Sustainable, Natural Pore Formers and Process Additives for the Ceramic Industry*

Nature offers an almost inexhaustible reservoir of usable functions that have always been present in the plant world. Each plant species has its own outstanding, individual characteristics. The innovative, "green" future technology of J. Rettenmaier & Söhne Group uses these valuable functions and properties and opens them up to all areas of life and modern industry. This article describes the function of these particles as natural pore formers and process additives.

Fig. 1
Products supplied by J. Rettenmaier & Söhne Group

1 Introduction

The J. Rettenmaier & Söhne Group (JRS) dedicated itself to research, development and processing of high quality organic fibres and particles derived from vegetable raw materials, e.g. cellulose, wood fibres or cereal and fruit fibres. JRS makes many features of these valuable natural substances available for industrial purposes. Caring for the ecological cycle is always a top priority. Therefore, sustainable vegetable raw materials will always be the basis of the Group's product philosophy in the future.

As an owner-managed, independent family business, the Group stands for innovation, long-term perspectives, reliability and security. The global orientation of JRS makes an optimal procurement of raw materials of the highest possible quality which is an important requirement in order to produce a wide variety of unique products. The Group's certified advanced production technology stands for top quality, innovative functionality and a perfect price/performance ratio.

JRS provides organic cellulose and lignocellulose particles modified for utilisation in the ceramic industry. One can expect high-class purity combined with constant product performance. Outstanding quality is guaranteed by certified quality control. High variety enables optimal usage. Different structures lead into different effects in your production process as well as for the performance of your final ceramic products. Tailor-made selection of natural particles allows controlled improvement of your application.

Natural cellulose and lignocellulose products are used as pore formers and to control the moisture distribution.

Advantages are:
- Control of pore volume, structure and size
- Short drying times
- Low reject rate
- Less cracks and fissures
- High flexibility of ceramic bodies.

The Group's products are available in various sizes and structures:
- Long fibres
- Cubic particles
- Granules
- Spheres
- Cellulose gels

and are manufactured out of different raw materials:
- Wood
- Cellulose
- Annual plants
- Recycled paper.

2 Usage as pore formers

During sintering the natural particles are completely burned out, so that pores remain. Pore volume, pore structure and pore size distribution are controlled. The study has been realised and elaborated by the staff of the Advanced Ceramics Group at the University of Bremen/DE. They followed an innovative approach based on usage of ARBOCEL particles as pore creators for ceramics. By variation of cellulose particle structure and size they evaluated the effect on pore character-

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J. Rettenmaier & Söhne GmbH + Co KG
73494 Rosenberg
Germany

www.jrs.de

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isation. Three different types of cellulose were used.

- Type 1: Cellulose particles: density of 1,49 g/cm³, average particle length of 18 µm, average particle thickness of 15 µm,
- Type 2: Microcrystalline cellulose granules: density of 1,53 g/cm³, average granule diameter of 150 µm,
- Type 3: Microcrystalline cellulose spheres: density of 1,50 g/cm³, average sphere diameter of 300 µm.

Investigations were made according to the processing mediated by ionotropic gelation developed by the Advanced Ceramics group. After the first step of alginate dissolution at slightly alkaline conditions, the aluminium oxide ceramic particles are added and then stabilised by trichloroacetic acid. Now the cellulose particles (15 vol.-%) are added. Following, the mixture must be cooled (<10 °C) before the calcium iodate as cross linker can be added. Calcium cations initiate the gelation. The green body is dried at 20 °C for four days. Shrinkage is around 10 %. Sample discs (27 mm diameter, 3 mm thickness) are cut and grinded.

Finally the gelled parts are sintered (at 1350 °C for 2 h), which leads to the chemical consolidation of ceramic particles. Simultaneously the cellulose particles are burned out, so that pores remain. Shrinkage after sintering is around 17 %.

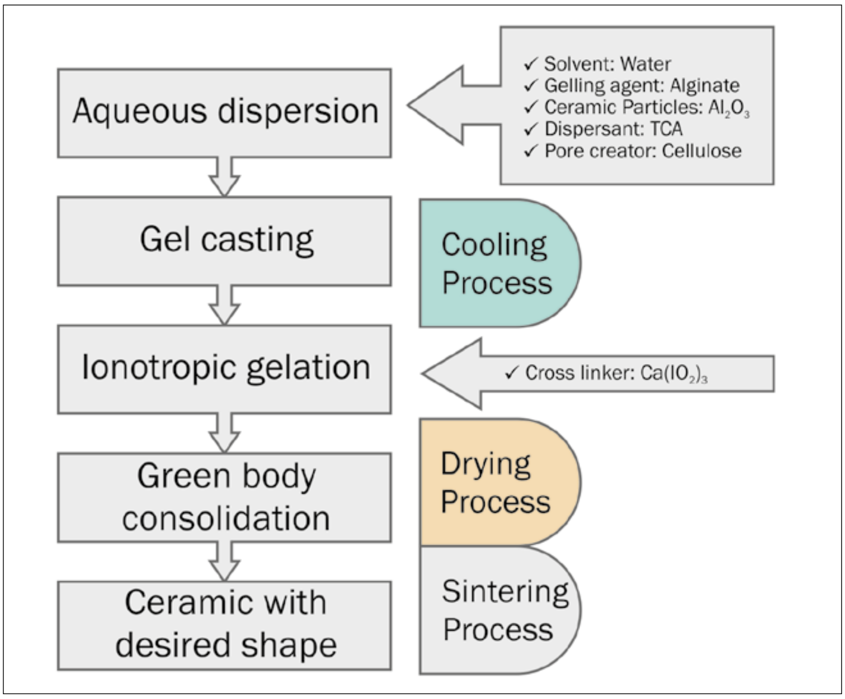

Fig. 2
Gelcasting process

3 Results

3.1 Pore structure

Cellulose is the raw material base of all three products. Microcrystalline Cellulose (MCC) is chemically treated to increase the amount of the crystalline content. Therefore, the structure of MCC is different from standard cellulose. This creates different pore structures after sintering:

- Cellulose particles → oblong pore channels
- MCC particles → nearly cubic pores
- MCC spheres → ball-shaped pores.

The pore structure is specifically controlled by choosing the equivalent particle structure.

3.2 Porosity/pore quantity

Pores can be differentiated in open pores, closed pores and a combination of both. The preferred kind of pore strongly depends on the requested functionality. Total

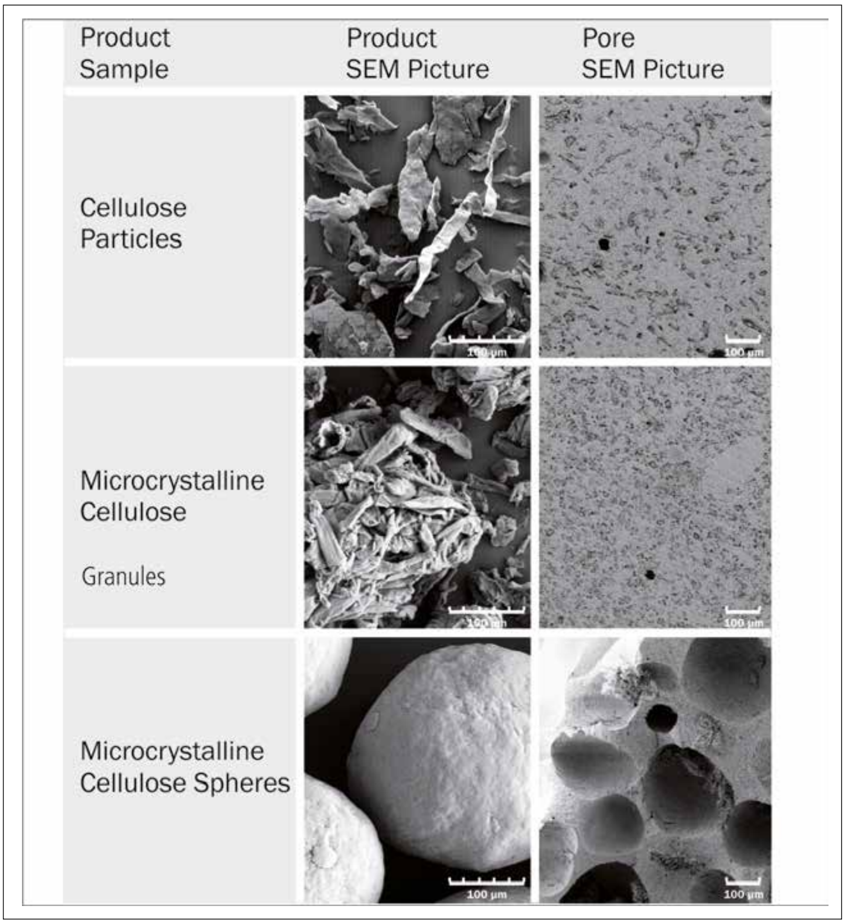

Fig. 3
SEM-micrographs

Tab. 1
Results summary

Product	Density (DIN 1094) [g/cm³]	Amount Pore Creator [g]	Amount Pore Creator [vol.-%]	d_{50} Particles [µm]	d_{50} Pores [µm]	Porosity, Total [%]	Porosity, Open (DIN EN 623 part 2) [%]	Shrinkage after Sintering (1500 °C, 2 h) [%]	Pores Structure
Cellulose particles	1,49	8,84	14	19,39	1,26	30	22	17	Channel
MCC granules	1,53	11,01	16	43,62	1,38	32	22	17	Cubic
MCC spheres	1,50	6,0	15	316,9	35,09	22	16	17	Spherical

porosity is defined as the sum of open and closed pores.
An increase of total porosity leads to an increase of open pores. Only closed pores will disappear starting at a total porosity level of nearly 10 %. The reason is that with a higher amount of pores, the single pores necessarily come into direct contact. The connection of several closed pores will result in the creation of new pore channels (= open pores).
Cellulose particles as pore creators that:

- create twice as much total porosity as used fibre content, e.g. 30 % total porosity realised by 15 % cellulose.
- follow the typical positive correlation of total porosity and open porosity, e.g. 30 % total porosity = 10 % closed pores + 20 % open pores and 40 % total porosity = 10 % closed pores + 30 % open pores.

3.3 Pore size
Pore size distribution is detected according to mercury intrusion porosimetry. The pore channel is defined by the contact area of the single pores. For fibrous particles the contact area corresponds to

the pore diameter. Here the particle diameter is uniform and therefore results in a unimodal pore size distribution. Due to the nature of cellulose particles the diameter is always in the range of 20–30 µm, independent from the particle length.

In consequence the pore size distribution is similar for all fine cellulose particles. In contrast to this study rougher cellulose grades (>1000 µm) tend to agglomerate, which causes coarser and varying pores. For granules and spheres the contact area varies. Variation of contact area leads to a wide pore size distribution (bimodal or multimodal). Even though the diameter of the cellulose granules is very uniform, granules tend to break at high shear forces during the ceramic production process. This leads into uncontrolled final granule sizes as well as contact areas. Pore size distribution is unpredictable and strongly depends on the production process parameters.

4 Discussion

One has to evaluate and discuss these results in context with the final ceramic application. Regarding the pore structure it could be possible to induce a controlled breaking behaviour of the ceramic part or to improve vessel growth in medical applications (bone replacements).

Increased porosity will lead to lightweight materials for the automotive industry, it can improve the thermal shock resistance for refractory ceramics and it can result in a higher inner specific surface area for catalyst carriers. For filtration applications specific pore sizes will enable a controlled permeability and a accurate separation of the single components. Microporosity will be an advantage for applications with high stability requirements.

5 Future

The next step will be to investigate the influence of pore structure, quantity and size on strength parameters.

There have to be also examined alternative natural fibres from the Group's portfolio like recycled paper fibres, wood fibres, fibres from annual plants (corn, oat) and speciality fibres/particles from e.g. nut husks or olive pits.

References

[1] Brandes, C.; et al.: Gel casting of free shapeable ceramic membranes with adjustable pore size for ultra and microfiltration. J. Amer. Ceram. Soc. **97** (2014) [5] 1393–1401. http://dx.doi.org/10.1111/jace.12877

[2] Brandes, C.; et al.: Aluminium acetate as alternative cross-linker for temperature controlled gelcasting and joining of ceramics. J. Europ. Ceram. Soc. **36** (2016) [5] 1241–1251. http://dx.doi.org/10.1016/j.jeurceramsoc.2015.12.011

[3] Brandes, C.; et al.: Gel casting of large area micro- and sub-micropatterned thin ceramic tapes. Ceram. Int. **42** (2016) [4] 5036–5044 http://dx.doi.org/10.1016/j.ceramint.2015.12.015

[4] Brandes, C.: Complex structured ceramic components by combination of temperature controlled ionotropic gelation and plastic processing. Dissertation, University of Bremen, Advanced Ceramics, 2016. http://publica.fraunhofer.de/documents/N-393788.html