Book of Abstracts
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Exploring a particle engineering toolbox of intensified processes to prepare precipitates with improved properties

C.P. Mark Roelands,[a] J.G.H. Brouwer,[a] J. van der Meer,[a] A.E.D.M. van der Heijden,[b] D. Verdoes[a]

[a]*TNO Science & Industry, Separation Technology, PO Box 342, 7300 AH Apeldoorn, Netherlands*
[b]*TNO Defense, Security & Safety, PO Box 45, 2280 AA Rijswijk, Netherlands*

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1. Summary

By development of a Toolbox consisting of innovative and intensified processes TNO aims for improved control over size, structure and shape of precipitates.
The Particle Engineering Toolbox aims for:

1. production of (sub)micron particles,
2. controlled production of (large) particles with narrow particle size distributions,
3. influencing habit and structure.

2. Extended Abstract

Approximately 70% of the chemical industry's products are produced in solid-state, many of them in crystalline form. In crystallization the function of separation, defined by yield and by purity, is integrated with the function of product formation. Crystalline products are defined by three characteristics: particle size distribution (PSD) e.g. mean and width of the distribution, structure e.g. polymorphs and solvates, and habit e.g. prisms / platelets / needles and aggregates / single crystals. These three characteristics control the product properties that are essential for their application: e.g. filterability, solubility and dissolution rate, color intensity or compressibility.

Using standard production methods (stirred batch vessel) the desired specifications for size, structure and habit are not always met. Especially reactive crystallization processes proceed in an uncontrolled way because of high and of varying supersaturation due to incomplete mixing. As a result undesired extreme expression of the three characteristics is not unusual: e.g. the formation of metastable polymorphs, needle-shaped crystals, a wide PSD and often aggregated particles. Desired are innovative techniques aimed at control over these characteristics. while the ability to produce crystals with improved characteristics enables novel, potentially high-value applications.

The TNO Particle Engineering Toolbox contains three patented techniques:

a. Rotating Crystallization and Separation (ROCS): controlled production of very small (sub)micron particles (0.1-10µm) with a narrow PSD and potentially a different shape. ROCS is a 'high-gee' technique, a form of Process Intensification by means of crystallization using membranes in an external centrifugal field. The process takes place under mild conditions considering pressure and temperature. Potentially the technique is combined with existing equipment for wet-chemical precipitation processes.

b. Membrane / Filter Assisted Crystallization (MAC/FACT): crystallization on the surface of heterogeneous seeds results in large particles that facilitate filtration by formation of a stable filter cake. With smart heterogeneous seeds (templates) it is potentially also possible to influence the structure and shape of the crystalline products. In principle seeds can be retrieved after use and recycled in the process. The process is proven on pilot-scale for water softening.

c. Helix tube reactor with intensified mixing (Helix): by continuous precipitation potentially small particles with a narrow particle size distribution can be obtained. The Helix-reactor combines intensified mixing (due to secondary circulation) with a low pressure drop. Scale-up can in principle be achieved by the scale-out principle. Apart from reactive and cooling crystallization this technique potentially allows for coating of particles.

The three innovative techniques are generic and can be applied for all precipitation processes: reactive, pH-shift and anti-solvent crystallization. An additional benefit is that the techniques can be used in combination with conventional equipment like stirred vessels. Applications are envisaged for different compounds: inorganic and organic, for example in specialties and fine chemistry, materials, electronics, pigments, food, and pharmaceuticals.

To illustrate the potential of these techniques two case studies for ROCS are highlighted. It is demonstrated for two compounds how the particle characteristics can be controlled. The inorganic compound manganese carbonate was made by reactive crystallization from aqueous solution. Monodisperse crystals of (sub)micron size and with spherical shape were obtained as shown in figure 1. The principle was demonstrated for batch and continuous process operation. Furthermore, an organic energetic material was crystallized using different combinations of solvents and anti-solvents. By varying the process parameters: concentration, ratio S/AS and the gravitational force monodisperse crystals were prepared as shown in figure 2.

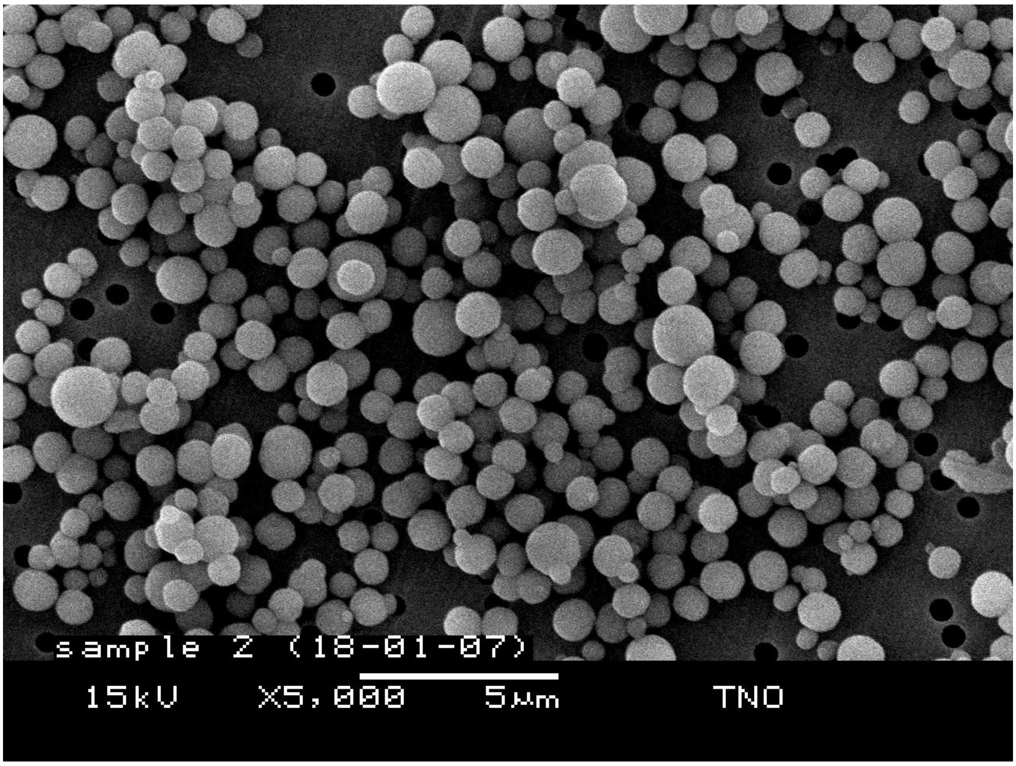

Figure 1: SEM picture of monodisperse $MnCO_3$ particles precipiated with the ROCS technique

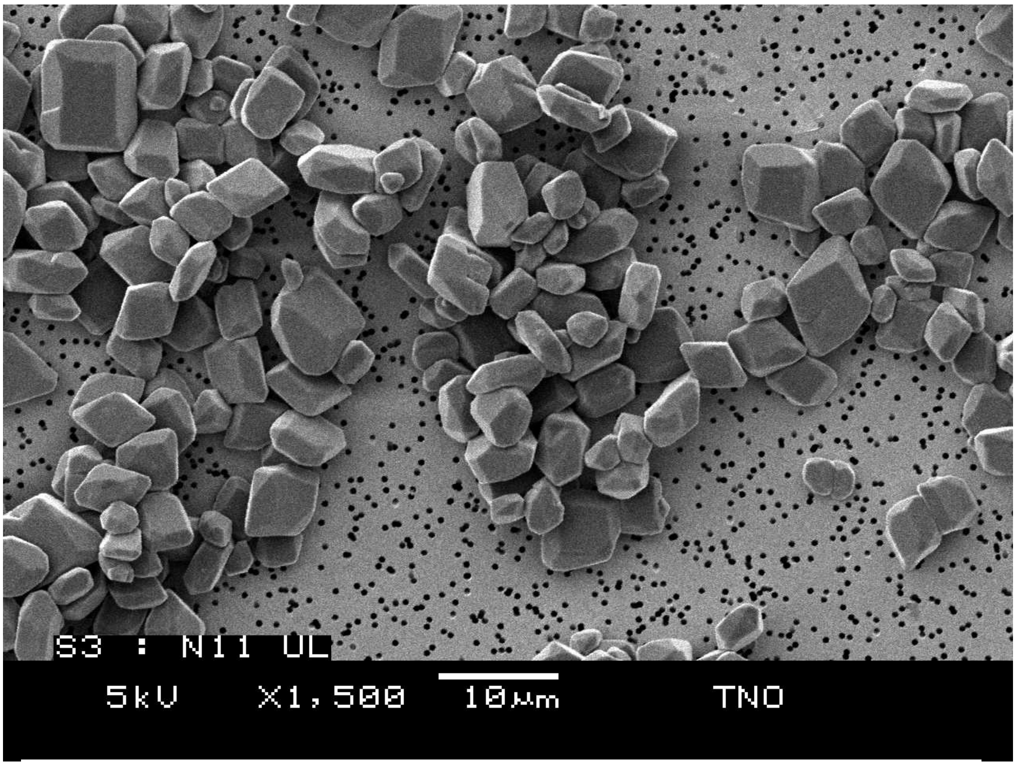

Figure 2: SEM picture of monodisperse crystals of an energetic material precipiated with the ROCS technique