

3D Printing of Salt as a Template for Magnesium with Structured Porosity

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Porosity is an essential feature in a wide range of applications that combine light weight with high surface area and tunable density. Porous materials can be easily prepared with a vast variety of chemistries using the salt-leaching technique. However, this templating approach has so far been limited to the fabrication of structures with random porosity and relatively simple macroscopic shapes. Here, a technique is reported that combines the ease of salt leaching with the complex shaping possibilities given by additive manufacturing (AM). By tuning the composition of surfactant and solvent, the salt-based paste is rheologically engineered and printed via direct ink writing into grid-like structures displaying structured pores that span from the submillimeter to the macroscopic scale. As a proof of concept, dried and sintered NaCl templates are infiltrated with magnesium (Mg), which is typically highly challenging to process by conventional AM techniques due to its highly oxidative nature and high vapor pressure. Mg scaffolds with well-controlled, ordered porosity are obtained after salt removal. The tunable mechanical properties and the potential to be predictably bioresorbed by the human body make these Mg scaffolds attractive for biomedical implants and demonstrate the great potential of this additive technique.

Porosity is desired in a broad range of materials for applications as catalytic supports, lightweight structures, and biomedical scaffolds.^[1–5] An established approach to obtain porous scaffolds is the technique of salt leaching.^[6] The technique is based on salt particles acting as a template that is infiltrated with the material of interest and later dissolved from the solidified scaffold material to generate porosity. Predominantly, sodium chloride (NaCl) is used as the salt because it is an abundant, nontoxic template material that readily dissolves in water without the need of organic solvents. Besides environmental considerations, NaCl is an attractive choice due to its biocompatibility, high thermal

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and chemical stability, and applicability to a vast range of scaffold materials. Indeed, salt templates have been used to achieve porosity in a wide variety of scaffold materials, including natural polymers such as silk fibroin,^[7] synthetic polymers such as poly(L-lactic acid),^[8] bulk metallic glasses,^[9] crystalline metals such as aluminum,^[10] and even magnesium, which is known for its high chemical reactivity.^[11] In these examples, the pore size of the final scaffold is defined by the size of the original salt particles or the salt aggregates used as template.

For all of these porous scaffolds, the salttemplating approach has led to random porosity with broad pore-size distributions.^[6,8,11] This reflects the polydisperse nature of the templating salt particles and limits our ability to control the porous architecture of the final scaffold. By contrast, recent advances in additive manufacturing (AM) have added freedom of design to the manufacturing of porous

materials, opening the possibility to create architectured gridlike structures with well-controlled porosity and pore sizes at the macroscale.^[5,12-15] While the pool of materials printable by AM is extending rapidly,^[16,17] materials that possess a high chemical reactivity remain a challenge to shape using additive technologies. Among such reactive materials, magnesium (Mg) is receiving increasing attention as a metallic biodegradable implant material for temporary bone replacement or osteosynthesis.^[18-20] This stems from its similarity in mechanical properties to bone, and its ability to induce new bone formation^[21,22] while also being bioresorbable.^[23] It is widely accepted that pore size,^[24-26] shape,^[27-29] directionality,^[30,31] and degree of porosity^[24,32,33] strongly influence cell viability and growth. To guide bone-tissue growth, large open porosity with pore sizes >300 μ m in combination with surface roughness appears to be most successful.^[24,34] Thus, the ability to shape Mg into structures with controlled porosity and pore size in a patient-specific geometry is highly desired.

Staiger et al.^[35] and Nguyen et al.^[36] previously reported a three-step process for indirect AM of Mg by printing first a polymer that was then infiltrated with an NaCl paste. The latter served, upon removal of the polymer, as a template for Mg infiltration. While being an important first approach to structuring Mg using AM, the additional processing step required to generate first the polymer template resulted in imperfect structure replication and was limited to geometries that allow NaCl infiltration into the template. www.advancedsciencenews.com





Figure 1. 3D printing of a salt (NaCl)-based paste to form an Mg scaffold with structured porosity via a series of debinding, sintering, infiltration and leaching steps. a) Chemical structures of the surfactants SDS and AOT used in the paste. These sulfonated surfactants are deployed to tune the interactions between the NaCl particles in the paraffin oil and thus adjust the paste rheology to allow for printing via direct ink writing (DIW). b) The optimized NaCl paste is 3D printable by DIW. After removal of the paraffin oil, the printed green body is calcined and sintered to result in a pure NaCl template, which can then be infiltrated with Mg melt. Leaching removes the NaCl template to generate an Mg scaffold with structured porosity given by the salt template. c) Macrographs of structures obtained after the individual process steps presented in (b). The scale bar corresponds to 1 cm.

To overcome these limitations, we present a route to chemically functionalize the surface of NaCl particles to produce a stable NaCl paste with flow behavior suitable for 3D printing via direct ink writing (DIW). The NaCl paste developed allows direct generation of 3D-printed NaCl templates with structured porosity defined by the printer's tool path (**Figure 1**). The 3D-NaCl template is eventually dried and sintered to gain sufficient mechanical strength for the subsequent infiltration of the desired scaffold material. To illustrate their suitability for metal infiltration, the sintered NaCl templates were infiltrated with Mg melt before being removed by leaching in a NaOH aqueous solution to obtain shaped Mg with ordered porosity.

For an NaCl paste to be DIW printable, several rheological requirements have to be fulfilled. First, the ink must flow under the pressure applied by the printer and should display shear-thinning behavior to facilitate the extrusion process.^[12,37] Second, the printed shape is only effectively preserved if the ink exhibits a finite yield stress that impedes the distorting action

of capillary forces.^[38] The finite yield stress also ensures enough elasticity to prevent sagging of the bridging filaments for the generation of grid-like structures.^[37]

Inks with such rheological properties are typically obtained by forming colloidal networks of weakly attractive particles.^[37,39,40] For the inks designed in this work, the interactions between the NaCl particles in the paste were tuned to obtain a weak colloidal network while maximizing the concentration of particles in the ink to ensure a long shelf life and shape preservation through minimum shrinkage after drying and sintering.

The hydrophilic nature of the NaCl particles results in prompt agglomeration in the hydrophobic oil used as the liquid phase of the ink. To reduce this agglomeration susceptibility and tune the particle–particle interactions, a surfactant was added to the paste. Sodium sulfate-based compounds were chosen for this purpose due to their ability to adsorb on the surface of the NaCl particles via the sulfate group.^[41] By adsorbing on the particle surface with the sulfate-head group and extending the hydrophobic tail toward the oil phase, the surfactant provides a steric barrier that counteracts the attractive van der Waals interactions between the suspended particles. Two surfactant compounds were studied to enable tuning of these interparticle interactions, namely sodium dodecyl sulfate (SDS) and bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) (Figure 1a). In addition to the molecular architecture, the chosen surfactants differ in their number ratios of hydrophobic tails to sodium-sulfate head groups, with SDS and AOT having a number ratio of 1 and 2, respectively. Paraffin oil was chosen as the liquid phase to disperse the surfactant-stabilized NaCl particles because of its higher viscosity compared to lowmolecular-weight organic solvents such as octane or decane (Figure 1b). A high-viscosity liquid phase usually prevents pressure-induced liquid-solid phase separation, also known as liquid phase migration, during the printing process. All these components were chosen according to biological safety standards to allow the developed paste to be applicable for biomedical purposes.

In order to determine the optimal concentration and type of surfactant for the formation of a weak interparticle network, we conducted a rheological study on salt-based pastes containing SDS or AOT as surfactant. All measurements were conducted with serrated plates to minimize the effect of wall slip (Figure S1, Supporting Information). The rheological response of the pastes was evaluated by both linear viscoelastic dynamic oscillatory and steady-state flow curve measurements (**Figure 2**). Representative curves of the storage modulus (*G'*) and the loss modulus (*G''*) as a function of the applied shear-stress amplitude are shown in Figure 2a for each paste composition. The shear yield-stress (τ_y) and plateau modulus (*G*₀) shown in Figure 2c were taken from the point of strong shear-strain deflection of the viscometry measurements in Figure 2b and the plateaus of *G'* in Figure 2a, respectively.

Overall, the rheological results show that the addition of surfactant can significantly reduce G_0 and τ_v of pastes containing ≈70 wt% of salt. In the absence of surfactant, the paste lacks shear thinning or finite yield stress, and thus requires a long time for stabilization during the rheological measurements. This results directly from the very strong particle-particle interactions and the presence of evolving heterogeneities within the pastes. The concentration of surfactant needed to disperse such agglomerates and achieve shear-thinning response is much lower for the AOT surfactant as compared to SDS. We hypothesize that the stronger dispersing ability of the AOT molecules arises from their twofold higher ratio of hydrocarbon tails relative to the head group. Indeed, the magnitude of the moduli and the yield-stress values of the paste were found to decrease at comparable conditions irrespective of the surfactant type, if the amount of surfactant is represented by the tail concentration, c_{tail} (Figure 2c). The results indicate that a threshold c_{tail} value of $\approx 10^{-4}$ mol g⁻¹ NaCl is needed to disperse the salt particles. This threshold is exceeded using absolute surfactant concentrations of 2.5 wt% AOT and 10 wt% SDS. Such analysis shows that the hydrophobic tail concentration on the NaCl-particle surface is a crucial design parameter for the rheological adjustment of the paste, and that it can be tailored by both the type and concentration of the surfactant.

For pastes containing 10 wt% SDS (SDS10), 2.5 wt% AOT (AOT2.5), and 10 wt% AOT (AOT10), τ_y was determined to be 22 Pa, 93 Pa, and 61 Pa, respectively. These values are in the order of magnitude of those previously reported for printable dense ceramic pastes (3–25 Pa)^[37] and printable ultrastable Pickering emulsions (51–660 Pa).^[14] No yield phenomena were observed for shear stresses up to 1000 Pa for pastes without surfactant (Surfactant0) and for pastes containing 2.5 wt% SDS (SDS2.5), due to the presence of too strong particle–particle interactions and of a rigid network that causes liquid-phase migration. The lack of a yield point and the overly high elastic properties at low shear stresses are unfavorable for DIW and hence these pastes could not be successfully printed.

In order to quantify the shape stability upon printing of the AOT2.5 paste, a bridging test was conducted. In this test, the extent of paste sagging as a function of bridging distance was determined as the *z*-deflection using profilometry (Figure 2e). While bridging distances of up to 1.5 mm were possible with tolerable sagging of below 0.1 mm, bridging distances exceeding 1.5 mm caused significant sagging up to 0.3 mm (Figure 2f).

The experimentally determined sagging at distinct bridging distances was compared to the theoretically expected values based on classical beam-bending theory (see Supporting Information). The maximum deflection δz_{max} of a spanning filament of diameter *D* can be estimated using the following relation:

$$\delta z_{\max} = \frac{a}{G_0} \frac{5}{12} \left(0.25 \ \rho_{\text{paste}} \ g \frac{L^4}{D^2} \right)$$
(1)

where G_0 is the plateau modulus, *L* is the distance between supports, *g* is the gravitational acceleration constant and ρ_{paste} is the density of the paste (1.75 g cm⁻³ for AOT2.5).

An additional parameter *a* was introduced in this equation to account for the reduction of the shear modulus to $G' < G_0$ during printing. This reduction results from the shear-thinning nature of the paste. Therefore, the parameter *a* is expected to depend on the process conditions such as extrusion speed, and on material properties such as recovery time to rebuild the elastic network upon extrusion and the size of the unsheared core in the extruded filament. Using the rheological data for AOT2.5, the theoretically expected δz_{max} matches nicely the experimental data ($R^2 = 0.9952$, Figure 2g) for *a* = 27.29. Equation (1) thus allows to directly relate rheological data to sagging, using a simple scaling relation which takes into account measurable geometrical and materials parameters.

Despite the beneficial effect of the surfactants on the rheological properties of the paste, the presence of organic compounds may lead to adverse effects in the next processing steps by increasing the shrinkage of the template during sintering, and by reacting with the salt and the molten metal during the sintering and infiltration processes. Differential scanning calorimetry (DSC) confirmed that the thermal degradation products of the sulfate-containing surfactants react with the salt to form a lowmelting-temperature compound during heating (Figure 2d). As the corresponding endothermic peak determined at T = 630 °C was detected for all pastes except for the surfactant-free composition and it increases in height with higher surfactant-head concentrations, we can infer that the presence of sulfate groups







Figure 2. Rheological and thermal analysis of the NaCl-based pastes. a) Representative examples of storage modulus (*G'*) and loss modulus (*G''*) evolution at increasing shear-stress amplitudes for the studied pastes. b) Steady-state measurements performed to extract the shear yield-stress of the investigated pastes (τ_p , indicated in red). c) The plateau modulus (*G*₀) and shear yield-stress (τ_p) as a function of the surfactant-tail concentration (c_{tail}). d) DSC measurements of the studied paste compositions quantifying the amount of eutectic NaCl–Na₂SO₄ phase formed. e) Topographical image obtained by profilometry characterizing the filament bridging ability of pastes containing 2.5 wt% AOT (AOT2.5). f) Optical image of the test structure used to assess the paste's bridging ability. g) Sagging (δz_{max}) of filaments as a function of spanning length (*L*). The experimental data was extracted from plot (e) (sintered condition, grey open symbols) and extrapolated to the corresponding green-body deflection expected (white filled symbols). The dotted line is a fitting curve based on beam-bending theory; Equation (1). The log–log plot of the insert illustrates the corresponding power-law dependency.

favors the formation of the low-melting-temperature compound. Chemical analysis by energy-dispersive X-ray spectroscopy (EDS) (Figure S4, Supporting Information) and thermogravimetric analysis (TGA) (Figure S5, Supporting Information) reveal that Na_2SO_4 is formed at the interface between the salt grains after sintering. While Na_2SO_4 itself has a high melting temperature

 $(T_{\rm m} = 884 \,^{\circ}{\rm C})$ and does not cause concerns regarding biological safety.^[42,43] it forms an eutectic composition with NaCl $(T_{\rm m} = 801 \,^{\circ}{\rm C})$ that features a significantly lower $T_{\rm m}$ of 628 $^{\circ}{\rm C}$.^[44] This corresponds well to the endothermic peak detected by DSC (Figure 2d). Such a low-melting-temperature eutectic reacts with the Mg melt to form a surface reaction product that affects adversely the flow behavior of the molten metal and eventually impedes its infiltration into the template. Consequently, the paste AOT2.5 was identified as the most suitable candidate for further analysis. Due to its high tail-to-head ratio, the AOT surfactant needs minimum concentration to achieve the desired rheological properties and leads to a low Na₂SO₄ residue concentration after sintering of the salt template.

Once the surfactant type and concentration were optimized, the selected NaCl-based paste was 3D printed by DIW into template structures with well-controlled grid-like architecture (Figure 1b). After removal of the paraffin oil by either printing directly on a filter paper or by Wick Debinding^[45] (see Experimental Section), the green body was sintered at 690 °C for 3 h. Sintering simultaneously decomposed the organic components and increased the mechanical integrity of the template structure by fusing the NaCl particles. The sintered NaCl template was then infiltrated with Mg melt by squeeze casting. Finally, the salt was dissolved via immersion in an aqueous NaOH solution,^[36] with a pH value adjusted to alkaline conditions to ensure fast dissolution of the template while protecting the Mg from severe corrosion. Examples of the porous structures after each individual processing step are shown in Figure 1c, illustrating the actual 3D-printed, sintered, and infiltrated NaCl templates, and the resulting Mg scaffold with structured porosity.

The ability to 3D print, sinter and infiltrate grid-like salt structures with tunable bridging lengths and filament diameters allows metal scaffolds to be digitally fabricated with precise control over their pore size, pore shape, porosity, and macroscopic geometry. To explore the vast design space available, NaCltemplate geometries with selected grid-like architectures were fabricated and further studied. In one architecture, samples with orthogonal single layers were printed with increasing horizontal spanning length. In another design, double-stacked layers were prepared as a possible way to generate pores with anisotropic cross-section in the final scaffold. The sample geometries were termed according to their spanning length in tens of micrometers (L) and the number of layers (N) between orthogonal filaments. This led to the single-stacked specimens L100/N1, L125/N1, and L166/N1, and the double-stacked sample L125/N2.

Macroscopic images of printed salt structures with these different geometries demonstrate the suitability of the ink for the creation of grid-like structures with tunable designs (**Figure 3**a). A relatively low linear shrinkage of about 13% and a volume contraction of 34 vol% were observed upon sintering of the dried templates (see Supporting Information). The overall low total shrinkage results from the high concentration of salt particles in the paste (70 wt%), which was achieved through the surface functionalization of the NaCl particles with the AOT surfactant. This enables a significant increase in solid loading while keeping the rheological properties of the ink within the required processing window. It is worth noting that the NaCl templates decreased in volume in an isotropic manner when Wick Debinding was used for liquid-phase removal. This is



important to facilitate production of templates with predictable geometry without crack formation or pore distortion after sintering.

Scanning electron microscopy (SEM) images of the sintered template structures (Figure 3b) provide further information about the sintered microstructure and the ability of the printed filaments to withstand distortion induced by gravity and capillary forces. The circular cross-section of the printing needle was successfully translated into circularly shaped NaCl struts after printing, drying, and sintering for all geometries studied (Figure 3b). In contrast to the high fidelity of the filament crosssection, the shape of the filaments along the printing direction was dependent on the bridging distance. Bridging distances of 1 mm and 1.25 mm were printed without substantial sagging, whereas gravity-induced sagging led to distortion of the intended geometry in structures with a filament bridging distance of 1.66 mm. This is in agreement with the findings of the bridging test shown in Figure 2e,f and reflects the fourth power dependence of the maximum deflection on the spanning length (Equation (1)). Besides sagging, gravity also resulted in partial vertical interpenetration of orthogonal filaments at the crossover points, leading to anisotropic shallower pores between the printed NaCl struts. This effect can be compensated by the vertical stacking of consecutive layers (L125/N2, Figure 3b), which allows for an increase in the pore size along the vertical direction. In fact, this is a useful strategy to print elongated strut architectures while keeping a needle with circular cross-section. The successful formation of such stacked layers reveals that the yield stress of the ink was sufficiently high to prevent capillaryinduced merging of the two overlapping filaments. High-magnification imaging of the template after sintering shows the high density, absence of voids, and low surface roughness (Ra) (Ra = $1.06 \pm 0.07 \,\mu$ m) of the NaCl-template struts (Figure 3b).

Mg scaffolds with different geometrical designs were generated by infiltration, followed by leaching of the distinct salttemplate architectures (Figure 3c,d). The resulting scaffolds were investigated in terms of surface quality and possible interfacial reactions between the metal and the salt. Analysis of the printed Mg structure confirmed that the good surface quality of the NaCl template was transferred to the Mg scaffold, which showed an average roughness of 0.85 μ m (see Supporting Information). Despite the formation of Na₂SO₄ at the interface, no major impurities were found in the Mg scaffold (Figure 3c and Supporting Information). This allows for the fabrication of Mg scaffolds with smooth impurity-free surfaces and tailored architectures after removal of the template (Figure 3d).

In addition to regularly ordered architectures, 3D printing also allows for the manufacturing of scaffolds featuring site-specific porosity and pore sizes. We demonstrate this capability by designing and printing exemplary NaCl templates with strut-center distances varying in the range of 0.8–1.5 mm within the same monolithic structure (**Figure 4a**). This enabled the fabrication of graded Mg scaffolds exhibiting pore sizes that increase linearly from 0.3 to 1.0 mm along one of the axes of the structure (Figure 4b). Because the strut diameter was kept constant, such variation in pore size was accompanied by a change in porosity from 9% to 59% throughout this particular axis of the NaCl structure. Simultaneous control of the spanning length (*L*) by the print design and the filament diameter



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Figure 3. Morphology of the produced NaCl templates and Mg scaffolds. a) Macroscopic images of printed and dried (green), and sintered NaCl templates. Grids featuring horizontal spanning lengths of 1 mm (L100/N1), 1.25 mm (L125/N1), and 1.66 mm (L166/N1) and double-stacked grids with 1.25 mm spanning length (L125/N2) were printed and sintered with minimal shrinkage. The scale bar corresponds to 5 mm. b) SEM images of sintered NaCl templates. The side view (upper images) reveals the circular cross-section of the struts. The top view (lower images) confirms the structural regularity of the prints. High-magnification imaging of the struts underlines the high sintering density and surface smoothness. The scale bars correspond to 0.5 mm except otherwise noted. c) Backscattered-electron (BSE) images and corresponding EDS chemical maps of the infiltrate (left) and Mg scaffold (right) confirm a distinct contamination-free interface. The scale bars correspond to 60 μm. d) SEM images of structured pores in the Mg scaffold resulting from a L125/N1 (left) and L125/N2 (right) NaCl template.





Figure 4. Microcomputed tomography (micro-CT) analysis of the Mginfiltration process accuracy using NaCl templates with periodic or graded strut distances in the range of 0.3 to 1 mm. a) Micro-CT 3D reconstruction of an NaCl template (top) and the resulting Mg scaffold (bottom). The red line indicates the location and direction of the cross-sectional cut for the pore-infiltration analysis in (b). The scale bars correspond to 2 mm. b) Experimental (blue) and theoretical (black/gray) analysis of the

(*D*) by adjusting the nozzle size should allow for independent tuning of the scaffold's local porosity and pore size, thus generating porous architectures with site-specific structures and properties. Furthermore, simple geometrical models can be used to derive design guidelines for tuning the local porosity and pore sizes of such manufactured scaffolds (Figure 4b). Assuming that the layer height reduces from *D* to *D** due to the gravity-induced vertical interpenetration of filaments, one can describe the porosity of the Mg scaffold (ρ_{Mg}) as $\rho_{Mg} = \frac{\pi D^2}{4D*L}$. In this analysis, the extent of vertical interpenetration (*p*) is quantified using the ratio $p = \frac{(D-D^*)}{D}$. By adjustment of *p*, it is possible

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to fit the above equation to the experimental data and show that our simple geometrical model describes the measured porosity ρ_{Mg} for p = 0.37 very well. In fact, p = 0.37 is in good agreement with the level of vertical interpenetration observed in cross-sectional SEM images of adjacent filaments (Figure 3b). This agreement between theory and experiments illustrates that the proposed geometrical model can indeed be effectively used to tune the porosity of the final Mg scaffold.

To fully benefit from the wide range of site-specific pore sizes and porosities covered by the proposed additive process, the replication step from the salt template to the metal scaffold must be sufficiently accurate. We evaluated the level of accuracy achieved through the infiltration and leaching process by conducting microcomputed tomography (micro-CT) scanning analysis of both the NaCl template and the resulting Mg scaffold (Figure 4a-d). Figure 4c shows corresponding cross-sections of tomograms obtained along the x-, y-, and z-direction. The accurate match of the overlaid micro-CT images of the NaCl template and the Mg scaffold for all directions (Figure 4c,d) underlines the good wetting of the Mg melt on the NaCl surface and the high fidelity of the process. An infiltration defect was detected in the center of the structure (dashed arrows in Figure 4c), which is believed to result from Mg shrinkage during melt solidification. Such shrinkage cavities are common in metal casting and can be avoided by active directional cooling. Whereas even small defects in the NaCl template are replicated in the metal scaffold (solid arrow, bottom, y-direction in Figure 4c), internal microporosity in the sintered NaCl structure

Mg porosity (ρ_{Mg}) of a scaffold fabricated from structures with gradually increasing spanning length L. The theoretical porosity values in Mg are taken here to be equivalent to the volume fraction of NaCl. $ho_{\rm Mg}$ is shown for varying extents of vertical interpenetration (p) into the nextlayer filament (top). A gradual increase of the NaCl-pore sizes between 0.3 mm and 1 mm (blue numbers) was achieved by varying L in the NaCl template between 0.8 mm and 1.5 mm (black numbers) (bottom). c) Superimposed images of NaCl (red) and Mg (blue). The top row displays a cross-section that highlights the continuous NaCl network, while the bottom row shows another cross-section depicting the continuous Mg network. The white solid arrows indicate micropores, which were transcribed if located on the surface of the NaCl (bottom, y-direction) and not transcribed when trapped within the NaCl print (bottom, x-direction). Defects in the infiltration process were observed (dashed arrows) due to shrinkage-cavity formation. The scale bar corresponds to 2 mm. d) Analysis of strut diameters of the sintered NaCl template (red) and pore diameters of the Mg scaffold (blue). e) Optical images of an infiltrated cube shaped by machining without distortion of the pore structure. f) Machined Mg scaffold obtained after leaching of the NaCl template.

remained unfilled after infiltration due to the closed nature of the micropores (solid arrow, bottom, *x*-direction in Figure 4c). The strut size of the NaCl template and the respective pore size of the Mg scaffold were found to correlate closely (Figure 4d), with a maximum mismatch of 0.03 mm. This corresponds to less than 7% for a printing-needle diameter of 0.51 mm. Given the high fidelity achieved through infiltration and leaching, the accuracy of the overall process was therefore found to be limited by the 3D-printing precision of the NaCl template rather than by the infiltration capabilities of the Mg melt.

Besides the high replication precision and the ability to deliberately vary the porous architecture of the final scaffold, this additive manufacturing technology can also be combined with subtractive methods to allow for further control of the macroscopic shape and finishing quality of the fabricated materials. We demonstrate this possibility by machining Mg-infiltrated salt templates into 3D parts of different macroscopic geometries and smooth surface finishing using conventional subtractive operations such as drilling, turning, and grinding. The mechanical stability and robustness of the infiltrated salt template are highly advantageous during shaping of relatively soft materials such as Mg. Moreover, machining does not affect the well-defined porous architecture provided by the template. To illustrate this, an infiltrated structure initially printed in cubic shape was machined into a torus geometry and examined after removal of the salt (Figure 4e). Upon leaching of the NaCl template, an Mg scaffold without detectable pore distortions was produced (Figure 4f), underlining the advantage of the rigid NaCl template in providing the mechanical stability necessary for post-processing of the Mg-infiltrated parts.

In conclusion, direct ink writing of salt-based pastes, followed by metal infiltration and leaching of the sintered salt templates, is an effective digital manufacturing approach to create Mg scaffolds with tunable porous architectures in a wide range of macroscopic shapes. Designing inks with high concentrations of surface-modified salt particles is crucial to achieve the rheological properties required for distortion-free printing and to minimize shrinkage during sintering of the printed salt template. Moreover, the organic molecules used for surface modification should not lead to compounds that may adversely react with the molten metal in the infiltration step. The good surface wetting of the Mg melt on the NaCl templates enables precise replication of even micrometer-sized features into the final porous scaffold. Because of their high mechanical stability, infiltrated salt templates can be machined before the leaching step, which increases further the versatility of the proposed processing route. This technology can potentially be extended to other scaffold materials that have so far been limited to random and poorly controlled porosity. The ability to control the porous architecture using this additive approach offers great advantages in 3D-cell culture and tissue engineering by enabling guided cell growth, or in lightweight structural applications by introducing anisotropic mechanical properties at an appreciated weight reduction.

Experimental Section

Materials: The surfactant bis(2-ethylhexyl) sulfosuccinate sodium salt (AOT) (97% purity) and paraffin oil (puriss, Ph. Eur., BP) were purchased from Sigma Aldrich. The surfactant sodium dodecyl sulfate (SDS) (99%

purity) was obtained from Acros Organics. The NaCl was purchased from J.T. Baker Chemical Co. Graphite powder (325 mesh, 99.9995% purity, metal basis) was obtained from Alfa Aesar. The Mg (99.95% purity) was purchased from non ferrum GmbH. An aqueous solution of HNO₃ (>65% purity) from Sigma Aldrich was used to remove the oxide layer on the Mg before infiltration. Nital solution (1 vol% HNO₃ in ethanol) was used for surface cleaning of the final Mg scaffolds.

Paste Preparation: The surfactant, either SDS or AOT, was dispersed thoroughly in paraffin oil by magnetic stirring overnight. After the addition of NaCl, the pre-paste was ball-milled at 300 rpm (planetary ball mill PM100, Retsch GmbH). A custom-made alumina milling jar and a mixture of two sizes of zirconia milling balls were used. For 100 g of paste, 125 g and 200 g of zirconia balls of diameters 5 mm and 15 mm, respectively, were used. Milling was performed for 3 h in total, divided into 20 min of milling spaced by 10 min pause to allow for cooling and thus prevention of thermal decomposition of the organic compounds. Pastes were prepared with 28.6 wt% paraffin oil (percentage of the total paste mass). The surfactant amount stated refers to its mass percentage with respect to the NaCl mass used. Surfactant concentrations of 0 wt% (Surfactant0), 2.5 wt% (AOT2.5, SDS2.5), or 10 wt% (AOT10, SDS10) were deployed.

Rheological Measurements of NaCl Paste: The viscoelastic rheological behavior of the NaCl pastes with different amounts of either SDS or AOT was characterized using a stress-controlled rheometer (oscillatory measurements: Gemini Advanced Rheometer, Bohlin Instruments: viscometry measurements: Anton Paar MCR 302, Anton Paar GmbH). A parallel serrated-plate geometry with 2 cm diameter and 1 mm gap was used to minimize wall slip (see Figures S1 and S2, Supporting Information). To evaluate the shear yield-stress (τ_v) , steady-state measurements were conducted by applying a logarithmically increasing shear stress from 1 to 1000 Pa. The value of τ_v was obtained at the point of sudden increase of shear stress (Figure 2b). In order to determine the plateau modulus (G_0), oscillatory measurements were performed using an amplitude sweep with a stress amplitude that increased logarithmically from 1 to 10 000 Pa. The frequency was held constant at 1 rad s⁻¹. G_0 was obtained from the plateau value of G' between 1 and 10 Pa for SDS10, AOT2.5 and AOT10 or between 100 and 500 Pa for Surfactant0 and SDS2.5. The rheological measurements were conducted at room temperature (RT) and were performed three to five times in the case of the oscillatory measurements to determine averaged values of G_0 or once in the case of the viscometry measurements to evaluate τ_{y} .

3D Printing: The 3D printed structures were prepared using a pressure-controlled direct ink-writing device (3D Discovery, regenHU Ltd.) with the corresponding software for the design of CAD files (BioCAD, regenHU Ltd.). Immediately before printing, the paste was mechanically mixed at 1000 rpm (RZR 2102 Control, Heidolph Instruments GmbH & Co. KG) for 5 min to assure homogenization, followed by degassing using planetary centrifugal mixing (Thinky Mixer ARE-250, Thinky Cooperation). Printing pressure and the xy-speed were set to 1.8 mbar and 8 mm s⁻¹, respectively. A straight stainless steel nozzle with an inner nozzle diameter of 0.51 mm (H. Sigrist & Partner AG, Matzingen, Art F560089_LB) was used to print orthogonal strut grids of different line spacing; namely 1 mm (L100/N1), 1.25 mm (L125/ N1), and 1.66 mm (L166/N1) to construct 10 mm \times 10 mm printed objects. Double-vertical stacking (1.25 mm \times 2 – L125/N2) was achieved by printing two layers on top of each other before printing the next layer with orthogonal orientation. For the graded sample, the horizontal strut distance was varied between 0.3 mm and 1 mm, corresponding to a strut-center distance of 0.8 to 1.5 mm, in steps of 0.1 mm. The triangular structures used to assess the paste's bridging ability were printed with the same set-up and printing parameters as described above.

Drying and Sintering: The removal of the paraffin oil was performed at room temperature either by the use of a filter paper or graphite powder. For the former, the parts were printed directly on a conventional filter paper, which absorbed the paraffin oil from the printed object. While this process is simple, cheap and can be accomplished without the use of additional chemicals, it resulted in slightly heterogeneous shrinkage



due to free contraction at the top of the print and restrained contraction at the contact to the filter paper (Figures 1c and 3). To achieve isotropic shrinkage, the filter paper was replaced by graphite powder. Since the prints are too soft to be handled at room temperature, the printed structures were submerged in liquid nitrogen to easily remove the sample from the supporting glass slide, followed by storage in graphite powder for 72 h to remove the paraffin oil by capillary forces (Wick Debinding)^[45] (Figures 2f and 4). Sintering was performed in a conventional resistance furnace (HT 08/17, Nabertherm) at atmospheric pressure. The temperature profile was defined according to the decomposition temperature of the organic components. The following profile was used: i) heating from room temperature to 200 °C in 2 h, ii) holding for 2 h for removal of paraffin oil, iii) heating from 200 to 400 °C in 2 h, iv) holding for 5 h to decompose the surfactant and residual paraffin oil, v) heating from 400 °C to 690°C in 5 h, vi) holding for 3 h to sinter the NaCl particles, and vii) cooling to room temperature.

Evaluation of Bridging Ability of Pastes: The experimental set-up was based on the work of Smay et al.^[37] A support structure was printed, consisting of two triangles with the same vertex, followed by printing of the spanning filaments across the support structure. The inner triangle and outer triangle had a vertex angle of 15° and 30°, respectively, and an equal height of 19 mm (see Figure 2f). The spanning filaments were printed perpendicularly to the bisector, starting at 3.0 mm from the vertex and at a distance of 1.5 mm between the print lines. For printing, drying, and sintering, the same protocols as previously described were followed. For the evaluation of the sagging behavior, the z deflection of the spanning filaments as a function of spanning distance was measured by optical confocal profilometry (Plu NeoX, Sensofar). Data acquisition and processing were carried out with the SensoSCAN (Sensofar-Tech, S.L.) and SensoMAP (Digital Surf) softwares, respectively. Further data processing and extraction of the z deflection were performed using the Gwyddion software (Gwyddion 2.47, GNU General Public License, http://www.gwyddion.net, 2016). The sagging was evaluated on the sintered scaffold and the data were extrapolated by accounting for the shrinkage of 13%.

Differential Scanning Calorimetry (DSC): To identify and determine the amount of eutectic Na₂SO₄–NaCl phase, DSC scans (DSC1 STAR^e System, Mettler Toledo) were run for sintered and subsequently ground pieces of paste. A sample mass between 1.5 mg and 3 mg was placed into an alumina crucible (30 μ L, Mettler Toledo), while the reference crucible remained empty. A scan was performed from 25 to 700 °C at a heating rate of 10 °C min⁻¹. Gas flow rates of Ar and N₂ were set to 30 mL min⁻¹ and 200 mL min⁻¹, respectively, and kept at all times during the experiment.

Infiltration with Mg: Sintered NaCl templates were infiltrated with Mg melt by squeeze casting. For the removal of surface oxides and impurities, conventional-pure Mg (99.95% purity, non ferrum GmbH) was first cleaned in 10 vol% HNO₃. The NaCl template was placed into a graphite crucible with the Mg placed on top, and finally covered by a mechanical punch. The Mg was inductively melted at 700 °C. The temperature was recorded by a thermocouple introduced in the crucible wall. Once the melting temperature was achieved, a pneumatic air pressure of 1.4 bar was applied onto the punch. The generator power was switched off immediately after application of the pressure, allowing the infiltrate to cool down to room temperature. The pressure was maintained until the crucible temperature was below the solidification temperature of Mg. Vacuum was kept below 10^{-4} mbar during the infiltration process.

Leaching of NaCl Template: The removal of the NaCl template was performed following a protocol established by Nguyen et al.,^[36] whereby the infiltrate was placed in aqueous NaOH solution (pH 13.6) and sonicated for 3 min. This was repeated twice, followed by 3 min of sonication in ethanol for final cleaning.

Particle-Size and Surface-Roughness Measurements: The particle size of the as-received salt grains and the NaCl grain size after paste preparation were analyzed by light microscopy. The as-received particle size was imaged (Polyvar-Met, Reichert) and measured (Image) software, version 1.50i, http://imagej.nih.gov/ij) to be 451.4 \pm 158.3 μ m. After the paste

preparation, the particles were washed with hexane in order to eliminate residues of nonvolatile organic components. The obtained particles were evaluated using a high-resolution digital light microscope (Keyence VHX-S660E, DE) at $3.8 \pm 2.9 \,\mu$ m. The surface roughness of the NaCl template and Mg scaffold was determined using the digital light microscope. The roughness was measured over a length of 80–300 μ m for a total number of samples of *n* = 5 (NaCl) and *n* = 12 (Mg).

Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy: To evaluate the morphology of the scaffold's surface and the chemistry of the infiltrate's interface, imaging with a scanning electron microscope (SEM) (Hitachi SU-70, Hitachi company) equipped with an energydispersive X-ray spectroscopy (EDS) detector (X-Max^N, Oxford Instruments) was performed. For all EDS scans, the acceleration voltage was set to 15 kV and the working distance to 15 mm. For the analysis of the pore structure and interface chemistry, the infiltrates were cut and thoroughly polished. Cutting was performed in a dry state without any solvents followed by polishing with a 4000 SiC grinding paper with isopropanol as a lubricant to avoid corrosive attack. For the final Mg-scaffold analysis, the cut infiltrates were leached, followed by an additional polishing step of the cut surface. The EDS analysis was performed at the edge of an Mg pore/NaCl strut of a L125/N2 infiltrate/ scaffold in cross-sectional preparation. Before imaging, the NaCl templates were sputtered with gold to enhance electron conductivity, and the infiltrates were sputter-coated with carbon to avoid heavy degradation at the NaCl-Mg interface promoted by galvanic coupling between Mg and gold.

Microcomputed Tomography: Micro-CT was performed on a dried and sintered NaCl template, and the corresponding Mg scaffold using a Scano μ CT 50 instrument (Scanco Medical). Scans were performed at an intensity of 8 W and 18 W, an energy level of 55 kVp and 90 kVp (peak kilovoltage), an integration time of 800 ms without frame averaging, and a nominal resolution of 10 μ m for the NaCl template and the Mg scaffold, respectively. The data were further analyzed using ImageJ software (version 1.50i, http://imagej.nih. gov/ij), where the strut- and pore-size of the NaCl template and Mg scaffold, respectively, were measured in the *x*-, *y*-, and *z*-directions on at least 150 struts each.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

DVANCED

Keywords

3D printing, direct ink writing, magnesium, NaCl, salt leaching

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