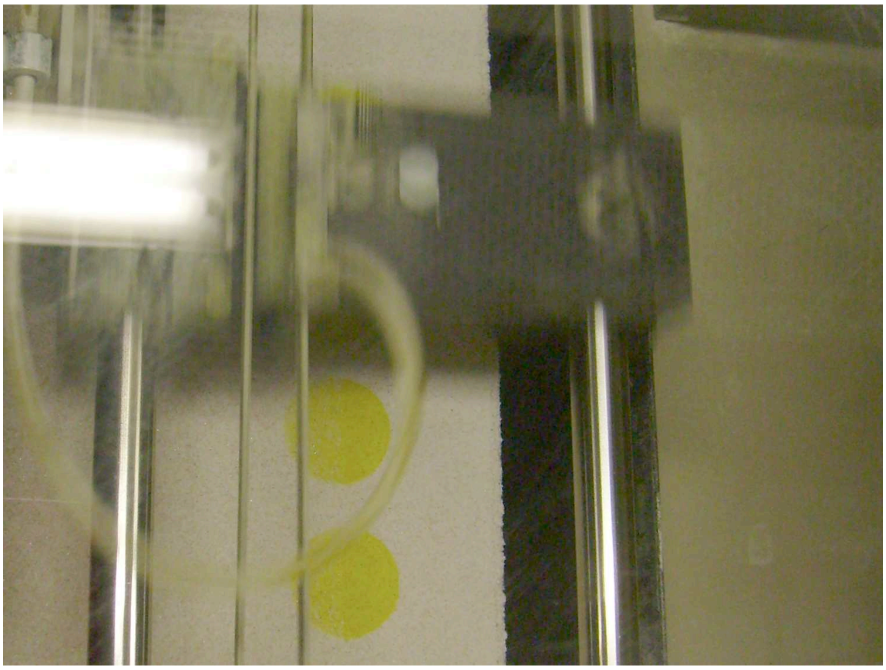

Figure 17. The printing in progress.

3 Results

In the first round of testing, substitute materials were used for the polymer and the zircon sand. Because of availability it was not possible to order octacrylamide/acrylate/butylaminoethyl methacrylate copolymer and it was substituted with methyl methacrylate after consultation with Professor Allan Easteal at the UoA Chemistry department. The zircon sand was replaced by zirconium oxide. The reason for this change was that the zircon sand ordered was of such a high level of purity that it was considered as a risk material and it was held up in customs. The use of the material had to be documented before it received permission to be sent. It took about 8 weeks for the material to get to NZ from the date it was ordered. Because of this the testing proceeded with the substitute materials. In the end the zircon sand had to be ordered from a different company where it could be delivered in a few days. However this order was in larger quantities (20 kg), with lower purity and larger grain size.

When the testing started, the focus was mostly on dissolving the polymer since, from the patent, it appeared to be the main strengthening factor in the material mixture. However the polymer was clearly not dissolving with the 2.5 % solvent in the fluid from the original patent. Hence the solvent from the patent was not an effective solvent for PMMA, after some research it was found that ethyl acetate was the best solvent suited for the task. When testing the solubility of PMMA in ethyl acetate it was found that it started dissolving with 10 % concentration and was fully dissolved with more than 25 % concentration. The problem was that ethyl acetate has the solubility of 1 ml/10 ml at 25 deg C in water so the fluid mixture could not contain more solvent than about 10 %, hence short time after mixing the fluid with more than 10% ethyl acetate it will separate and float on top. This was not observed in the PMMA/ethyl acetate test because the fluid was mixed directly to the PMMA and to the same height. When the material mixture was tested with 10 % ethyl acetate in the fluid the polymer seemed to dissolve at a lower rate or not at all, this was most likely because of the addition of other materials. It was however possible to make a hard material mixture by using just ethyl acetate as the fluid, but this was discarded because of the volatile nature of the solvent.

From the patent it states that the finished sand-cast should be put in the oven to harden after printing. Hence the polymer was supposed to further dissolve when heat-treating the material mixture before casting can be done. Heat-treating was tested, but did not observably increase the strength of the material mixture. This was most likely due to that the PMMA does not have any cross-linking.

After the zircon sand was obtained and small-scale tested, the material mixture was still not strong enough for use in casting. The next step was to full-scale test the material mixture on the 3D-printer to see how this would affect the hardness, shape distortion and surface quality of the product. The results from the printing concluded that the material recipe in the patent would not give a strong enough material. However the primary hardness ingredients turned out to be magnesium oxide and monocalcium phosphate and in the patent those ingredients only summed up to 2 weight percent of the sand mixture. When investigating the magnesium phosphate cement the optimum weight ratio of monocalcium phosphate to magnesium oxide was found to be 68.5 %:31.5 %, not 36 %:64 % as described in the patent, and the sand filler to cement weight ratio to be 64.3 %:35.7 % not 97.67 %: 2.33 % as described in the patent. The patent states: "…all parameters listed herein are meant to be exemplary and actual parameters depend upon the specific application for which the methods and materials of the present inventions are used. It is therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended clams and equivalents thereto, the invention can be practiced otherwise than as specifically described" [3]. It is likely that the example in the patent was not meant for casting, but differs to prevent companies copying the recipe directly.

Therefore new weight ratios were developed and the new recipes were tested. In the small-scale tests with new recipes the material turned out much stronger. Different fluid compositions and heat-treatments were tested to get a better understanding to the new mixture, however they did not affect the strength of the material. When testing this material mixture full-scale the material was weaker and had an uneven surface. The reason for the strength difference from the small-scale testing was most likely due to the saturation setting of the printer. For the next tests the print settings were changed to full saturation. In

Figure 18. The final products being taken out of the printer.

the next test the strength of the material was more similar to the material mixture from the small-scale testing. The surface texture however was not satisfactory. The cause of this is likely that the polymer in the sand has a relatively high mesh 100 – 300 μm and hence the polymer is being dragged over the surface, instead of being deposited on printing areas when the counter-roller is applying the next layer of material. An uneven distribution of the sand was not clearly observed during the TDP. It is however likely that this happens on such a small scale that it cannot be seen and becomes more clear when the final product has dried and been taken out of the printer, see Figure 18 and 19.

The sand and fluid was also tested with 175 and 200 μm layer height (which is the highest setting). In the 200 μm test the solvent content was reduced to 2.5 % to see if this had any effect on the surface finish. However either of these tests increased the surface quality and the final product got weaker. This could be due to the higher layers leads to less total fluid being deposited on the print and hence lesser saturation. The distortion of the print was difficult to observe due to uneven surface, but not large enough to be seen as the main concern for the material mixture. The poor surface finish is the property of the material mixture that needs to be investigated further following the tests done in this project. See Table 14 for an overview of all the tests.

Table 14. Overview of the pros and cons of the various full-scale tests from section 2.3 (recipe 1) and 2.5 (recipe 2).

Full-scale test	**Pros**	**Cons**
Recipe 1 test 1	Good spreading of the sand and fluid, good resolution, cheap sand ingredients and less fluid used.	Poor surface quality and no material strength.
Recipe 1 test 2	Good spreading of the sand and fluid, cheap sand ingredients and good resolution.	Poor surface quality, no material strength and more energy needed to heat the system.
Recipe 1 test 3	Good spreading of sand and fluid, cheap sand ingredients and good resolution.	Poor surface quality, long drying time, more energy needed to heat the system and no material strength.
Recipe 2 test 1	Good spreading of sand and fluid, good resolution and less fluid used.	Very poor surface quality and weak material.

Recipe 2 test 2	Good spreading of sand and fluid, good resolution and strong material.	Very poor surface quality.
Recipe 2 test 3	Good spreading of sand and fluid.	Very poor surface quality, low resolution and weak material.
Recipe 2 test 4	Good spreading of sand and fluid and a more nature and working environment friendly fluid used	Very poor surface quality, lower resolution and weak material.

4 Discussion

There are several factors that are important for materials that will be used for TDP of sand moulds. The balance of the sand and the cementing components, fluid composition and the material grain size, all have to be satisfactory before the material can be used in an industrial setting. These factors and how the material mixtures performed in this project are discussed below.

4.1 Spreading of the material

Both in the first and the second full-scale testing, the material seemed to be spreading satisfactorily. The large grain size of the PMMA can however be a factor in the poor surface on the final print, but this did not seem to be a problem when observing the printing and spreading of the sand. In spite of this at one point in the second test with the new sand recipe, it was observed that some of the sand was being dragged outside the printing area. This was clear from the colouring added to the fluid.

4.2 Deposition of the fluid

During printing the fluid was depositing satisfactory with both the normal composition (see Table 6) and the composition with less solvent. This is probably due to the printing aids added to the material to prevent clogging and give free flow, and that the fluid mostly consists of water that is not harmful to the print system and has good viscosity properties. The low amount of solvent also prevents the fluid attacking the tubing or other plastic parts of the print system.

4.3 Strength of the material

The first round of full-scale testing did not result in satisfactory strength, but with changing the recipe, the material mixture became much stronger and in the second full-scale testing, the strength was acceptable for use in casting. This was not confirmed due to the lack of equipment to test material with this relatively low strength. However according to the director at the rapid prototyping centre, Professor Olaf Diegel, it was strong enough to be removed from the printer and to be transferred to a drying oven for the polymer to further dissolve and/or harden depending on if the polymer used has cross-linking (as described in chapter 2.4.3).

4.4 Shape distortion

In the first test the material was to weak to conclude if there was any shape distortion. In the second full-scale testing the final product was strong enough to be taken out of the print and be observed. However the uneven surface made it difficult to conclude if the distortion of the final product was due to the poor surface quality or distortion. By observing the cylindrical component (see Figure 18) it can be seen that the final product did not display any major distortion.

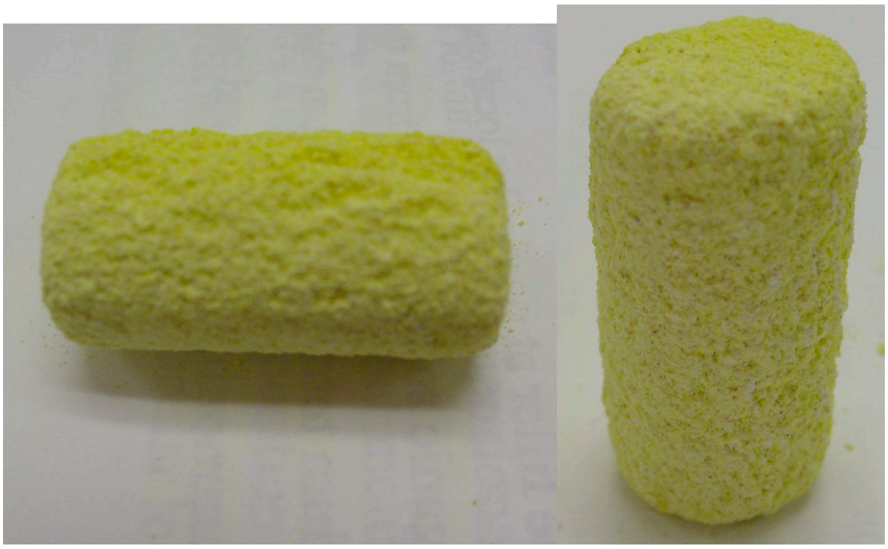

Figure 19. Final product from a cylindrical shape.

4.5 Refractoriness

The refractory properties of these compositions were not tested in this project. The final compositions were not of sufficient quality to be tested with molten metal. However zircon sand is known to have very good refractory abilities and since the sand consists of 57.7 weight percent zircon sand it is likely that the refractoriness of the material mixture will be satisfactory.

4.6 Permeability

This was not tested in this project, and is difficult to conclude without testing it with the instruments described in the theory section.

4.7 Surface finish

The surface on the first full-scale test components seemed better than in the second test. However this was difficult to conclude quantitatively due to the weak nature of the material, but it was not satisfactory for casting purposes. In the second round of testing the surface was clearly unsatisfactory (see Figure 19 and 20) and this property has to be improved with further work and tests with the material. From what has been discovered in this project the poor surface quality of the material was most likely caused by the factors mentioned below.

Figure 20. The printed disc shape form the fourth full-scale test, the poor surface quality can easily be observed.

Too much cement material in relation to the amount of sand material, the 1:1 ratio of cement and sand makes the material mixture stronger, but the phosphate and magnesium oxide cementing reaction could take place unevenly. Hence the large amount of cement material, and its distribution, could be the reason for the uneven surface. The surface quality in the first round of full-scale testing was marginally better than in the tests with the new recipe. This could be because the first sand recipe had less cementing ingredients.

The fluid composition could also be the reason for the uneven surface. Since the sand recipe in the patent was not strong enough for use in casting it is reasonable to assume that the fluid recipe has also been changed. Changing the amount printing aids like isopropanol and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate to optimise the wetting and to control the bleeding of the fluid in the sand could increase the surface quality.

The polymer grain size is likely the most important reason for the uneven surface. If the particle size is larger than the layer thickness of the printing settings the particles will not be distributed along the surface but rather be dragged in front of the roller (see Figure 21) and be dropped in the waste material bin on the end of the print area, which can be seen as an opening on the right side of picture 17 and 18. Even when the layer thickness was increased to 200 μm most of the PMMA still had a larger grain size than 200 μm. Accumulation of larger grains in front of the counter-roller mechanism will cause the surface, on which the sand is being deposited, to be distorted due to the larger grains scraping the surface. The difference from the normal sand and the sand collected from the waste material bin was observed and as it can be seen from Figure 22 the waste material had a higher concentration of PMMA.

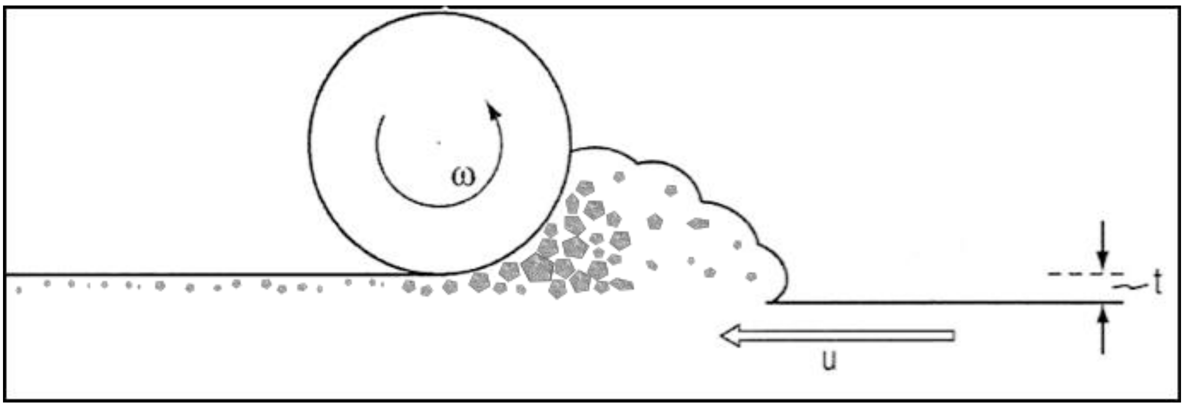

Figure 21. Illustration of a counter-roller cross-section, the grey objects are the accumulated PMMA and t is the layer thickness. ω is the rotation of the counter-roller and u is the movement of the sand relative to the counter-roller.

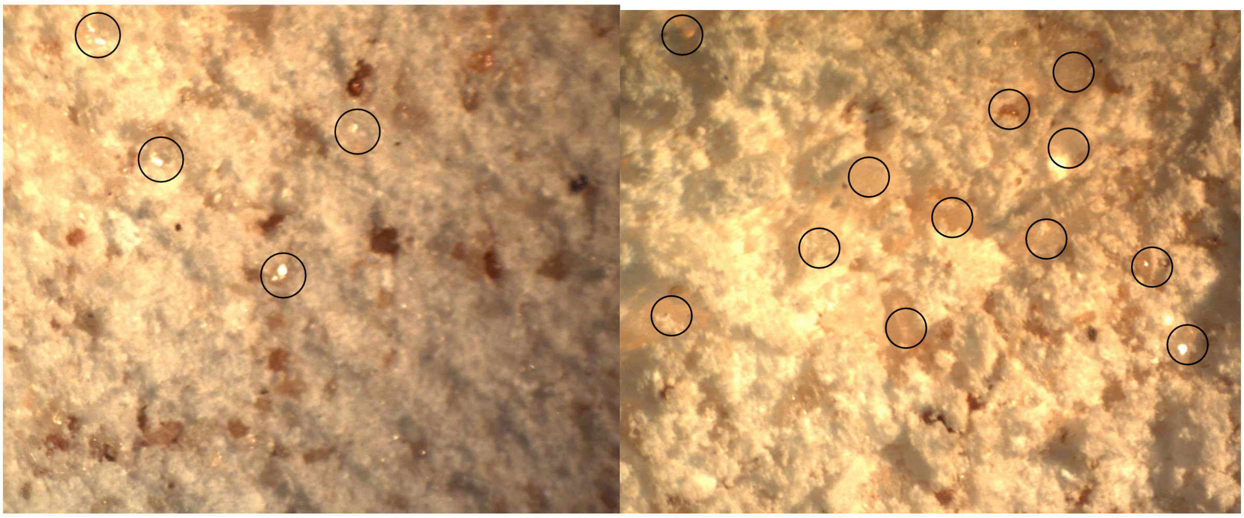

Figure 22. Picture to the left is the sand mixture and the picture to the right is the sand collected from the waste collector at the left side of the printing area. The large transparent grains are the PMMA and they are circled to make them more visible.

The saturation of the material can also be a factor in the uneven surface. Too much saturation can affect the cement settling and drying properties, and hence make a more uneven surface than with less saturation.

The print settings are different for all the Z Corporation materials. There are individual settings for saturation, temperature, layer height, bleeding compensation and more. The reason for the uneven surface could be that the material mixture needs particular settings to make the surface even. This could be printer settings that are outside of those in the current software. This is especially relevant when it comes to the fluid deposition.

5 Conclusion

The main problem with the material mixture developed in this project was the surface quality. For further testing this is the factor that should be considered when further developing the recipes for both the sand and the fluid. The printer settings are also something that should be considered to optimise the printing quality on the final product. For further testing there are several points that should be further investigated to understand the properties of the material and to identify the cause of the poor surface quality:

- Testing the material in full-scale on the printer without the PMMA to see if this will affect the surface finish on the mixture.
- Try different fluid compositions in the full-scale testing to see if adding more printing aids will solve this problem. It may also be possible to remove the PMMA solvent completely to see how this affects the surface quality.
- Making a new sand mixture with more sand particles and less cement particles to see if the amount of cement affects the surface finish.
- Changing the printing parameters to more extreme values. Even though different parameters were tested in this project, there are still many variables that can be changed to optimise the print quality. One option is to see if the variables can be changed outside the existing material parameters (i.e. saturation optimised to the specific material, higher temperatures than 38 deg C and thicker layers >200μm).

These are by no means the only factors that could affect the print quality of the final product, but rather what have been observed in this report and therefore the most likely factors to the poor surface quality. It is suggested that these point should be tested to increase our understanding the properties of the material mixture and develop a better recipe.

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Appendices

Appendix A – Material safety data sheets.

All material data in the following tables are found on the Chemgold Global website using the Chemgold II engine. It is officially used by UOA to find the MSDS on chemicals and materials. Accessed from:

http://www.library.auckland.ac.nz/databases/learn_database/public.asp?record=chemweb

Sand:

Material	Hazard Warnings	Prevention	Response
Zicron	Causes mild skin irritation, causes eye irritation	Wash thoroughly after handling	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, If skin irritation occurs: Get medical advice/ attention, If eye irritation persists: Get medical advice/attention.
Zicronium oxide	Causes skin irritation, causes serious eye irritation	Avoid breathing dust/fume/gas/mist/vapours/spray, wash thoroughly after handling, use only outdoors or in a well-ventilated area, wear protective gloves/protective clothing/eye protection/face protection.	IF INHALED: Remove to fresh air and keep at rest in a position comfortable for breathing, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Call a POISON CENTER or doctor/physician if you feel unwell, If eye irritation persists: Get medical advice/attention.
Magnesium oxide	Causes serious eye irritation, may cause damage to organs by skin contact.	Do not breathe dust/fume/gas/mist/vapours/spray, wash thoroughly after handling, do not eat, drink or smoke when using this product, wear protective gloves/protective clothing/eye protection/face protection.	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, IF exposed or if you feel unwell: Call a POISON CENTER or doctor/physician, If eye irritation persists: Get medical advice/attention.
Monocalcium phosphate (anhydrate)	Causes skin irritation, Causes serious eye irritation, Slightly harmful to aquatic life.	Avoid breathing dust/fume/gas/mist/vapours/spray, Wash thoroughly after handling, Use only outdoors or in a well-ventilated area, Avoid release to the environment, Wear protective gloves/protective clothing/eye protection/face protection.	IF INHALED: Remove to fresh air and keep at rest in a position comfortable for breathing, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Call a POISON CENTER or doctor/physician if you feel unwell, If eye irritation persists: Get medical advice/attention.

Methyl methacrylate homopolymer	May cause allergic or asthmatic symptoms or breathing difficulties if inhaled, May cause allergic skin reaction	Avoid breathing dust/fume/gas/mist/vapours/spray, Use only outdoors or in a well-ventilated area, Contaminated work clothing should not be allowed out of the workplace, Wear protective gloves/protective clothing/eye protection/face protection, In case of inadequate ventilation wear respiratory protection.	IF ON SKIN: Wash with plenty of soap and water, IF INHALED: Remove to fresh air and keep at rest in a position comfortable for breathing, IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing, Call a POISON CENTER or doctor/physician if you feel unwell, If skin irritation or rash occurs: Get medical advice/attention, If experiencing respiratory symptoms: Call a POISON CENTER or doctor/physician, Wash contaminated clothing before reuse.
Zinc oxide	Very toxic to aquatic life, Harmful to terrestrial vertebrates.	Avoid release to the environment.	Collect spillage
Limestone (calcium carbonate)	Nonhazardous		

Fluid:

Material	Hazard Warnings	Prevention	Response
Water	Nonhazardous		
2-amino-2-methyl-1-propanol	Harmful if swallowed, Causes skin irritation, Causes serious eye irritation, Harmful to aquatic life.	Wash thoroughly after handling, Do not eat, drink or smoke when using this product, Avoid release to the environment, Wear protective gloves/protective clothing/eye protection/face protection.	IF SWALLOWED: Call a POISON CENTER or doctor/physician if you feel unwell, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Rinse mouth, If eye irritation persists: Get medical advice/attention.
Isopropanol	Highly flammable liquid and vapour, May be harmful if swallowed, Causes mild skin irritation, Causes serious eye irritation	Keep away from heat/sparks/open flames/hot surfaces. - No smoking, Keep container tightly closed, Ground/bond container and receiving equipment, Use explosion-proof electrical/ventilating/lighting equipment, Use only non-sparking tools, Take precautionary measures against static discharge, Wash thoroughly after handling, Wear protective gloves/protective clothing/eye protection/face protection.	IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Call a POISON CENTER or doctor/physician if you feel unwell, If skin irritation occurs: Get medical advice/ attention, If eye irritation persists: Get medical advice/attention.
2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate	Causes mild skin irritation, Causes serious eye damage.	Wear protective gloves/protective clothing/eye protection/face protection.	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Immediately call a POISON CENTER or doctor/physician, If skin irritation occurs: Get medical advice/ attention.

Carbon tetrachloride	Fatal if swallowed, Causes skin irritation, Causes serious eye irritation, Suspected of causing cancer, Causes damage to organs by skin contact, Harmful to aquatic life, Ecotoxic to terrestrial vertebrates	Obtain special instructions before use, Do not handle until all safety precautions have been read and understood, Do not breathe dust/fume/gas/mist/vapours/spray, Wash thoroughly after handling, Do not eat, drink or smoke when using this product, Avoid release to the environment, Wear protective gloves/protective clothing/eye protection/face protection, Use personal protective equipment as required.	IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, IF exposed: Call a POISON CENTER or doctor/physician, IF exposed or concerned: Get medical advice/ attention, Rinse mouth. If eye irritation persists: Get medical advice/attention.
Ethyl Acetate	Highly flammable liquid and vapour, Causes serious eye irritation	Keep away from heat/sparks/open flames/hot surfaces. - No smoking, Keep container tightly closed, Ground/bond container and receiving equipment, Use explosion-proof electrical/ventilating/lighting equipment, Use only non-sparking tools, Take precautionary measures against static discharge, Avoid breathing dust/fume/gas/mist/vapours/spray, Wash thoroughly after handling, Use only outdoors or in a well-ventilated area, Wear protective gloves/protective clothing/eye protection/face protection.	IF ON SKIN (or hair): Remove/Take off immediately all contaminated clothing. Rinse skin with water/shower, IF INHALED: Remove to fresh air and keep at rest in a position comfortable for breathing, IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing, Call a POISON CENTER or doctor/physician if you feel unwell, If eye irritation persists: Get medical advice/attention.

Appendix B – Material experiment data table.

All material data in the following tables are found on the Chemgold Global website using the Chemgold II engine. It is officially used by UOA to find the MSDS on chemicals and materials. Accessed from:

http://www.library.auckland.ac.nz/databases/learn_database/public.asp?record=chemweb

Sand:

Material	Chemical Formula	MOL weight	Density	CAS-Number	Melting Point
Zicron	$ZrSiO_4$	183.308 g/mol	4.60 g/cm^3	14940-68-2	2823 K
Zicronium oxide	ZrO_2	123.218 g/mol	5.68 g/cm^3	1314-23-4	2988 K
Magnesium oxide	MgO	40.3044 g/mol	3.58 g/cm^3	1309-48-4	3125 K
Monocalcium phosphate (anhydrate)	$CaH_4P_2O_8$	234.050 g/mol	2.22 g/cm^3	7758-23-8	382 K
Poly(methyl methacrylate)	$(C_5H_8)_2)_n$	Varies	1.19 g/cm^3	9011-14-7	433 K
Zinc oxide	ZnO	81.408 g/mol	5.61 g/cm^3	1314-13-2	2248 K
Limestone (calcium carbonate)	$CaCO_3$	100.087 g/mol	2.71 g/cm^3	471-34-1	1098 K

Fluid:

Water	H_2O	18.015 g/mol	1.00 g/m^3	7732-18-5	273 K
2-amino-2-methyl-1-propanol	$C_4H_{11}NO$	89.140 g/mol	N/A	124-68-5	310 K
Isopropanol	C_3H_8O	60.100 g/mol	0.79 g/cm^3	67-63-0	184 K
2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate	$C_{14}H_{26}O_2(C_3H_6O.C_2H_4O)_x$	395 g/mol	0.98 g/ cm^3	9014-85-1	N/A
Carbon tetrachloride	CCl_4	153.82 g/mol	1.59 g/cm^3	56-23-5	250 K
Ethyl acetate	$C_4H_8O_2$	88.105 g/mol	0.90 g/cm^3	141-78-6	190 K

Appendix C – Problem description

THE NORWEGIAN UNIVERSITY
OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF ENGINEERING DESIGN
AND MATERIALS

MASTER THESIS SPRING 2010
FOR
STUD.TECHN. ØYSTEIN HEDEN KÅLÅS

PATTERNLESS DIRECT MOLDING OF SAND CASTINGS
Direkteforming i sandstøping uten fysisk modell

In this thesis an investigation of different methods of patternless molding of sand castings is carried out. The different methods of patterless molding shall be reviewed and special focus shuld be on 3D-printing of molds. These molds should be usable for iron based alloys (like cast iron and steel).

The benefits of the investigated methods for rapid prototyping purposes shall be evaluated.

Practical tests shall be proposed and executed in lab scale if facilities are made available for the student.

The thesis should be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Undervisning". This sheet should be updated when the Master's thesis is submitted.

The thesis shall be submitted as two paper versions. One electronic version is also requested on a CD or a DVD, preferably as a pdf-file.

The contact person is Jim Metson

Ole Ivar Sivertsen
Head of Division

Morten A. Langøy
Professor/Supervisor

NTNU
Norges teknisk-
naturvitenskapelige universitet

Institutt for produktutvikling
og materialer

Appendix D – Problem description changes

Changes in the problem description as discussed over e-mail:

"Hei, Øystein her fra Auckland Uni mail

Fikk følgende mail fra Sarat, hva tror du?

mvh

Øystein Kålås
- Show quoted text -

---------- Forwarded message ----------
From: Sarat Singamneni <sarat.singamneni@aut.ac.nz>
Date: 16 February 2010 15:41
Subject: Re: Project description
To: ykls001 ykls001 <ykls001@aucklanduni.ac.nz>

Hi Oystein,

Looking at the proposal, it seems, the best line of thinking for you is to investigate and find probable materials for 3D printing of moulds suitable for ferrous applications. This would mean trying different compositions of foundry sands, binders and test them for suitability as 3D printing materials and also test them for casting steels. While the facilities we have here are suitable for this kind of experimental research, the overall outcome depends on how intuitive you are with the materials choice.

Cheers
Sarat

>>> ykls001 ykls001 <ykls001@aucklanduni.ac.nz> 16/02/2010 2:54 p.m. >>>

Dear Sarat and Darius,

This is Øystein the Norwegian Masters student. Thank you for the presentation of the Rapid Product Development Centre. I have attached my Masters project description and presentation. If you have any questions about the project feel free to contact me (on this e-mail or phone 0211563144). The project it is due by end of June (30/06/10).

The project description is not necessarily final, it can be specified or altered to make the cooperation more interesting for you.

A copy of this e-mail is sent to my supervisor at NTNU, Morten Langøy.

Best regards,

Øystein Henden Kålås

|

Morten Langøy: to me

Hei,

Ser veldig bra ut.

Morten

Fra: ykls001 ykls001 [mailto:ykls001@aucklanduni.ac.nz]
Sendt: 17. februar 2010 00:49
Til: Morten Langøy
Emne: Fwd: Project description
- Show quoted text –"