Additive Manufacturing of 3D ceramic structures for a step change in performance in industrial application as sorbent and catalyst

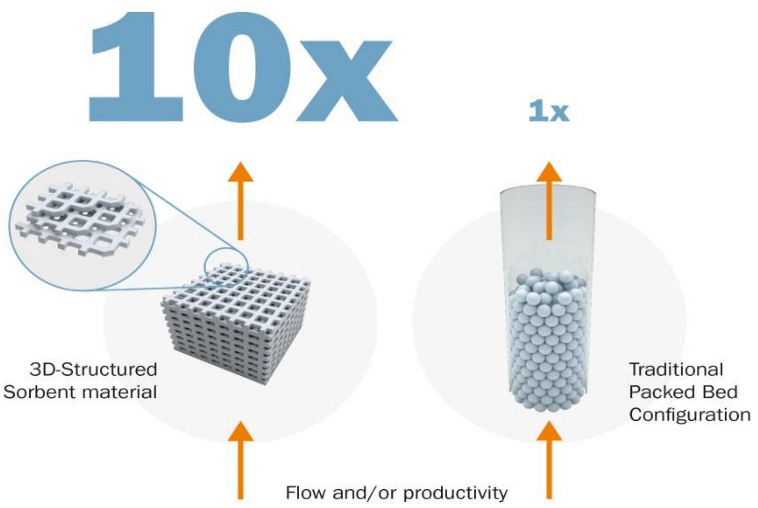
--------------------------Reflections from a business development perspective--------------------------

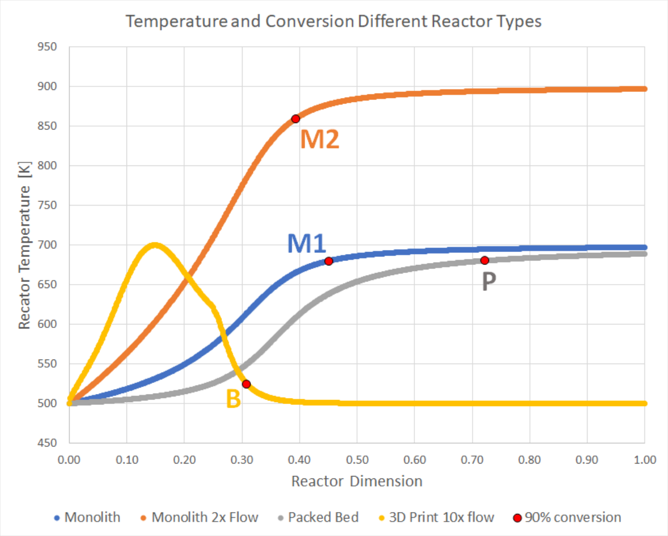
Summary

Additive Manufacturing (AM) of ceramic structures will enable complex design of sorbents and catalysts with improved operational performance in various areas. AM technologies like 3D-printing have several advantages compared to current subtractive manufacturing technologies, but also come with challenges like proper ceramic paste preparation and skillful post-processing like de-binding and sintering. The 3D-CAPS project focusses on the application of 3D-printing of silica and hydrotalcites to make improved 3D-structures for the sorption of CO2 from industrial (off-)gases.

Introduction

Additively Manufactured (AM) ceramic structures applied in the chemical industry promise better mass transfer, pressure drop, heat exchange, selectivity, flexible form factors, recyclability, safety, change out time, start/stop, albeit at a higher cost, compared with packed bed reactors, and similar advantages (except pressure drop) compared with honey comb structures. These advertised improvements imply that smaller and less expensive plant (on a life-cycle basis) are possible. The purpose of the 3D-CAPS project is to investigate what reduction in size is possible for a sorbent process (with the same throughput):





Some theoretical work has been done to explain why it is plausible that a plant based on AM structures could be 10x smaller, compared with traditional packed-bed reactors, with the same production capacity, along the following lines (fig. 2).

Consider:
P: traditional packed bed
M1: traditional monolith
M2: same monolith, but with 2x the flow of reactants
B: printed monolith, but with 10x the flow, distributed input of gases, and integrated heat extraction. The red points show the position in the reactor when 90% conversion is reached. Then we need to look at pairs of reactors for comparison.

P->M1: because of the much narrower range of times for which the gas remains in the reactor (the residence distribution), the monolith achieves 90% conversion at 45% of the reactor length, compared to the packed-bed that requires 72% of the bed. The monolith also has the advantage of a much smaller pressure drop.

M1->M2: the amount of gas to be processed is double, i.e. its flow rate. This leads to a much higher exit temperature of the bed (twice the temperature increase for M1). Note the 90% conversion is reached quicker (at 39% of reactor length) even though more must be processed because the average bed temperature is higher, which gives a higher reaction rate. The reason not to increase the flow rate even more, is because the temperature will eventually lead to several problems - integrity of the catalyst, and cost of reactors being the most important.

M2->B: This 3d-printed reactor is designed such that the flow is distributed along the first 20% of the reactor, and that heat is extracted along the hole of the reactor. The flow is 5x larger than M2, and even 10x larger than M1. The integrated heat function and distribution of incoming gases causes the 90% conversion to be reached at already 31% of the reactor length.

B->P: the flow in the 3d-printed reactor is 10x higher than the packed bed, and the 90% conversion is hit at 31% of the reactor length, compared to 72% of the reactor length. In this case the performance is thus 23x better.

Caveats: this is a very simple (excel) model of a reaction, and of the difference in residence times between a packed-bed and a monolith, we have chosen a distribution between these too as the 3d-printed bed. To be sure, we do not yet know, how we will integrate the distribution of incoming gas along the reactor length, or how we will integrate the heat extraction, but these things should be possible if we can print any shape we like in multiple materials.

Application improvement area 1: sorbents

The petrochemical industry, like other industries such as power plants and steel companies, have used amine solutions (like MEA, DEA and MDEA) to remove CO2 from industrial (off-)gases for a long time. In these processes, the gas stream that has to be treated is passed through a column filled with amine solution. The CO2 reacts with the amine and stays behind in the solution, which is regenerated in a parallel column.

This process is applied in hundreds of plants in the world but has its challenges as well. First of all, the amine solutions will gradually contaminate due to e.g. sulfur containing trace components in the gas stream. In addition, the solution degrades over time due to the inherent process conditions. Finally, these are not simple (from a process control point of view) operations that also require tall columns, effectively making it expensive and difficult to apply in e.g. off-shore applications.

Application improvement area 2: catalysts

The petrochemical industry (i.e. refineries, chemical plants) has been using heterogeneous catalysts (e.g. ceramic particles loaded with precious metal) to accelerate most of their chemical conversions processes for many decades. The catalyst particles are deposited in a reactor vessel or column for a period of say 5 years. The reactants are entered from one end, and the products are exited from the other end. If heat is needed or generated in the conversion process, it can be supplied or removed via the wall of the vessel, via the entering reactants or exiting products, or via an inserted pipe system.

This proven technology has several areas of inherent improvement. During the deposition process, but certainly during the 5-year operating period, maldistribution of the catalyst particles may occur, due to pressure shocks and flow deviations. This in turn may lead to a maldistribution of the reactant flow through the reactor, that may lead to unwanted temperature differences over the reactor, with (in the case of exothermal reactions) hot spots as a result. These hot spots may lead to co-sintering of catalyst particles, which aggravate mentioned maldistribution, and may complicate catalyst removal during the next shutdown.

In addition, the heat supply or removal via an inserted pipe system is troublesome, as extreme reaction conditions may lead to corrosion, and the presence of the catalyst particles to erosion of the pipes.

Finally, the catalysts particles themselves may erode during deposition and during service, which leads to reactant flow maldistribution due to clogging caused by different particle sizes and fines generated.

Solutions

a) Current

Industry nowadays are using structures to generate improvements, in catalytic and especially in sorbent applications.

However, these products are predominantly made from metal, which implies that several problems are not addressed, including footprint and size.

b) AM

With the advent of Additive Manufacturing (AM) technologies like 3D-printing, it has become possible to make tailor made structures of ceramic materials that can help address abovementioned improvement areas.

AM structure design is done with appropriate simulation and design programs, which produce a digital file of horizontal slices from the envisaged 3D-structure. These data are transferred to the AM machine of choice, and the structure is subsequently produced pixel by pixel and layer by layer. A typical resolution is around 20 micrometer.

Compared to traditional subtractive manufacturing technologies, AM enables complex 3D structures that amongst others will integrate mixing, optimize throughput, reduce pressure drop and increase heat exchange.

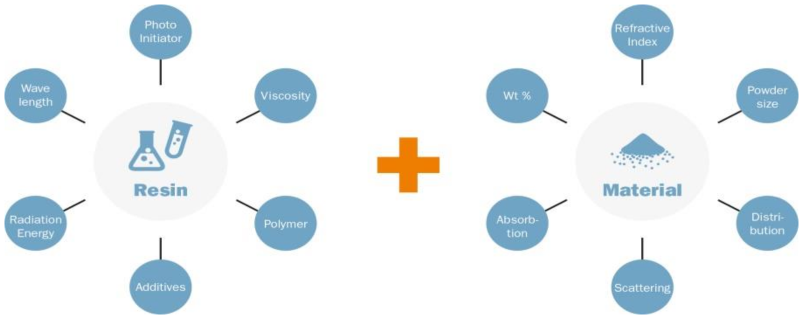
Properly applied and combined, these improvements will result in more complex but more integrated sorption and catalytic 3D structures and installations, that in turn will be smaller, lighter and more energy efficient. Consequently, petrochemical plant will be cheaper to build (capex) and operate (opex). In addition, the potential smaller size and lower weight will enable installation of e.g. (CO2) sorption units where space and weight come at a premium, like off-shore production platforms.

AM challenges

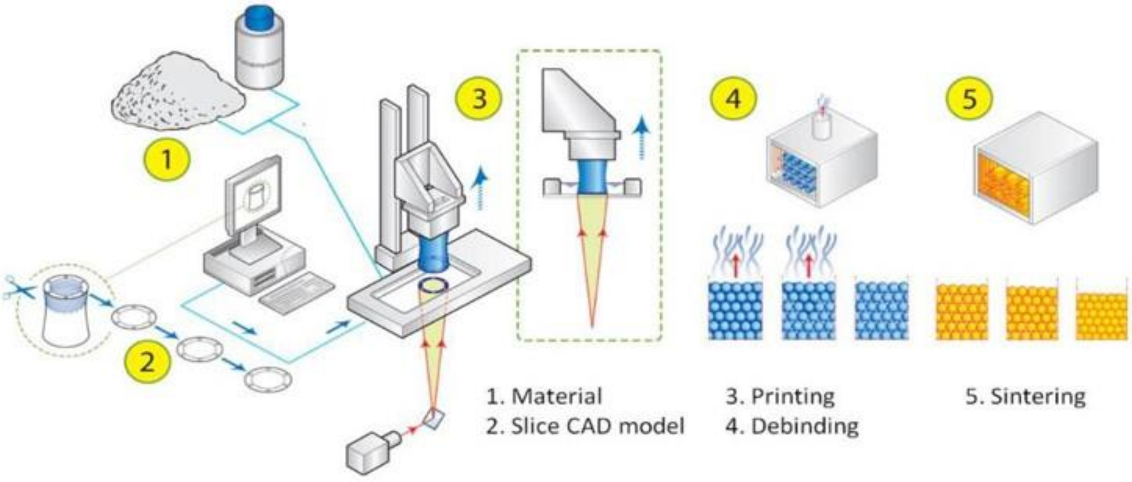
Whilst AM has a large potential, there are challenges with these manufacturing technologies as well. The chain to AM-produce 3D ceramic structures has the following components:

1. starting material prep → 2. AM manufacturing → 3. de-binding → 4. sintering

1. The choice of ceramic material, particle size distribution and choice of binder are essential to achieve the right final product properties:



2. There are several AM technologies available for ceramics nowadays, like DLP (digital light processing and FFF (fused filament fabrication) (both variants of ceramic 3D-printing) and co-sintering technologies. The most commonly used technology is DLP:



The choice of which AM method to use to make a certain product depends on a) the choice of starting material and b) the required properties (e.g. structural strength and surface porosity) of the product. As a consequence, in various occasions producers for example opt for surface treatment before or after sintering.

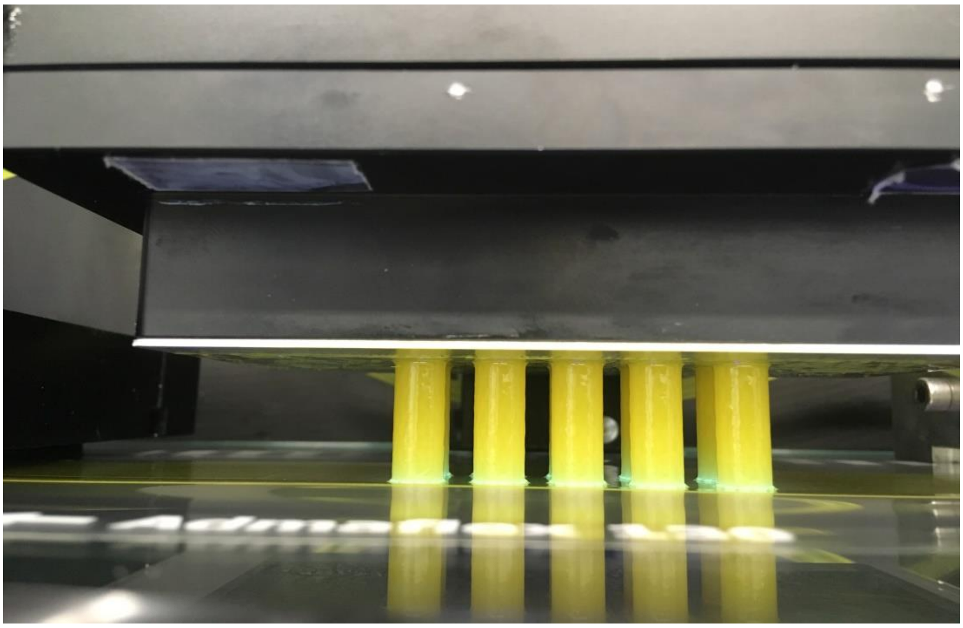
3. The de-binding in step 3 is important from an operational point of view, as too fast temperature increases of the green product will lead to micro-cracks.
4. Finally, the sintering step is crucial for the final strength and dimensions of the product. This finishing is sometimes more governed by art than by science, (operator skills/ experience).

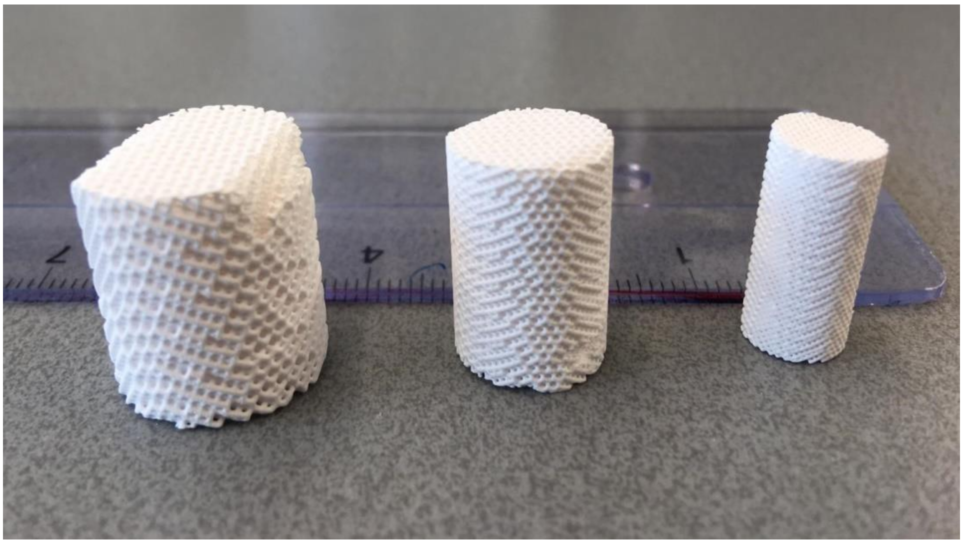
All 4 steps have an influence on the characteristics of the final 3D structure, like strength, surface porosity etcetera, so knowledge about the impact and control of each step, as well as the overall integration of them, is essential to achieve a satisfactory final product.

AM next steps

For the proper application of these 3D-structures to sorbents and catalysts, the optimal design of the 3D-structure itself with respect to flow/throughput optimization, pressure drop reduction and maximum heat exchange surface at the right locations is very important. In other words: before the 3D slice file can be made to manufacture the structure, there will be various complicated computational flow dynamics (CFD) runs and iterations, to optimize the structure for its ultimate application.

The currently running ACT 3D-CAPS project is a good example, as it aims to optimize, design and manufacture (via 3D-printing) structured sorbents from various starting materials like silica and hydrotalcite to remove CO2 from industrial (off-) gases in a much more efficient way than current solvent technologies. Below a picture of the 3D-CAPS printing process, as well as of the resulting development product:





Other similar technology development and demonstration projects are currently starting (e.g. ZEOCAT-3D[1], to manufacture optimized AM produced zeolytic catalysts), and under development.

Such projects are important to gather enough evidence that AM production of 3D-structures for sorption and catalysis indeed bring about a disruptive reliable step change that will convince industry to start to embrace this promising new route to sorbents and catalysts.

---

[1] A H2020 project, April 2019 expected start