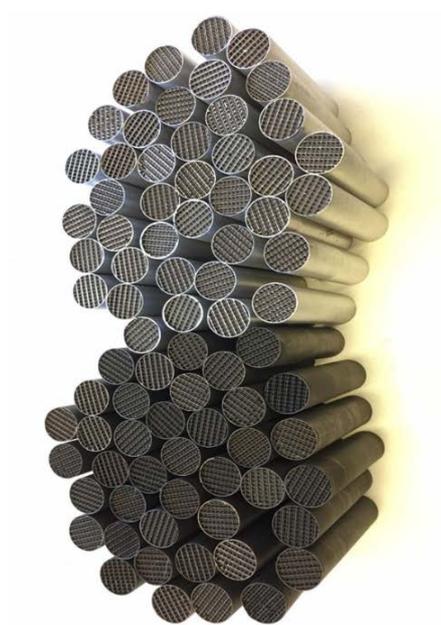# PRINT CR3DIT

Booklet of recommendations for manufacturing catalysts supports and reactors by Additive Manufacturing

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Table of Contents

1. Description of the Deliverable

1.1. Purpose

In order to share the knowledge acquired from their work and results, PRINTCR3DIT partners aim to provide some specific recommendations for the manufacturing of catalysts supports and reactors by additive manufacturing technologies.

1.2. Contents

The deliverable contains the common procedure applied for the 3D manufacturing of catalyst supports and reactors. The most relevant printing cycles applied in the project for each technology used are described and highlight, as often as necessary, potential issues encountered and how to solve them from a design and/or process point of view.

2. Introduction

For a large amount of catalytic reactions, the management of heat transfer is key to avoid formation of hot-spots in the catalyst bed, catalyst deactivation, pressure drop, inefficient usage of catalyst…It has been shown in the recent year that the use of structured catalysts (e.g. monoliths, foams) helps to improve heat and mass transfer properties in chemical processes. Among them, open cellular structures combine high specific surface area and high porosity leading to low pressure drop and high heat transfer rate when they are made from thermal conductive material. Different studies try to correlate geometries of these cellular structures (cell size, struts diameter…) to the above parameters but results depend highly on irregular morphologies of the cellular structures coming from their manufacturing process. To overcome these problems, Additive Manufacturing was recently used to allow the manufacturing of reproducible periodic and regular structured catalytic supports for highly endo- and exothermic reactions [1, 2, 3].

PRINTCR3DIT project also focuses on this topic. Adding the concept of "process intensification", which aims to manufacture chemical products in a more sustainable and efficient way, the project aimed to design modular and structured geometries using CAD softwares before being 3D printed by means of 2 additive manufacturing techniques depending on materials and applications: FDM (Fused Deposition Modelling) and DMLS (Direct Metal Laser Sintering) technologies were used to manufacture respectively catalysts and reactors which will then be tested in real conditions at the end of the project.

Fused Deposition Modeling technology is the most widely used and affordable of printing techniques for prototyping or for end-use parts manufacturing. It is a filament-based technology where a temperature-controlled head extrudes a thermoplastic material layer by layer onto a build platform. If needed, a support structure is created where needed and can be built in a water-soluble material.

Regarding DMLS technology, this technique is particularly useful for producing controlled lattice or reticular structures to be placed inside catalytic reactors. DMLS technology is one of the most common procedures to 3D print metal components, from fine powder of different materials (such as Steel, Aluminum, Titanium and some alloys), under the action of a high-power laser, which selectively "sinters" the powder grains, bonding them together, layer by layer, until the final 3D volume is complete.
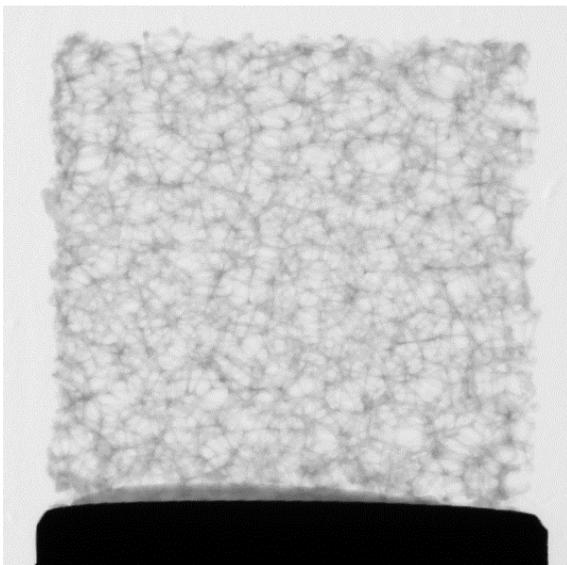
3. Obtaining of catalyst supports by Fused Deposition Modelling technology
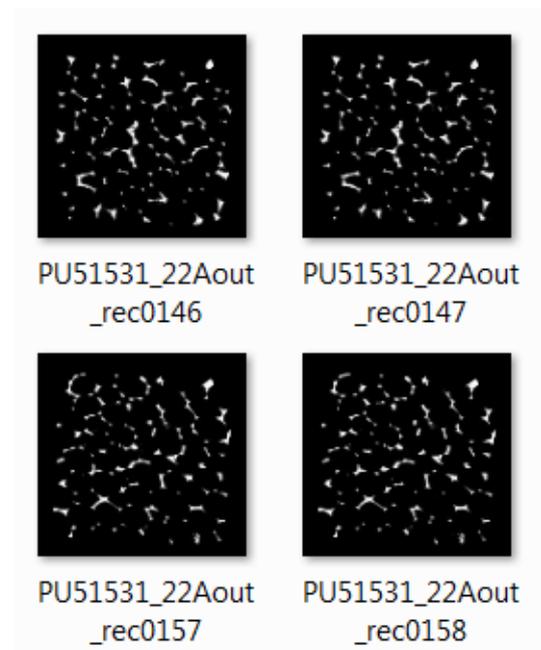
3.1. Preparation phase

3.1.1. Model preparation

➤ STL file from tomography

In order to facilitate the design process of modular open-cell structures, a tomography of an already existing foam was performed for comparison. Attempts has been done starting from 30PPI polyurethane foams tomographies (Image 1). 3D foams are cut into layers by the tomography equipment. Folder obtained at the end of tomography contained all ".jpg" pictures files of each layer obtained (600 pictures in our case) (Image 2). The number of files depends on the resolution chosen. Once ".jpg" files obtained, ImageJ software allows to computationally reconstruct the foam (Image 3). The 3D file obtained has a ".obj" format. As Fused Deposition Modelling 3D printers work mostly with STL files, the ".obj" file is converted into STL file format using Netfabb software (Image 4).

Image 1: Tomography of a 30PPI cubic foam

PU51531_22Aout_rec0146   PU51531_22Aout_rec0147

PU51531_22Aout_rec0157   PU51531_22Aout_rec0158

Image 2: Examples of 4 jpg files among 600 obtained after tomography

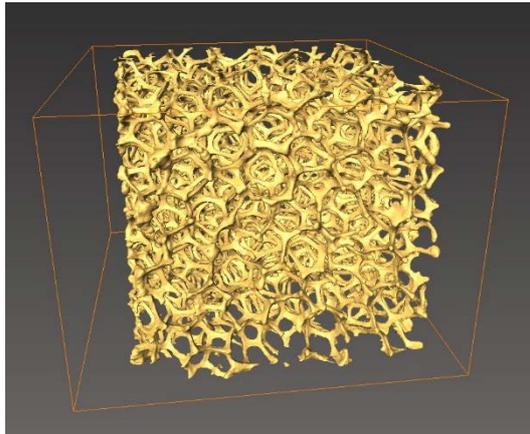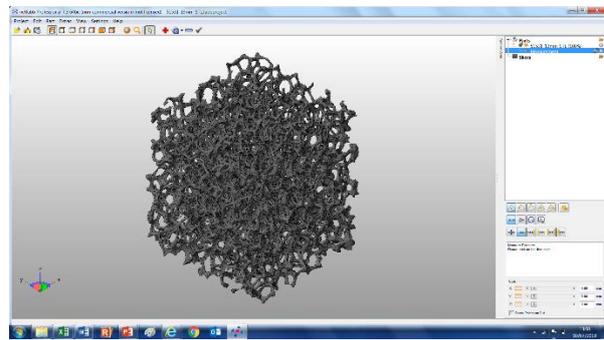*Image 3 : Reconstruction of the foam with ImageJ software*

Image 4: Foam with Netfabb software

Attempts of printing 3D parts obtained from tomography with a commercial 3D printer (Ultimaker 2) using usual ABS (Acrylonitrile-butadiene-styrene) material, with different nozzle diameter (400µm and 250µm) led to a failed feature (Images 5 and 6).
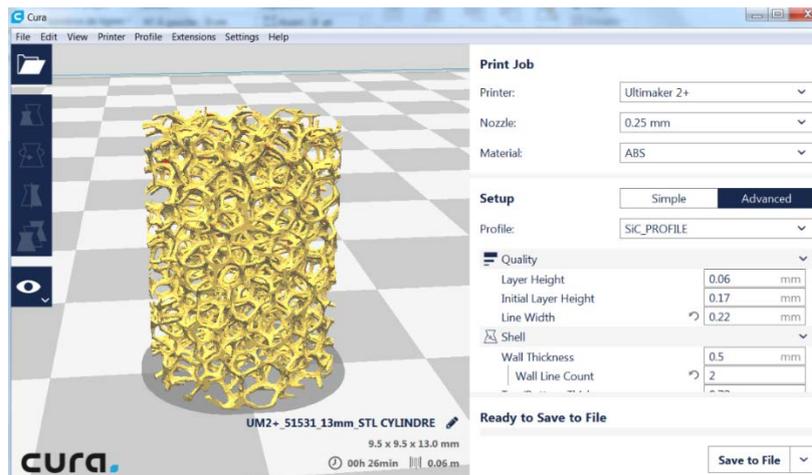
Image 5: Foam design in Cura software (Ultimaker 3D printer)

Image 6: 3D printed foam obtained from tomography (ABS material)

The magnification of foam struts in Netfabb software shows diameters of struts between 170µm and 190µm (Image 7). Such small dimensions allows fast catalytic reactions (which is important in order to intensify the processes) but lead to poor mechanical properties of the catalyst. Printing such dimensions with a FDM printer is known to be very difficult due to "wall thickness" limitation: this parameter is defined as the distance between one surface of the model and its opposite surface. It depends on the "slice thickness" which depends itself on nozzle diameter (50% nozzle diameter < slice thickness <75% nozzle diameter). Printing below these values can cause brittleness, warping, collapse, etc… of the 3D part.

Image 7 : Magnification of foam struts with Netfabb software

Different attempts to print monoliths with different wall thicknesses while varying different process parameters (nozzle diameter, slice thickness) to establish design rules relative to FDM technology with a commercial printer Ultimaker, based on ABS material led to features given in the Table 1.
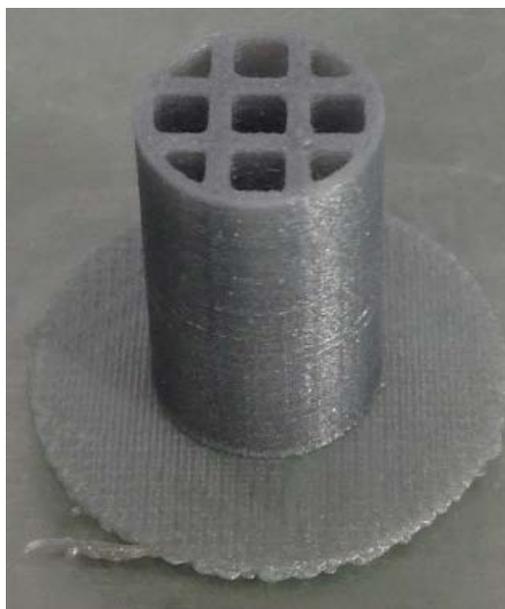
Image 8 : 3D monolith used to establish printing design rules

Nozzle diameter (µm)	Slice thickness (µm)	Minimum wall thickness (µm)
250	180	700
400	300	1300

Table 1: General rules obtained for FDM technology

Based on this observation, the design of an open-cell foams-like structures has been initiated taking into account the limitations of the technology.

> ➢ STL files from geometry generator software

Considering designs rules of printing, decision was taken to design of open-cell foams-like structures using Blender, an open-source geometry generator software. The use of open-cell foams structures offers the advantage of being considered as the repetition of a representative unit, which largely simplifies the construction of the computational structure. To fully define the geometry of the support, it is necessary to enter some basic information in the software, easily provided through a script file written in Python language: unit cell topology (such as Kelvin cells or cubic cells); values of the corresponding geometric parameters (for example, length and diameter of struts, tilt and twist angle); and number of cells present in each direction (x, y and z).

All these parameters were assessed (see paragraph 3.2.2) considering the final geometry of the catalyst, the desired porosity of the open-cell structure, the ratio between cell diameter and quantity

of material (in order to have a high geometrical surface for catalyst deposition) and also constraints on printing ("wall thickness" parameter).

Blender produces a STereoLithography (STL) file representing the entire structure. This file format is the most adequate for 3D printers.

> ➢ Reducing STL file size

STL file stores information about 3D models. This format describes only the surface geometry of a three-dimensional object (without any representation of color, texture, etc…). The basic idea is to tessellate the 2 dimensional outer surface of 3D models using tiny triangles (also called "facets") and store informations about the facets in a file: the more triangles used, the better the definition of the 3D model but the bigger the file size.

In PRINTCR3DIT project, original files for FDM printing were provided by University of Porto in STL format obtained from Blender with a very good resolution. As slicing of these stl file took too much time using CANOE slicer software, files size was decreased using Netfabb software: number of triangles was decreased while keeping a good printing resolution.

3.1.2. Slicing of STL file and export

The last step before printing is the slicing of the stl file. This is done through a software (a "slicer") which cuts the computational part entirely in slices and gives the machine all the necessary indications to realize the printing: positioning of the part, thickness of the layer, quantity of matter to be deposited, speed of the extruder, speed of movement of the heating nozzle and bed, filling density of solid objects... The result is an encoded file that contains all the information read by the printer. Some of thhe most known slicers are SlicR (free of use), Cura (free of use), MakerWare and ReplicatorG.The sliced file format is always a G-code that is a standard of industry for driving the numerical-control machine tools. Encoded file is then exported to the control software of the printer either directly (Repetier/slicR in our case) or with USB cable, SD card, etc.

Some important parameters are tuned at the step of STL file slicing in order to optimize the printing quality, taking into account the nature of the material and the design of open-cell structures to be printed. The most important are listed below. A new G-Code is generated each time one of the parameter below is changed in slicer software:

-   The "layer height" parameter: it corresponds to the thickness of material deposited for each slice. The thinner the slices, the slower the print, but the better the resolution of the print. As explained in section 2.2.1, layer height is linked to nozzle diameter of the printer and to "wall thickness" parameter. In order to decrease as much as possible the "wall thickness" parameter (which is linked to the struts of the open-cell structures), printing have been attempted using 180µm layer height / 250µm nozzle diameter.

    Two drawbacks were identified: 1) due to a big number of layers, the printing was too slow to be considered acceptable from an industrial point of view and 2) the R&D 3D filament manufactured in PRINTCR3DIT project didn't suit to such a small nozzle diameter leading to unexpected stops during 3D printing.

    Finally a layer thickness of 300µm with a 400µm nozzle diameter showed 3D printed struts diameters corresponding to those observed on the design (0,9 < d < 1,5mm). 3D printing with such layer thickness/nozzle diameter and home-made 3D filament allows regular

printing. Moreover, as "thick" struts are mechanically more resistant, the geometry of open-cells does not require supports. However, it can be noticed that increasing struts diameters above 1mm may lead to diffusional limitation which doesn't fit with fast catalytic reactions and process intensification.

- The "infill" parameter which allows to define the quantity of matter (in percentage) to be deposited inside the "wrap" of the 3D part and the pattern of deposition. In PRINTCR3DIT project, as open-cell foam structures do not contain a significant amount of matter, the percentage has been chosen to be 100% of filling with rectilinear pattern.

- The "printing speed" parameter: for common amorphous 3D printing materials (ABS, PLA…), fast printing speed can be applied (80-100mm/s in general). When printing materials that are less usual, as high temperature 3D filaments (polycarbonate (PC), Polyester (PET)) or crystalline thermoplastic filaments (polyethylene (PE), polyetheretherketone (PEEK)), slow speed printing is recommended. In PRINTCR3DIT project, the R&D 3D filament required slow speed at 30mm/s otherwise unexpected stops during printing were observed, due to bad progression of the filament in the nozzle.

- "Retraction" parameter: while retracting the 3D filament back up to the hot-end of the printer, "retraction" parameter allows to relieve pressure from the melt zone of the nozzle so that the 3D filament isn't being forced through the nozzle during non-print moves, avoiding oozing and stringing. In PRINTCR3DIT project, due to the nature of the formulated material, no retraction was applied to the filament and the maximum travel speed of 150mm/s was chosen for non-print move to avoid stringing through the foam structure during printing.

3.2. Printing phase

3.2.1.   Material choice

The wide application of 3D printing is limited by printable materials. Currently, only thermoplastic polymers with low glass transition temperature and suitable melting viscosity, powder formed materials and a few photopolymers could be used in 3D printing, depending on the technology used. However, these limited materials could not meet the significant number of requirements of diverse industrial application and thus the diversity of materials must increase. Synthesis of matrix materials with special properties, discover of new reinforcement and discover of suitable mixing composition are critical to increase the versatility of composites printing technology. Sustainable materials are also promising to be developed to reduce material cost and environmental impact.

In PRINTCR3DIT project, a ceramic precursor has been 3D printed by Fused Deposition Modelling starting from 3D filament specially tuned for this application. The 3D filament was made of a core portion of a ceramic precursor and the shell was made of a usual thermoplastic matrix known to be extruded (as ABS or PLA). The bi-component 3D filament was then extruded to form the 3D shape. Whereas 3D ceramic precursor part was printed without any problem as soon as the bi-component 3D filament was well processed, shape of the final 3D ceramic part obtained after high temperature thermal treatment could feature defects, amplified if those defects were already present at precursor steps. That's why particular attention should be paid at 3D printing steps to avoid later defect. Moreover, due to shrinkage observed after high temperature

thermal treatment, dimensions of the precursor foam should be accurately calculated in order to obtain the right dimensions for the 3D ceramic part. The first loop of attempts allowed to determine the shrinkage and the right dimensions of the foam precursor to be printed.

3.2.2. Printer preparation

Once the printing material has been chosen, a few adjustments have to be made to the 3D printer to start printing the 3D file (Image 8). Most of these settings are done using the printing control software. It is used to heat the extrusion head, to control the movements of the printer during the test phase, to start the printing, and to obtain important information about the behavior of the printer during printing. Most 3D printers have their own dedicated software whereas open-source 3D printers are compatible with most of existing softwares including: ReplicatorG, Makerware, Repetier, Cura, etc.

Using the control software and corresponding instructions, the first step is to check the optimal displacement of the X and Y axes and the Z-shaped plate.

It is then important to check that the extrusion head is well positioned with respect to the printing bed. For a correct printing, a sheet of paper slid under the print head set to zero will just pass under the head

After the filament has been correctly inserted in the gear wheel, the print head is then heated up to the melting temperature of the 3D filament. Once the temperature is reached, a few centimeters of filament are extruded: the filament must flow smoothly without sticking to the nozzle.
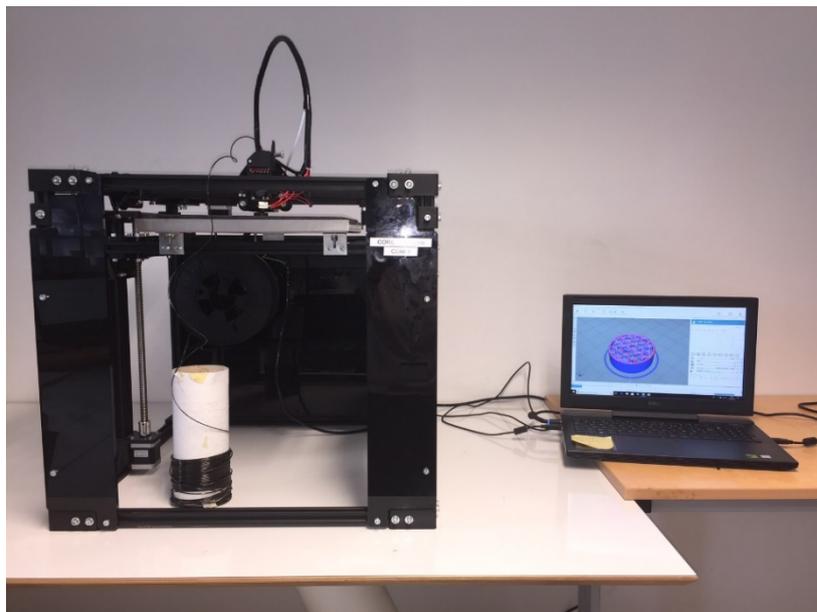
Image 9: Printing on FDM printer in CANOE facilities

3.2.3.   Printing processing

If all the previous conditions are gathered (file properly prepared and sliced, good physical settings of the printer, convenient material chosen), the printer is ready to print. Important parameters are given by the printing control software: printing time, number of layers to be built, length of filament to build the entire part.

The control software allows to visualize the evolution of the part in real time during its printing: printhead movements, layers built, remaining time (Image 9).
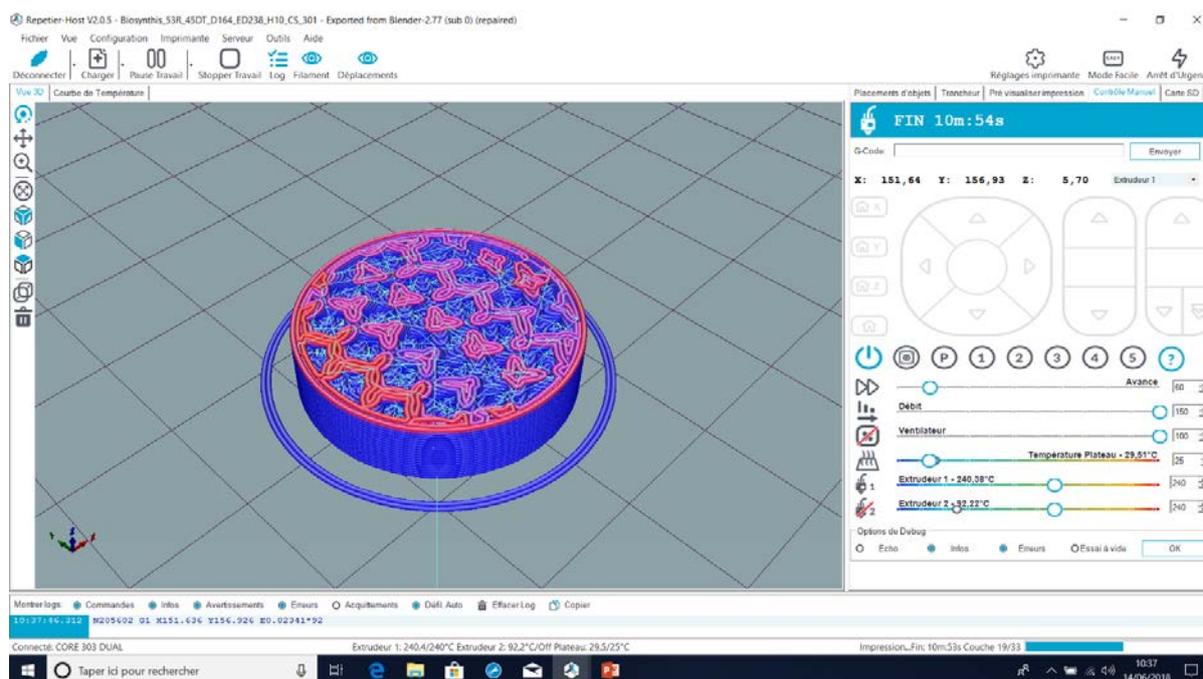

Image 10: Example of the Repetier display showing the 19 first layers of a 3D foam

In this part, the different steps leading to the 3D printing of a final catalyst will be described, with different issues encountered.

➢ Kelvin cell proof of concept

Once it has been shown that STL files obtained from tomography couldn't be printed, Blender software was used to design open-cell structures. As first trials to evaluate Fused Deposition Modeling in printing open-cell structures, it was decided to choose Kelvin cell geometry as unit cell, given their wide use as foam structures, being nearly the optimum shape for packing a volume with equal-size objects with minimal surface area. The structure should be designed taking into account the following constraints:

- The geometry of the catalyst : cylindrical with an external diameter of 22.8 mm, a wall of 1mm and a height of 17 mm
- Porosity of the foam: increased porosities from 40 to 70% were designed in order to be close to the porosity of usual catalytic foams (around 50%) but also to take into account printing limitations. It allowed also to evaluate the capability of the 3D printer.

- Printing limitations: in order to vary the porosity of the structure, struts diameters were chosen as adjustable parameter (instead of cells number) taking into account that no dimensions should be lower than 800µm (referring to "wall thickness" parameter).

Four geometries with 4 different porosities were designed using Blender and stl files were generated for 3D printing. All the 4 structures were easy to print with ABS material (Image 10).
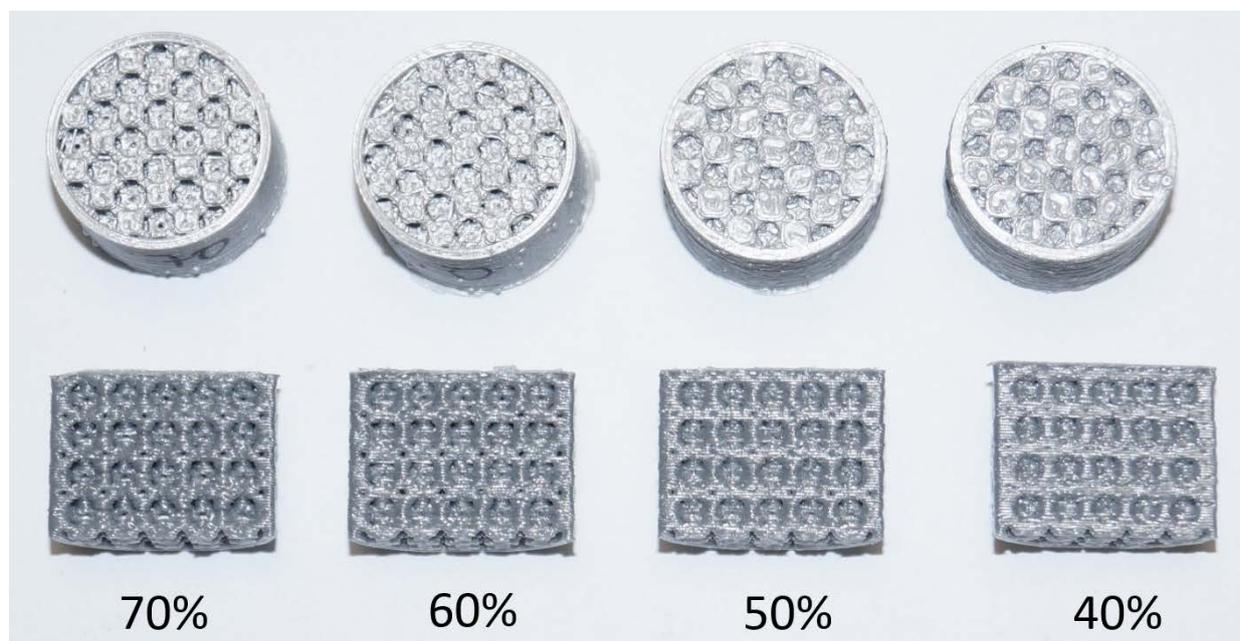
Image 11: 3D printed parts in ABS with 4 porosities between 40% and 70%

The structure with 70% voidage appears "airy" whereas the one with 40% voidage seemed more closed. Open cell structures (foams), such as Kelvin cells, are typically used in packings of high porosity, to reduce the pressure drop in the reactor. In our setup, the geometry with a porosity of 40% showed closed cells in some regions. On the other hand, structures with 50%, 60% and 70% porosities were printed with success with PRINTCR3DIT formulated material and used for further experiments (image 11). This first loop of trials allowed also to evaluate the shrinkage of the 3D part printed after high temperature thermal treatment that convert it in ceramic material. A shrinkage coefficient has then be applied to all later 3D printed foams.

| 70% | 60% | 50% |

Image 12: 3D printed parts with 3 higher porosities with PRINTCR3DIT formulated material

> ➤ Toward cubic cells structures

Based on the fact that Kelvin cells are not the best options for porosities below 60%, a decision was taken to base the design on cubic cells topology. 4 new designs with porosities close to 50% were also proposed by University of Porto : they are all based on cubic cells that have been either rotated of 90° or double tilted by 45DT (the foam is inclined 45 degrees in both directions perpendicular to the axial direction) or both at the same time. Printing were realized with standard procedure for ABS material (nozzle diameter 400µm, printing speed 80mm/s, etc…) with no difficulty (Image 12).

| Cubic regular | 45DT | 90R | 90R/45DT |

Image 13: First 3D printed parts in ABS with 4 designs based on cubic cells

An original approach used in PRINTCR3DIT project was to use CFD (Computational Fluid Dynamics) tools to determine geometries with good performance. For example, STL files of geometries presented in image 13 were generated in Blender software and simulated using CFD tool to assess the mixing efficiency, the heat transfer efficiency and the pressure drop. The geometries chosen to be printed were found by CFD to have good performance.

Using CFD simulations, the 90R/45DT geometry was chosen due to its better mixing efficiency and acceptable pressure drop. As this geometry was easy to print even with PRINTCR3DIT

formulated material, it was chosen for the manufacturing of first ARKEMA's and BIOSYNTHIS's catalysts.

> ➢ Final cubic cells structures as catalyst supports for catalyst manufacturing

In order to improve mass transfer in the catalyst, 3 new designs and STL files based on cubic cells with same inclination but different torsion, cell size and struts diameter were generated: Varying the strut diameter and unit cell size leads to different porosities of the open-cell structure and consequently modified the pressure drop, as confirmed by CFD simulations. In doing this, it is expected that the foams with smaller cells and smaller struts diameter will be more active from a catalytic activity point of view: as the geometrical surface per unit volume increases, more catalysts will be deposited.

| Struts diameter : 1mm | Struts diameter : 1mm | Struts diameter : 1,54mm |
| Porosity : 0,56 | Porosity : 0,61 | Porosity : 0,52 |

Image 14: Design evolution of 3D printed parts in ABS based on cubic cells

After printing of the three 3D parts (Image 13), preliminary results have beenobtained:
- 3D parts with the smaller struts diameter (1mm) and higher porosity (60%) didn't mechanically support the experiment. The structures collapsed because of lack of matter. A good compromise should be chosen between quantity of matter in the 3D part and its mechanical resistance regarding to constraints it is facing.
- Pressure drops were measured: for the same porosity, pressure drop of 3D parts with higher struts diameter and larger cell size is bigger.

To conclude, Fused Deposition Technology was easy to implement for the manufacturing of catalytic supports precursors once that the relevant material has been formulated.
The different geometries designed with the geometry generator software Blender were printed without need of supports and without changing process parameters whatever the porosity, cell size or struts diameter. To be noticed that all software used for catalysts manufacturing by FDM technology (printer control software Repetier/slicR, geometry generator software Blender or repair software Netfabb) are open and free of use which makes this technology as accessible as possible.
One limitation observed with FDM technology concerned the "wall thickness" parameter that is the minimum thickness that can be printed without collapse. FDM technology is not the best technology to reach the small dimensions that have often to be reach for open-cell

foams. **PRINTCR3DIT project showed that this disadvantage can be override by using a strategy of printing that connect 2D CFD simulation and a correct tuning of the foam design by a geometry generator software. The study highlights the importance of the "struts diameter" parameter: a compromise should be found between the technology limitation, the mechanical resistance of the struts and the catalyst diffusional limitation which may happen in fast catalytic reactions that allow process intensification.**

4. Obtaining of functional geometries by means of DMLS technology

4.1. Preparation phase

4.1.1. Model repair and preparation

Original files were provided by SINTEF in STL format, with an optimum compromise between number of triangles (file weight) and working resolution. Minor adjustments to initial design are done using either Rhinoceros 4.0 (for geometric STL modification) or Materialise 3Matic software (for minor triangles meshes modification or repairs). However, it was no necessary to work in depth into the 3D models since the original quality was good enough for the working process.

Regarding the work preparation, main complexity comes inherently related to the DMLS technology, which is implementation of supports. In addition, supports are one of the most important points in DMLS process.

Supports have multi-function:

➢ Bear the weight of the printed structure within the powder bed. Help evacuate internal heat, accumulated through the sintering process.

➢ Attach the part to the platform.

It is important to remark that usually there is not a single valid support strategy. That mainly depends on the manufacturing engineering and expertise of the technical staff involved. However, there are some premises a given support configuration should fulfil:

✓ Easiness of elimination: implement over accessible sides of the parts. Include gaps or offsets between larger areas of supported structures, so it can be easily removed. Ensure that the design of the support is practical to be removed manually, instead of using time-consuming milling operations.

✓ Heat evacuation: based on typical heat-transfer mechanisms; applies in the interphase between support-part ("tooth" design)

✓ Avoid massive powder accumulation: Hollow spaces in lower sections of the part, between support structures, to avoid stuck powder.

✓ Avoid risk of internal delamination (due to internal residual stresses): include radius instead of sharp edges, reinforce interphases between part surface and support, so the supports does not rip-off from the part when thermal stress becomes higher in upper layers of the process.

✓ Improve surface quality: optimum orientation of the part with the powder distribution blade (or "recoater") movement; otherwise, this will produce "stair effect" in the part surface. In addition, surfaces colliding with supports attachment have worse quality.

Support implementation in the 3D parts is done with Magics software. This tool automatically detects those areas that might require supports, depending on the orientation, and include them. The user is able to modify, remove or include new ones, though.

Another point of interest in the work preparation is the orientation of the parts within the building platform. A main direction should be established: holes and critical geometries have better resolution in the XY plane. If those are placed in other direction, some distortions might take place, this is especially critical for channels, since the cross-section could be compromised and might need support structures inside.

There is high interest in self-supportive structures. These are particularly useful in PRINTCR3DIT applications, since lattice designs are very complex and support removal becomes a costly time-consuming and difficult execution task (if possible). In order to achieve that, and as a "rule of thumb", inclinations below 45º should be supported. Above that, structures are considered self-supportive (always dependent on the length), as can be seen in the image below:
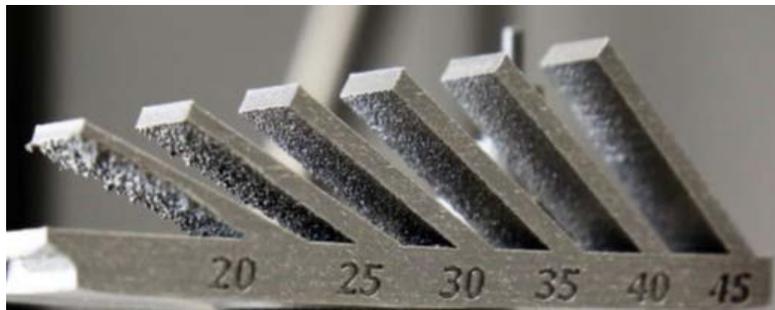
Image 15: Dependence of angular design and material behaviour

4.1.2. Slicing of STL file and export

In all cases, once the work preparation is ready and support structures have been successfully implemented in Magics, slicing is done through EOS software (manufacturers of the machine). From this software, 3D .STL files are converted to .SLI files (layers), which could be exported and interpreted in the machine control.

4.2. Printing phase

4.2.1. Material choice

Material used along the PRINTCR3DIT project was primarily aluminum. In DMLS technology, the most common reference for this material is the alloy AlSi10Mg from EOS manufacturer. AlSi10Mg is a typical casting alloy with good casting properties and is typically used for cast parts with thin walls and complex geometry. It offers good strength, hardness and dynamic properties and is therefore also used for parts subject to high loads. Parts in EOS aluminum AlSi10Mg are ideal for applications which require a combination of good thermal properties and low weight. Conventionally cast components in this type of aluminum alloy are often heat treated to improve the mechanical properties, for example using the T6 cycle of solution annealing, quenching and age hardening. The laser-sintering process is characterized by extremely rapid melting and re-solidification. This produces a metallurgy and corresponding mechanical properties in the as-built condition which is similar to T6 heat-treated cast parts. Therefore such hardening heat treatments

are not recommended for laser-sintered parts, but rather a stress relieving cycle of 2 hours at 300 °C (572 °F).

At a certain point in the project schedule, stainless steel was also used. There are several grades of steel to be used in DMLS technology; the steel chosen is PH1. It is a pre-alloyed stainless steel in fine powder form. The chemistry of EOS StainlessSteel PH1 conforms to the compositions of DIN 1.4540 and UNS S15500. This kind of steel is characterized by having good corrosion resistance, high hardness, and excellent mechanical properties, especially in the precipitation hardened state. This type of steel is widely used in variety of medical, aerospace and other engineering applications requiring high hardness, strength and corrosion resistance. Standard processing parameters use full melting of the entire geometry with 20 μm layer thickness, but it is also possible to use 40μm layer thickness to increase the build speed. Using standard parameters the mechanical properties are fairly uniform in all directions. Parts can be machined, spark-eroded, welded, micro shot-peened, polished and coated if required.

In addition, regarding the material, it is worth highlighting that due to the layer wise building method, resulting parts have a certain anisotropy, which can be reduced or removed by appropriate heat treatment. However this will still occur, so it should be taken into account that there is a main direction (building axis direction) where mechanical properties will be, usually, lower than in any other. This is common to all DMLS materials.

4.2.2. Printer preparation

Printer preparation is, in all cases, done according to EOS standards. This means fresh powder loading in the feeding platform, leveling powder surface with the recoater blade, and upload new job according to the preparation and slicing done before.

4.2.3. Printing processing

In this part, most relevant printing cycles in the project will be described, in order to illustrate potential issues found, and how to solve them from a design and process point of view.

➢ *Bursting pressure trial specimens.*

First printing runs within the project framework were performed on tubes with different angles, so burst pressure test could be carried out by SINTEF. Inlets and outlets were 90º, but the transition between them varied with different radius values. This is a very good example of the issue described previously: the **main goal was keeping inlet and outlet cross sections (circles) as good as possible**.
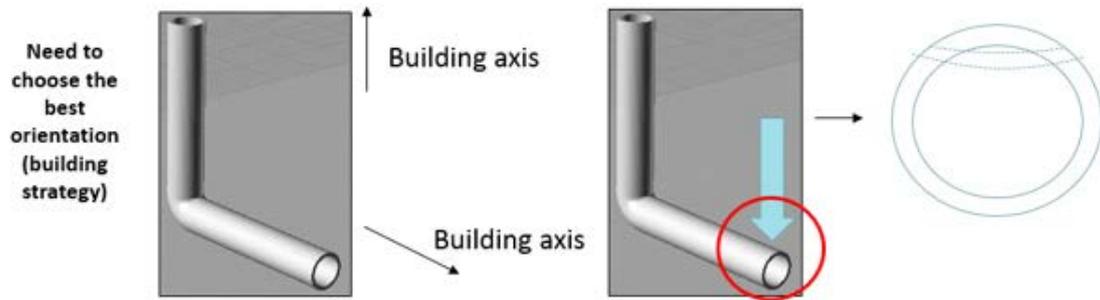
Image 16: Selection of priority building axis (left): a main direction is going to be compromised. Effect of printing out of the building axis (right) resulting in geometric distortions

However, due to the angular difference between them, it was not possible to guarantee similar quality (regarding geometric/dimensional tolerances) in printing, without need of supporting. This problem was solved by **nesting the tubes at 45° configuration to the building platform**, as can be seen below:
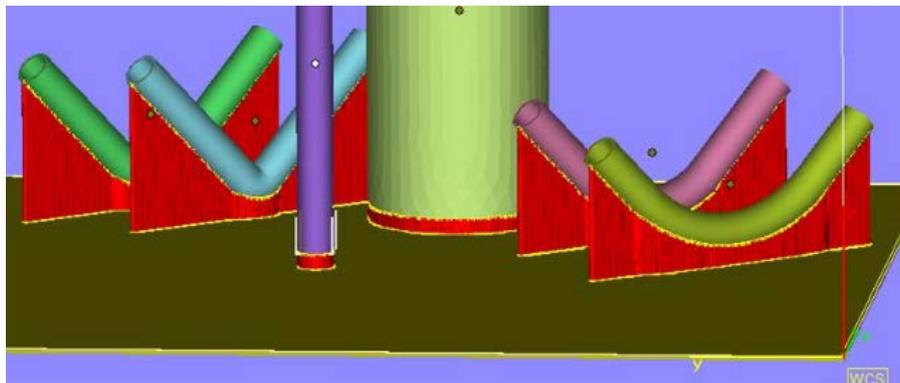
Image 17: Nesting of burst pressure test specimens in Magics software

Final results can be seen in the next picture:

Image 18: Final printed tubes, after supports removal

➢ *Miniature reactor*

The first attempt to print a reactor was done at the beginning of the project, according to SINTEF design. The design featured internal channels, with just one inlet/outlet. As previously mentioned, another point of interest with the DMLS technology is loose powder removal. In open structures, it should be easier to have access to the volume trapped inside each cavity but this becomes difficult with internal channels. **Loose powder tends to get stuck and it is difficult to clean**. The smaller the size of the hole, the harder it would be to carry out this task. With the original design proposed by SINTEF (18 x 38 mm), there was not enough room for powder removal, so internal channels were full of loose powder. Therefore, the part was not functional. The reactor was scaled up until the minimum size for properly cleaning the internal parts, which was 2,6 times original size. Results can be seen in the picture below:
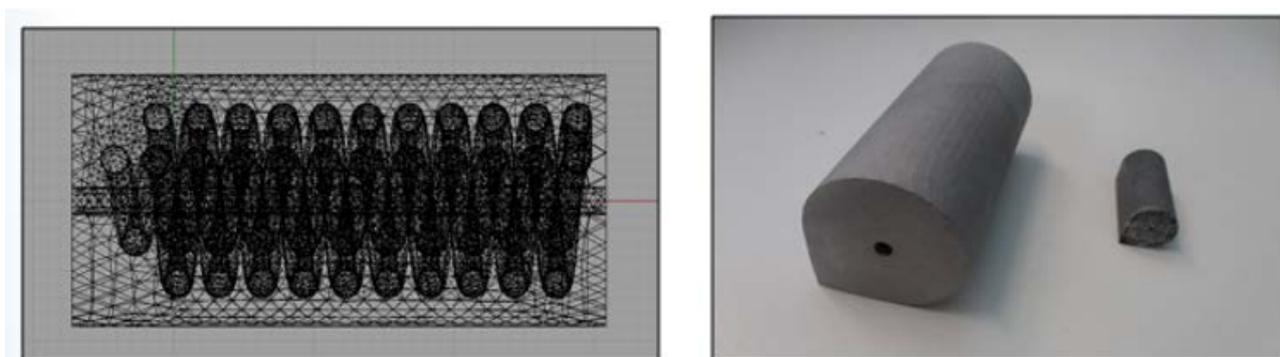
Image 19: Internal design of the reactor (left) and comparison between original size and scaled model (both printed)

> ### Kelvin-cell proof of concept

Prior to printing the lattice foams (or "meshes") to be inserted within reactor tubes of the demonstrator unit, a first printing proof of concept was carried out. The design was made of "Kelvin cells" stacked together. The original size of the cell was very small (5 x 5 x 5 mm), so the unitary modules could not be printed, due to the limited resolution of the equipment with such thin walls. Therefore, the part was not formed at all over the building platform. The model had to be scaled up, just like the miniature reactor, up to 4 times the original size. By that size, **the "ceiling" of each cell was large enough to theoretically require supports implementation** (more than 3 mm of dome). However, **it was possible to print the structure without them.** The results can be seen in the picture below, comparing original sized cube (not formed) and the upscaled version:
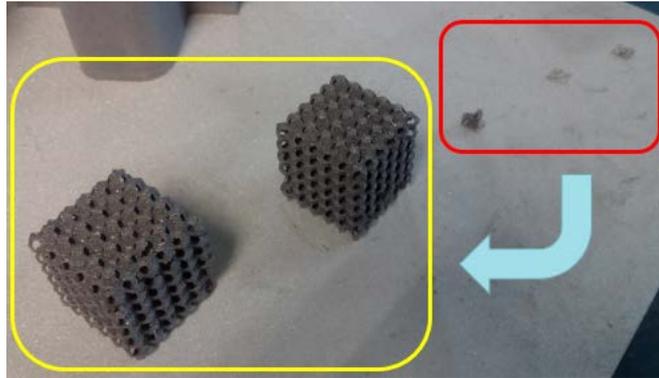
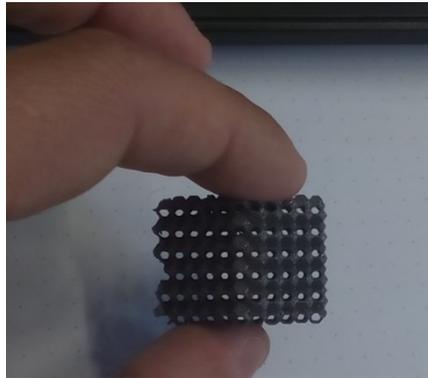*Image 20: Original size cubes (red) and 4 x scaled cubes (yellow)*

Image 21: Support less through holes in the Kelvin Cell structure

➢ ***Tubes with embedded lattice structures: proofs of concept with different mesh designs***

The associated work with these designs, and successive iterations, was the core of the manufacturing role within the project frame. The first stage consisted on performing printing trials with different mesh designs, proposed by SINTEF. Iterative properties of the mesh were checked by SINTEF, regarding three main morphological features:

✓ Wall thickness
✓ Spacing
✓ Tilt angle

Thus, 8 probes were designed and manufactured in aluminum. Mesh designs were integrated in generic tube part (Ø1"). Out of those 8 models, 5 featured straight mesh designs all through the length of tube and the other 3 featured different tilting angles. The breakdown of iterations is as follows:

• Wall 03, Spacing 10
• Wall 03, Spacing 15
• Wall 03, Spacing 20
• Wall 10, Spacing 20
• Wall 06, Spacing 20
• Wall 06, Spacing 20, RH 30
• Wall 06, Spacing 20, RH 30, Θ 30
• Wall 06, Spacing 20, RH 45, Θ 45

It is important to highlight the fact of tilted geometries beforehand, since **the best printing strategy for those designs is** clearly **up straight over the building platform**. Therefore, the tilting angle design will favor printing without need of supports (as explained in the previous case). However, **due to the small spacing between bars of the mesh**, and the small amount of material involved on each joint between cells of the mesh, **it is possible to print the lattice structure without need of supports.**

Image 22: Samples of tubes with embedded lattice structures, 8 different designs

The resulting lattice structures are very thin, so those might not be indicated for resisting severe mechanical loads.

Half sections of those designs are printed as well, in order to check visually the quality of the internal lattice structure. With such a thin wall, so close to the equipment operative resolution, it is possible that some parts of the mesh do not print properly, so the whole structure could fall down (or, at least, lose stiffness), since they are lacking supporting material below. Pictures are shown next, along with some microscopy pictures taken by SINTEF:

Image 23: Half sections of the lattice tubes (left); microscopy pictures of the mesh walls (right)

The result is that no printing defect is observed above 500 microns; the printing is very consistent in that range of measure.

However**, a collateral issue is observed in this case, regarding the non-sintered powder stuck inside.** This is not exactly the same case as described previously with the "miniature reactor", since the size of the access to the lattice are clear and large enough, but **the internal mesh hinders powder removal along the tube length.** After being cleaned, particles of powder still keep coming out of the tubes. With DMLS technology, **it is not feasible to use liquid-based solution to free the powder**, because liquid particles will bond with the metal grains and form larger particles, which are even harder to pull out. That being said, **the only feasible solution is mechanical vibration**. This should be performed carefully though, given the fragility of the lattice structure.

> *Tubes with embedded lattice structures: material comparison and working resolution*

In the stage of proof of concept, these tubes are also tested printing in stainless steel (PH1, previously described) in order to compare qualities in the resolution of the mesh. One of the designs of the tubes are printed with the following results:

Resolution: ~100 µm / 20-50 µm

Al. VS PH1
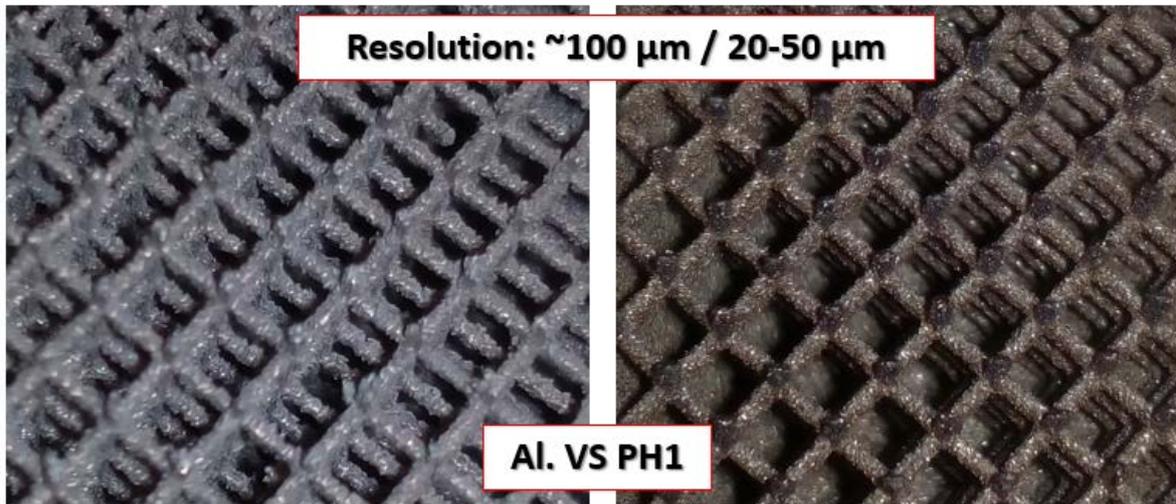
Image 24: Aluminium mesh (left) vs Steel mesh (right). Differences in resolution and surface roughness can be seen

It is possible to see the difference when comparing both finishes. Operative resolution when working with steel is higher than with aluminium. In addition, the surface roughness is worse with aluminium. From the theoretical material datasheet of EOS, typical accuracy to be achieve with aluminium is around 100 microns, while steel is lower than half that value (25-50 microns). About the surface roughness, for aluminium is typically between 15 and 19 microns (Ra), and for steel is between 7 and 9 microns (Ra).

On the other hand, for this particular application, aluminum is a much more interesting material due to thermal properties. However, the goal of this case of study is showing the difference when working with different materials in DMLS technology, which does not only affect intrinsic mechanical properties of the material, but also the solution and surface quality that are possible to achieve.

> *Tubes with embedded lattice structures: larger tubes for demonstrator unit*

After the initial proofs of concept, it is decided that DMLS tube parts will be used to fill the catalyst reactor prototype, which will act as the demonstrator unit for the project. From a manufacturing point of view, there is an important change between printing of validation test parts and functional units, mainly due to the required length. Hence, the reactor pipe has a length of 7.5 meters, which will be split into 4 sections of 1.875 each one. Extra material is added to both sides of the tube, in order to guarantee enough free space to securely cut and finish off the edges of the tube, since they should be stacked together. With that considered, total length is 19.5 mm.
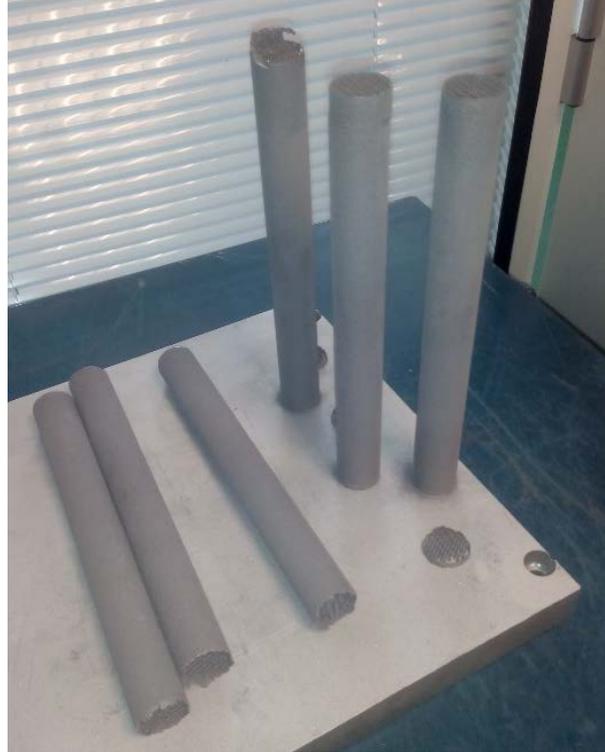
About the internal mesh design, the selected iteration was the one with the following features:

✓ Internal gap: 1.75 mm

✓ Wall thickness: 0.3 mm
✓ Surrounding thickness: 0.5 mm

In line with the tests performed in previous tasks.

All that considered the results of the frost printing attempts is shown below:

Image 25: Results of first printing attempt

Some issues occurred here, all related with the same fact: the height of the tubes given the aspect ratio of the geometry. Basically, the tubes are too large for such a small base, causing defects especially noticeable when printing at upper layers:

o **Breakage of the tubes by the base section**: given, in turn, by two factor, the thin wall of the tubes, which offers low stiffness against severe bending efforts and the design of the encounter edge between tube and building platform.
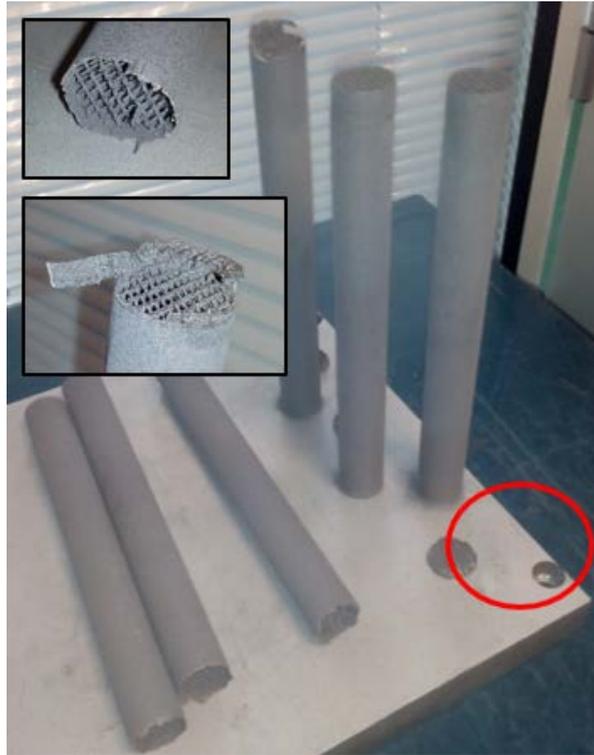
Image 26: Breakage of the tubes from the building platform

o **Displacement of upper layers**: the tube vibrates under the action of the reacoater spreading a new layer of powder and touching the edges in the previous layer. The accumulation of this effect in the upper layers produces a displacement on upcoming layers. Therefore, the structure has an offset in the X-Y positioning, as shown in the images below:


Image 27: Displacement of upper layers

The solution for those two issues was applying re design concepts to the initial models, by adding some radius in the tube/base interphase, instead of sharp edges, which accumulates

internal stress, in order to reinforce the whole structure of the tube. Reinforcement on the tubes there helps avoiding breakage and reduce vibrations when working in upper layers.

The next resulting iteration, after changing the design could be seen below:

Image 28: Batch of tubes printed after re design

The results are much better regarding the previous issues, so it was possible to move forward into the production stage for all the required tubes. From this point of view, 40 units are required. The maximum amount of tubes in one single printing cycle is 24 units, so this is carried out. In the next picture, an intermediate layer can be seen:
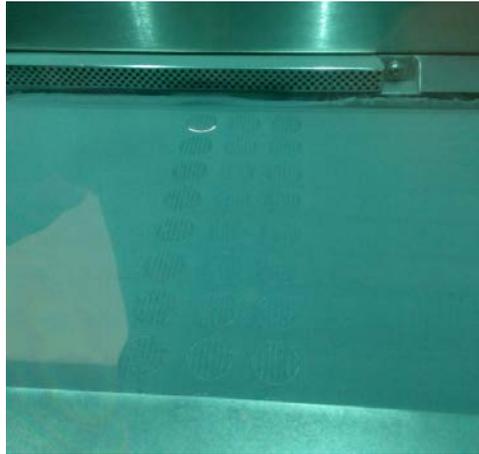
Image 29: Printing cycle in the final batch manufacturing stage

Finally, the quality of the mesh is checked through microscopy in order to get detail on the mesh quality:
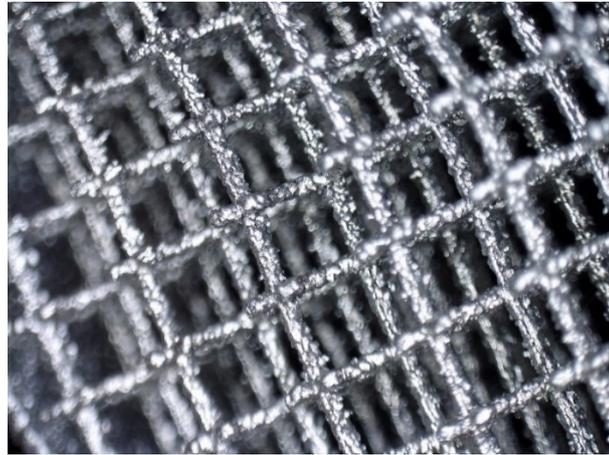

Image 30: Mesh quality inside the lattice structure

> ### *Stainless steel integrated reactor.*

In the final part of the project, technical work focuses in stainless steel material and the possibility of printing a whole reactor in one single part. Besides the chemical interest of this initiative, **what is more interest of this case is illustrating the inherent problem to DMLS techniques of internal stress caused by thermal action within the part, and different approaches to solve them from the manufacturing engineering perspective.**

The initial design is provided by SINTEF and can be seen in the image below:
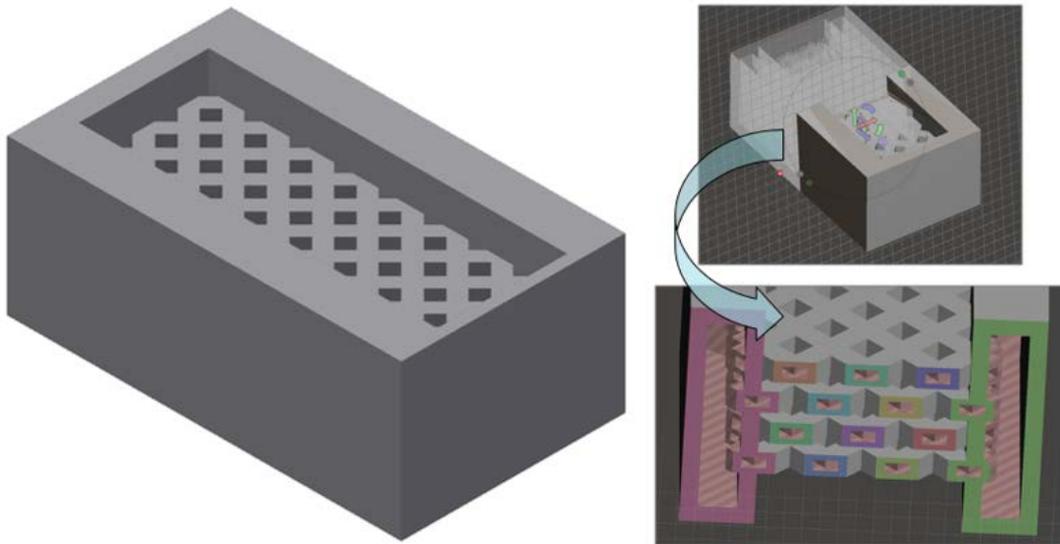
Image 31: Design of reactor by SINTEF

The design has some features that need to be printed in a certain position, according to the criterions shown before throughout this document, used in previous cases. Therefore, horizontal and vertical nesting strategies should be avoided: in the first case, a lot of support would be needed; in the second one, some minor geometries inside each channel would probably collapse, since they do not have support to be built over.
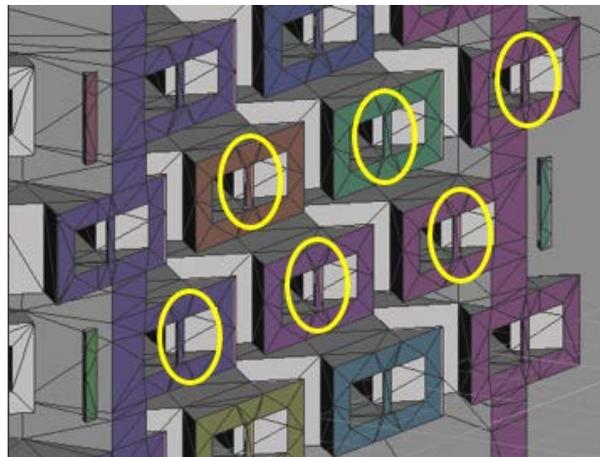
Image 32: Non supported geometries in a z-axis building strategy

Optimum solution to both guarantee geometric quality inside the channels and avoid massive support requirements is placing the reactor at 45º tilting angle. A half section of the reactor was printed first time to check inside quality. The nesting strategy within the building platform could be seen below:
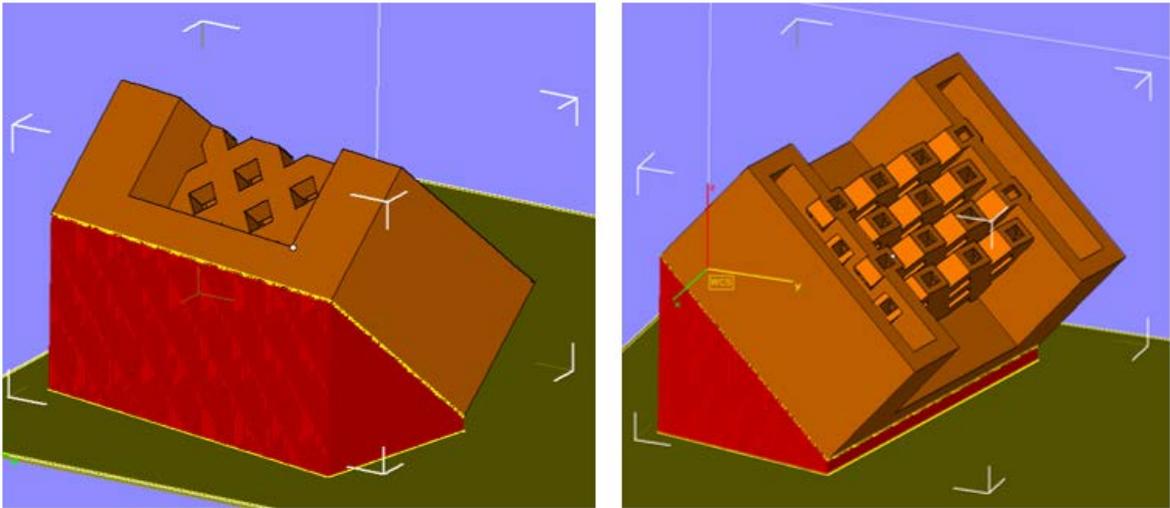
Image 33: Nesting strategy for the half section of the reactor

As shown above, the only requirement for supporting the geometry is the base of the reactor, at 45°. The initial approach for support strategy is based on "honeycomb" hollow supports, which covers the whole projected base while minimizing the amount of material used.
Printing is carried out as usual:

Image 34: Printing process for the half section of the reactor

Printing results are shown below:
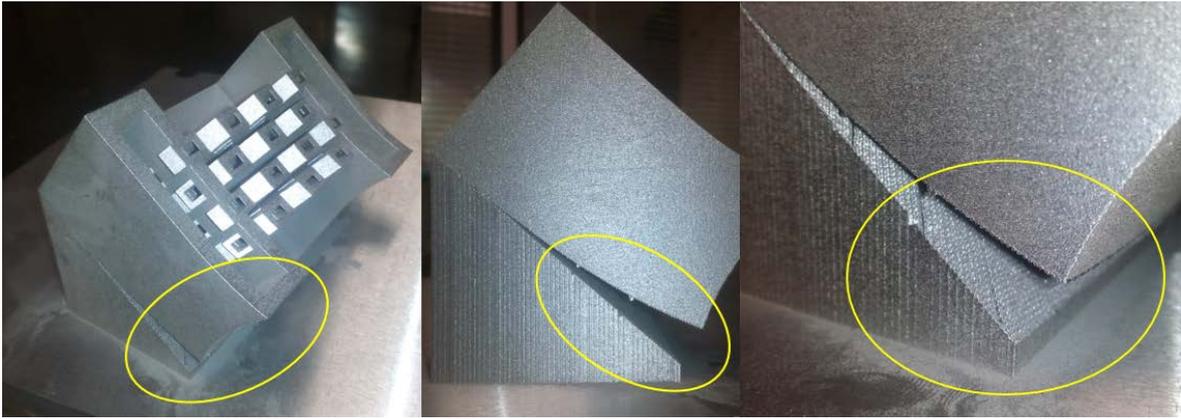
Image 35: Printing results of first printing test

What happened in that case is that the **thermal stress, accumulated layer after layer but especially critical when printing the base of the reactor** (very thick, where more material is found) was so high that the part tends to warp. **This only could have been avoided by the support structures, forcing the part to hold its original position. In this case, since the support strategy was based on honeycomb and therefore, very weak, the warping force was higher and the result was the breakage though the interphase.** On the positive side, the nesting strategy was correct for preserving the quality of the inner geometries, as can be seen in the image below:


Image 36: Internal channels quality

The second approach was to keep the same support design but increase the surface contact between the base of the reactor and the supports. Previously, it was based on point contact; the goal was to switch to surface contact. This way, there is more chances to be able to restrain the warping forces during the printing cycles. Results are shown below:
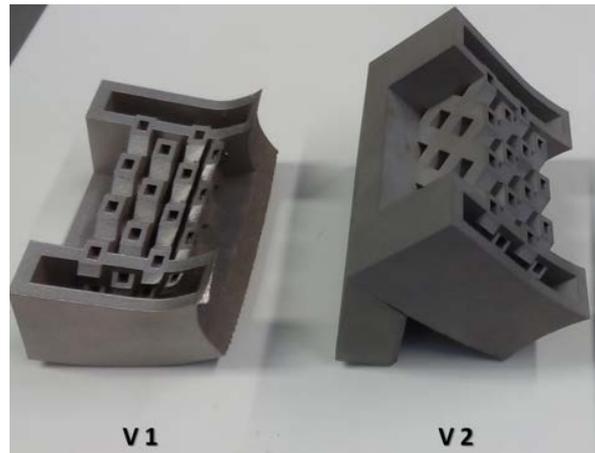
Image 37: Results of second iteration. First iteration (left) and second iteration (right)

Although this is an improvement over the initial approach, the part still warps and breaks in the support interphase. Hence, **it is necessary to increase the stiffness of the support to endure the existing forces within the part base. This can be strengthen by adding more material into the initial design**. The other side of the spectrum of solutions is **implementing a solid support, taking all the volume below the base of the part**. This would be the third iteration, with results shown below:
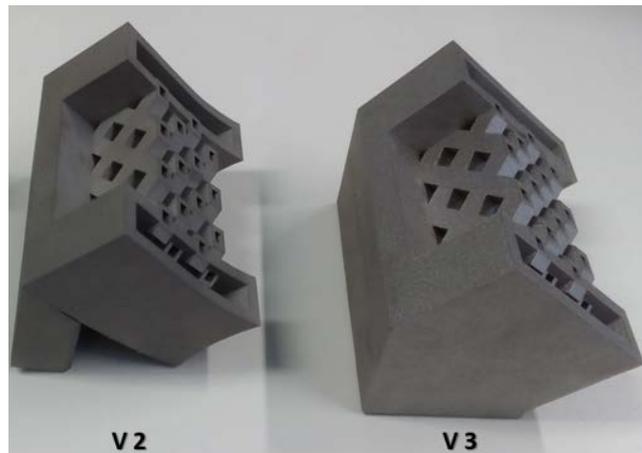
Image 38: Results of third iteration. Second iteration (left) and third iteration (right)

Apparently, the issue has been partially solved. The strength of the new supports avoids the warpage of the part, which is a good point. However, under closer inspection of the parts, some defects can be seen:
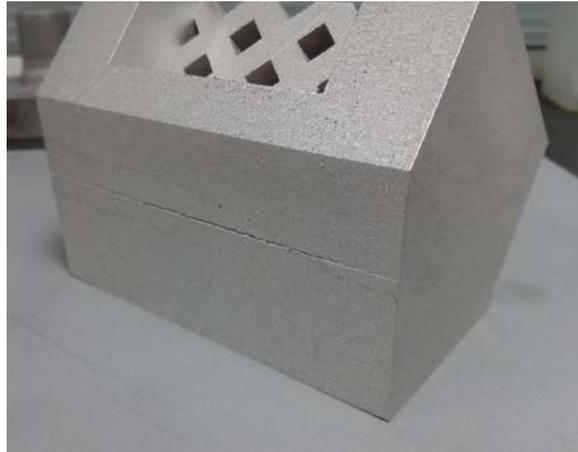
Image 39: Defect in the third iteration of the printing cycle: internal cracks

An internal crack appeared in one of the side of the support. This probably would not have affected the reactor itself, but it is worth analyzing the issue from manufacturing engineering point of view: this solution would not be valid from a theoretical point of view since **the increase of anchoring area is done at the cost of increasing sintered volume. Increasing sintered volumes means adding more internal stress to the initial one**, which was already enough to cause warpages. To sum this up, **the potential solution could have become part of the issue.**

The design premise for the next iteration is clear: **maximizing contact area while keeping the support volume to the minimum**, so material accumulation and thermal stresses could be avoided. This can be done, but it is necessary to clarify that **commercial software will not reach that point of detail, so supports have to be drawn manually based on selected CAD systems.** The process is **having supporting elements with variable cross sections, going from higher thickness when closer to the part/base to lower ones**, **in the middle of the support**. This way, the concentration of mass will not be located in the middle section (just where the crack appeared). This design is done with Rhinoceros software tool:
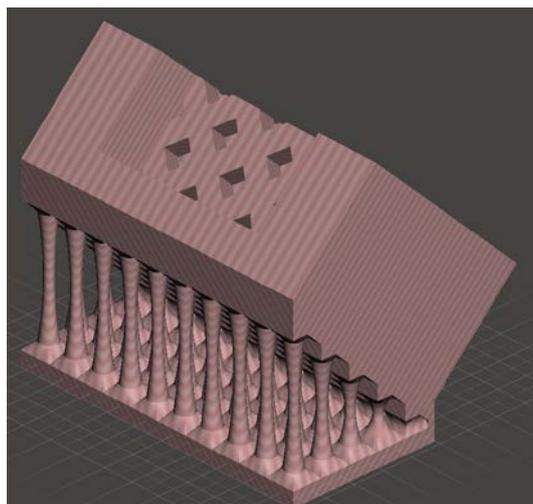

Image 40: New supports designs

With this new design, the supports volume is 62% of the previous one, which is a notable decrease. The results are shown below:
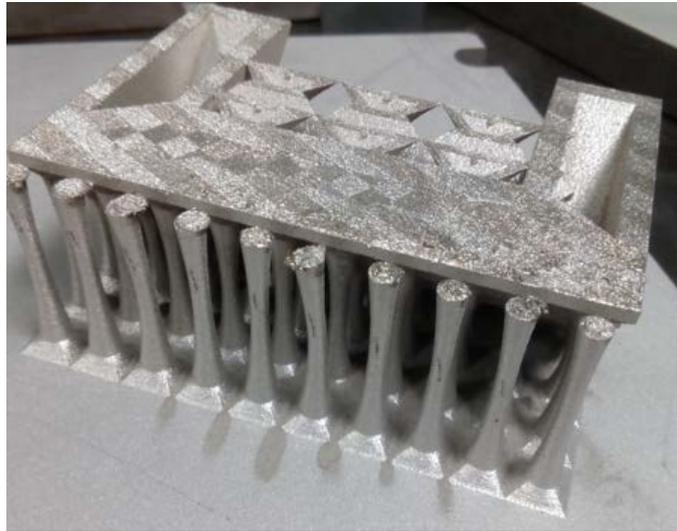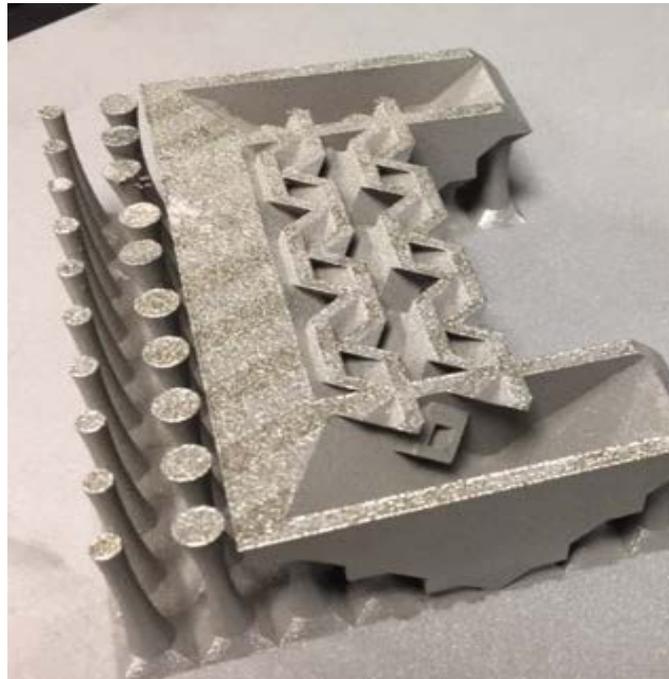

Image 41: Results of fourth iteration

In this case, the reactor integrity seems to be ok, but the supporting columns suffered from deformation, both bending and layers displacements. **This is because the part suffers the influence of a bending effort from the other side (the non-supported one)**. Since the anchoring works better this time, thermal stress moves to the non-supported base, causing a bending point over the support columns. A way to solve this would be adding new support columns (with the same criterion) to that base, as seen in the next picture:
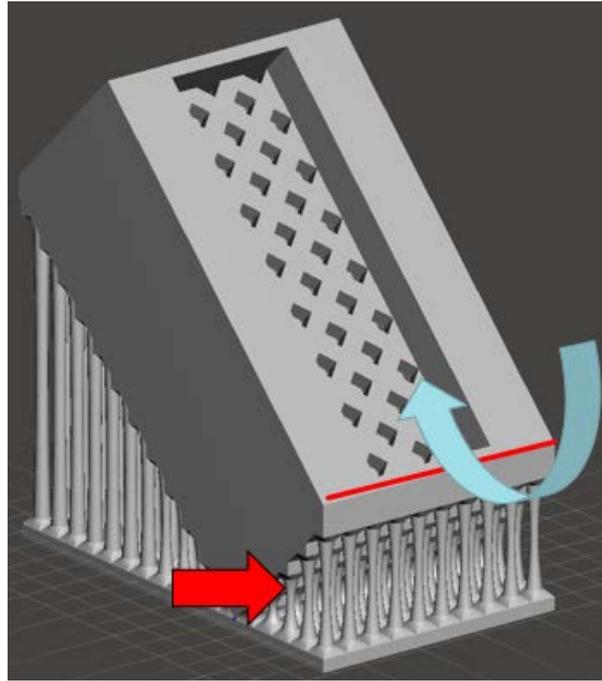
Image 42: New support strategy in both bases

This is empirically carried out on the next iterations; results are shown below:

Image 43: Results of fifth iteration

The printing run does not finish properly this time either. **Note that the supports are too fragile, and minor deformation implies the recoater crashing against them and thus, stopping the process**.

The main issue with this case of study is the reactor design, since the wall thickness is too high for the sintering process. Mass accumulations imply higher risks of thermal stress, which turns into warpage effects. What is more, these effects have only been evaluated in half section of the reactor. When trying to print the whole reactor, it is practically impossible for supports (no matter which the design would be) to endure the accumulated stress through the length of the reactor.

To sum up, **this is a good case to illustrate that not all designs are suitable for DMLS technology, independently of the freedom to modify support designs.**

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