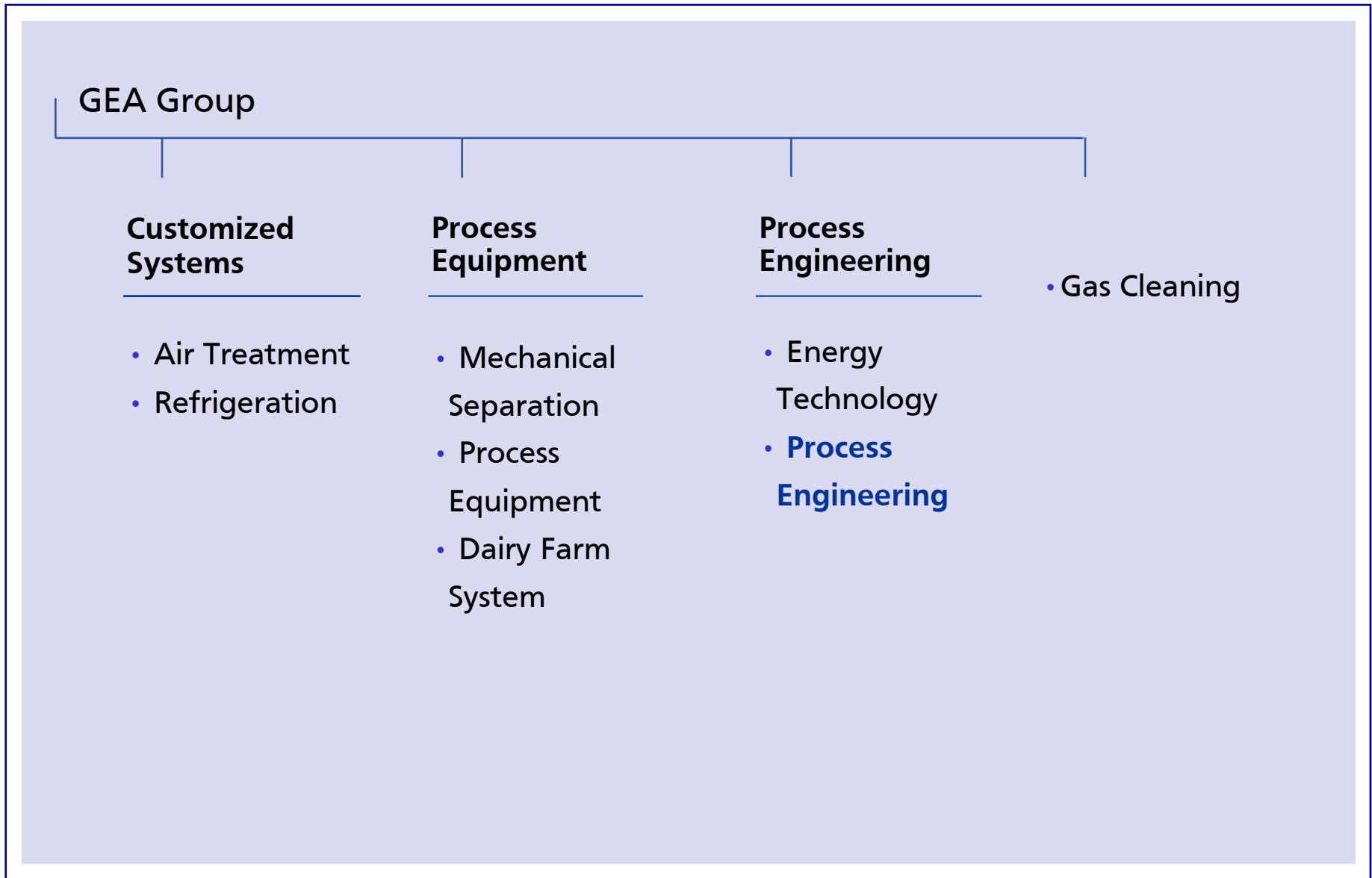


Niro Process Technology B.V.

Melt Crystallization & wash column separation
i-SUP 2008
Brugge

April 23, 2008

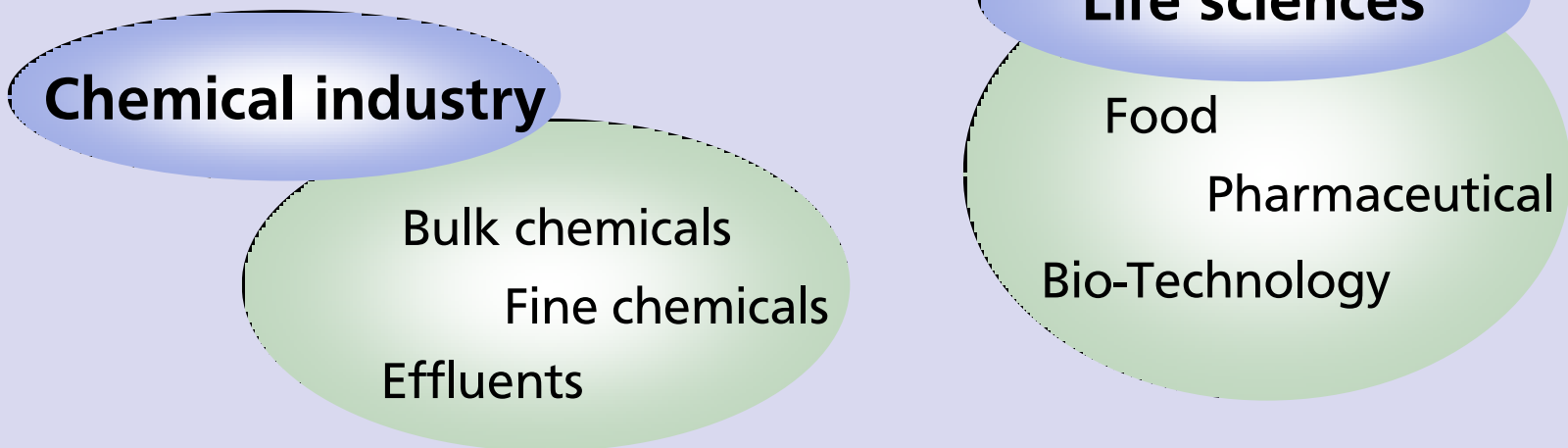


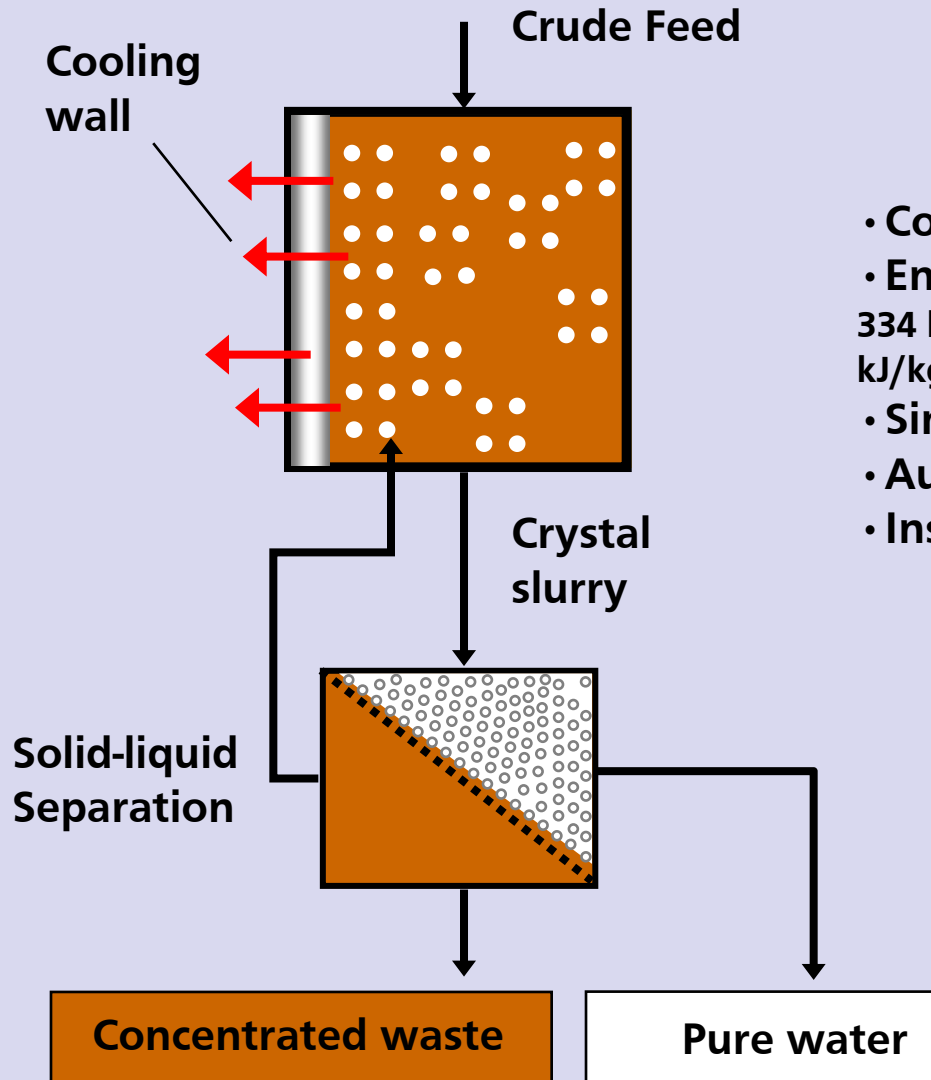


Niro PT core technologies:

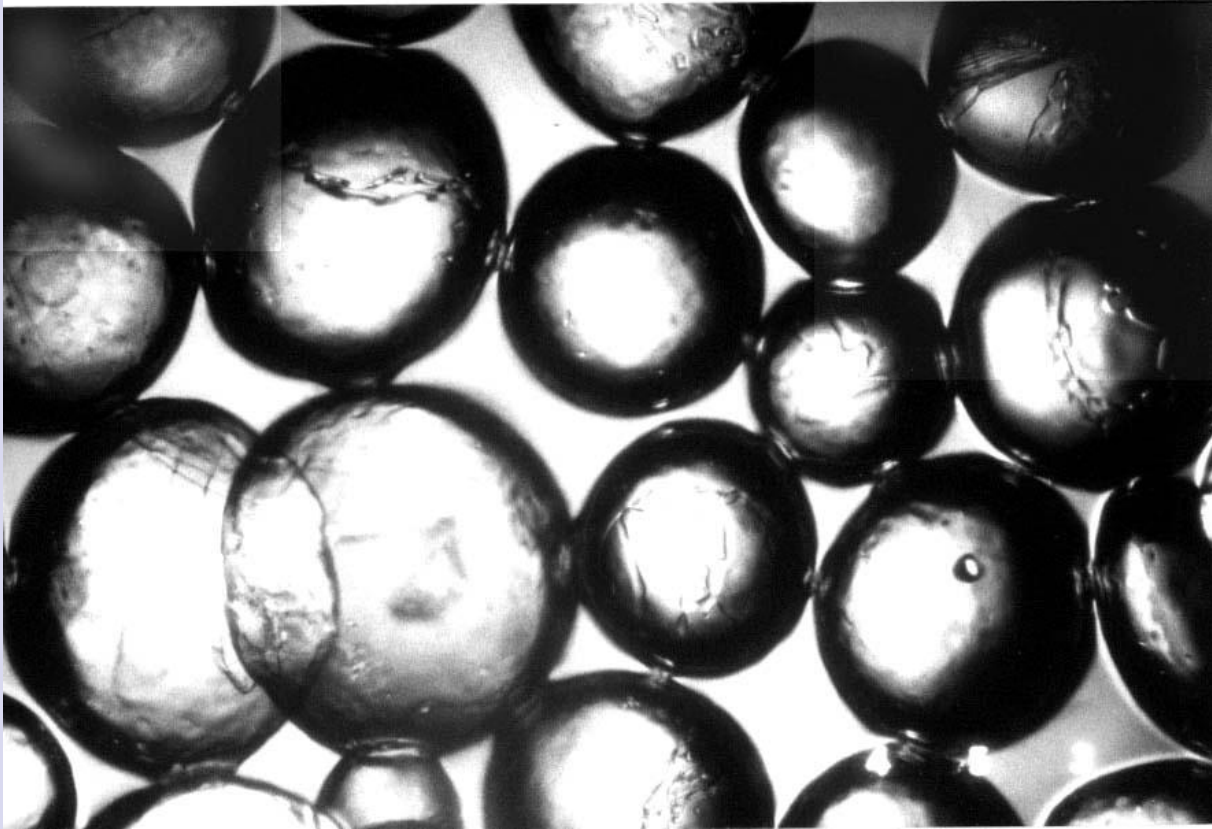
- Freeze concentration technology
- Melt crystallization technology
- Wash column separation technology

Main application areas:





- **Continuous operation**
- **Energy efficient** (heat of crystallization = 334 kJ/kg versus heat of evaporation 2200 kJ/kg)
- **Simple temperature control points**
- **Automatic reject discharge**
- **Insensitive to normal feed variances**

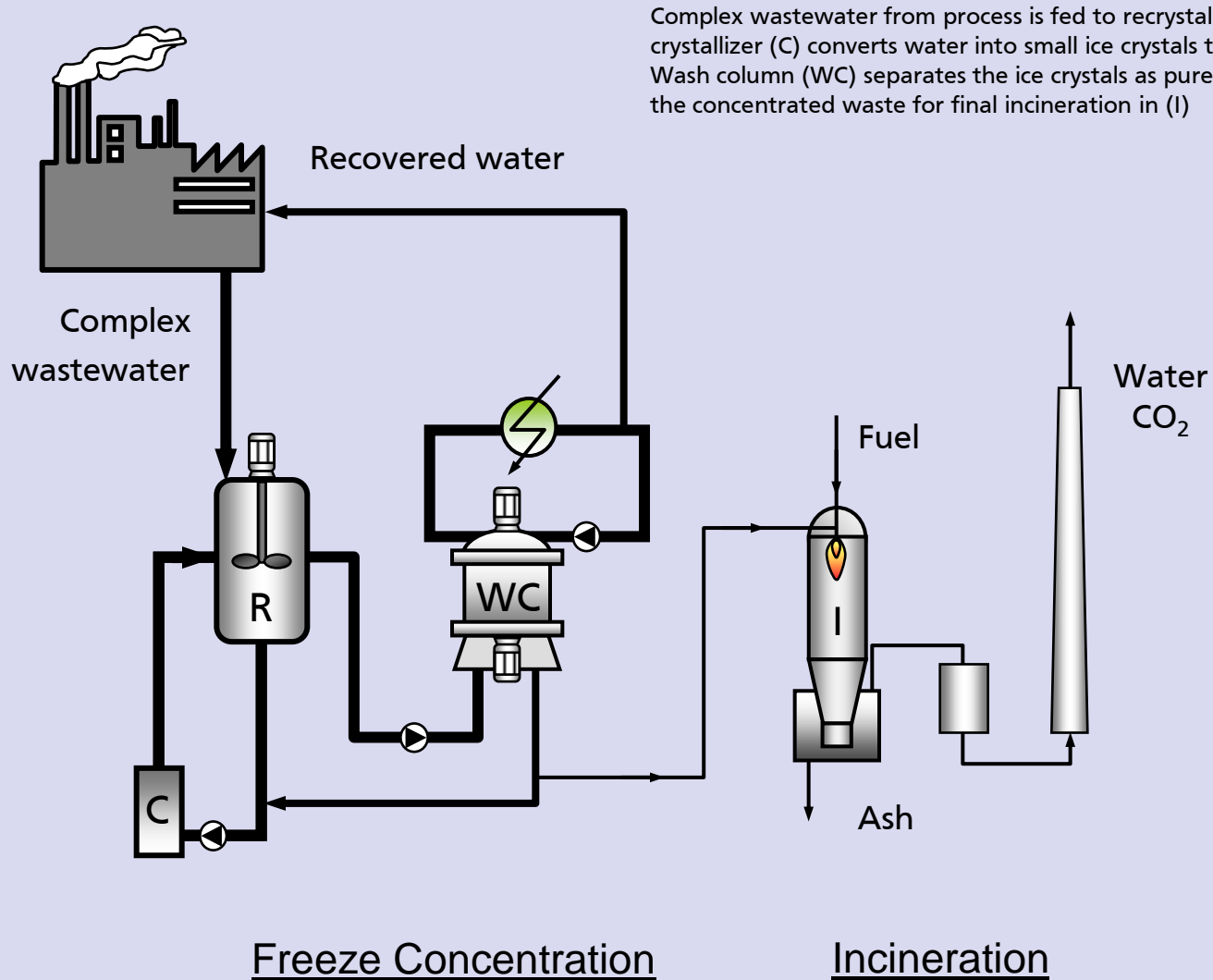


**SPERICAL
CRYSTALS**

**DIFFERENT SIZES
(0.2mm- 1mm)**

**100% PURE ICE
(NO
INCLUSIONS)**

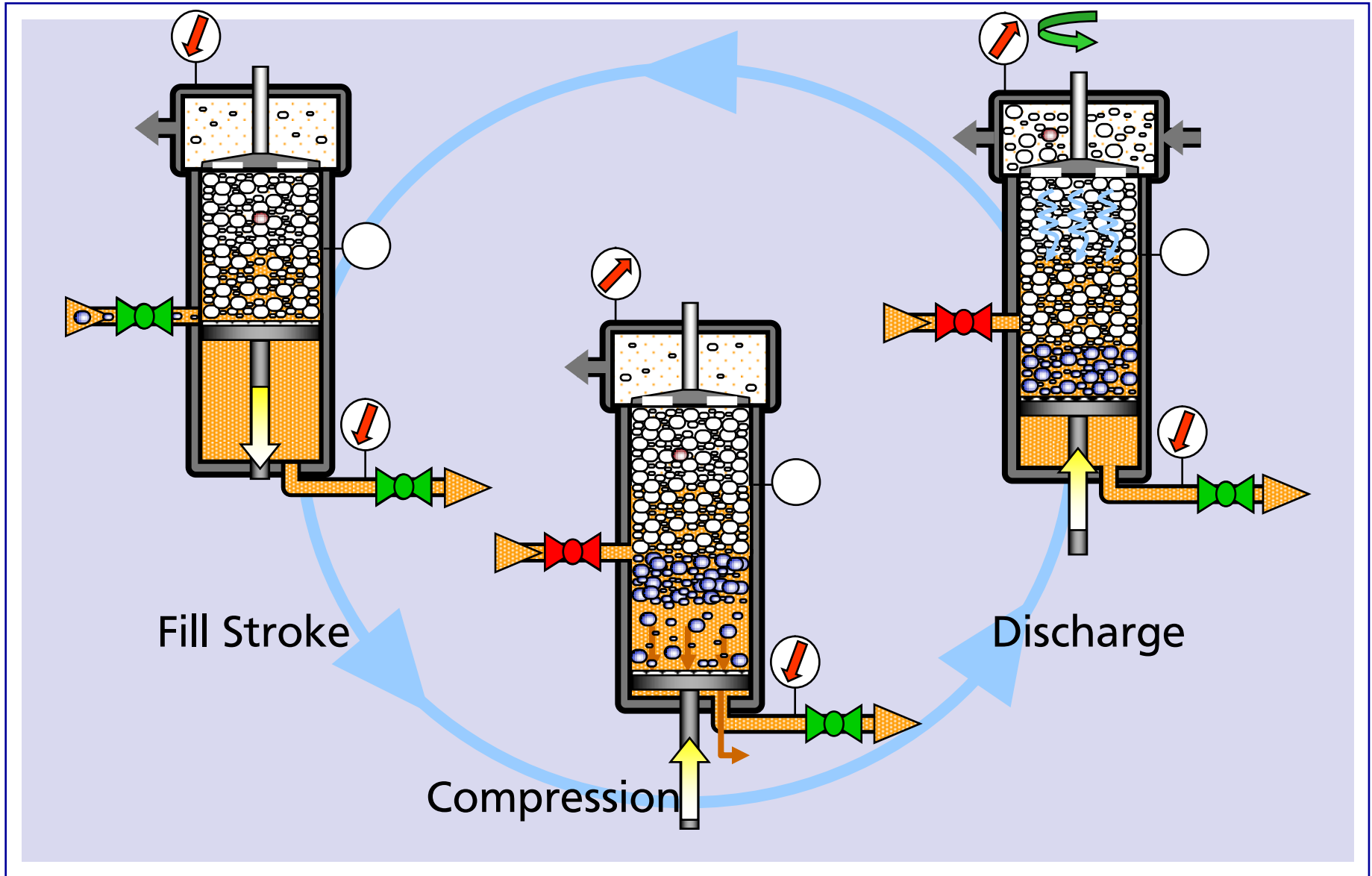
Incineration and Freeze Concentration



Complex wastewater from process is fed to recrystallizer (R) where crystallizer (C) converts water into small ice crystals that grow in (R). Wash column (WC) separates the ice crystals as pure water leaving the concentrated waste for final incineration in (I)

Freeze Concentration

Incineration

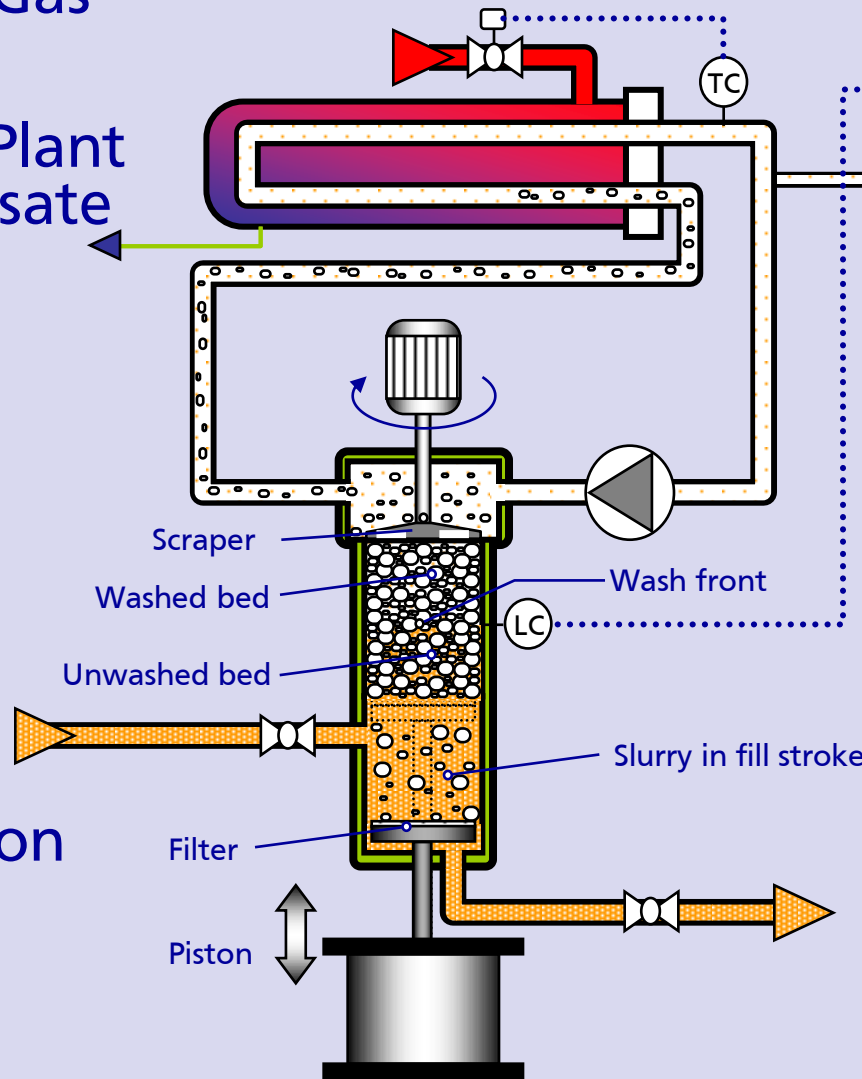


Steam or Hot Gas
from
Refrigeration Plant
Condensate
Return

Pure
Water

Slurry from
Crystallization

Concentrated
Product



Acetaldehyde

Propylene oxide

Propionaldehyde

Ethyl benzene

Phenol

Methylphenylketone

Methylphenylcarbinol

β -Phenylethylalcohol

di-Phenylethylether

Molybdenum

Acrylonitrile

mono-Propyleneglycol

Ethanol/ Methanol

Sodium acetate

Sodium formate

Sodium benzoate

Sodium bicarbonate

Sodium carbonate

Sodium hydroxide

Acetic acid

Formaldehyde

Acrylic acid

Calcium sulfate



Typical concerns:

- Is the continuous Niro melt crystallization process feasible for concentrating the waste water under consideration?
- What purity of the water is achievable?
- What amount of water can be separated off?

Typical figures:

Test period:	5 days - <i>Allows concentration and steady state operation.</i>
Water Purity:	<100ppm TDS
Capacity:	10 l/h
Filling volume:	160 l



Feed Concentrate „pure“ water
90% H₂O 55% H₂O H₂O

Purity of the separated water:

Comp. 1	< 20 ppm
Comp. 2	< 5 ppm
Comp. 3	< 1 ppm
Comp. 4	< 1 ppm

25 <	TOC	<	45 mg/l
40 <	COD	<	120 mg/l

Purification Ratio:
> 1,000

Waste water concentration plant

Crystallization Plant

Capacity: 185,000 MTA
Impurities: < 50 ppm

Niro PT



Shell,
Singapore

Waste water concentration plant

Crystallization Plant

Capacity: 400,000 MTA
Impurities: < 50 ppm

Niro PT



Shell,
The Netherlands

Freeze Concentration



Beer

Freeze concentration provides the perfect cold separation technique for quality retention in sensitive products.

Freeze Concentration may be feasible if the waste stream has:

- Low concentration < 15% total solids
- Volatile organic components; evaporation will still contain impurities
- Water soluble salts.
- Variable composition.
- Hazardous organic components that require disposal and are harmful to standard bio-treatment systems

Crystallization from solution (homogeneous mixture of more than one species)

Melt crystallization (molten solid)

Suspension based

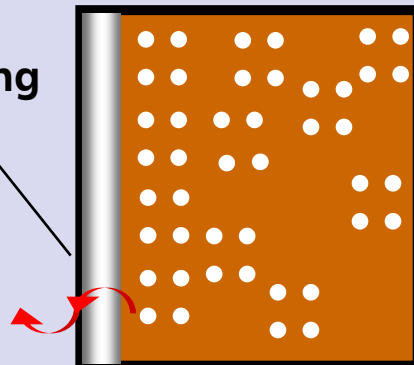
Layer crystallization

Crystallization from the melt (molten solid)

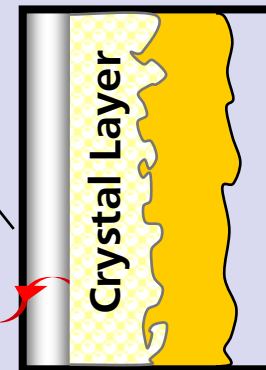
Static

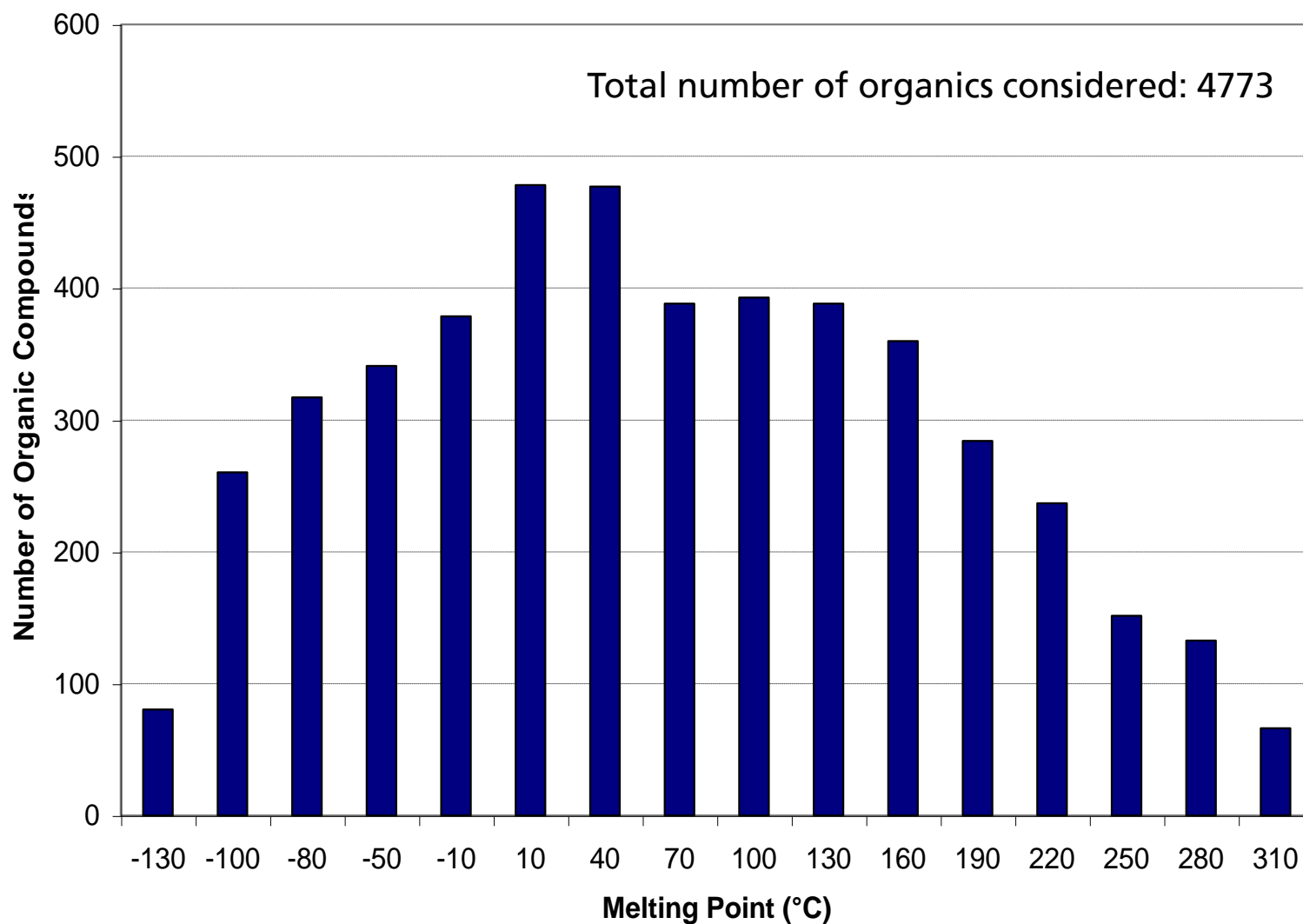
Dynamic

Cooling wall

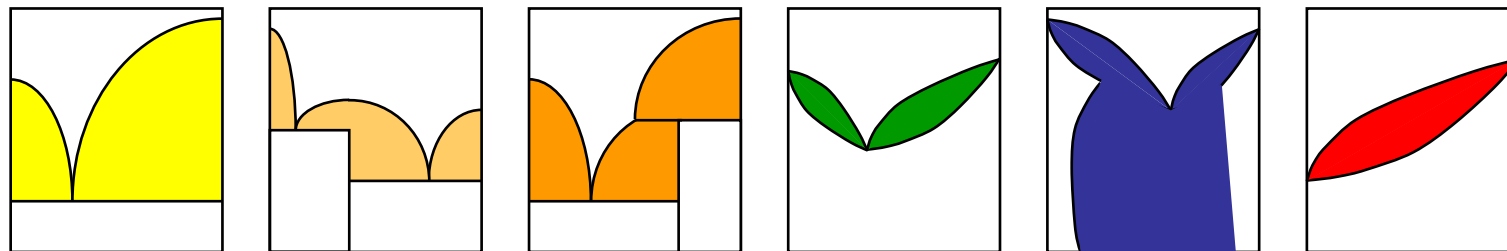








Cooling wall





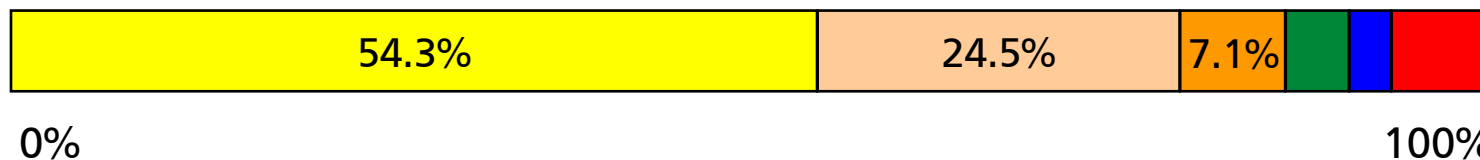
Data from Ulrich, Lu, Glade
Seminar "Grundlagen und Anwendungen der Kristallisation" im Haus der Technik (2000), Essen

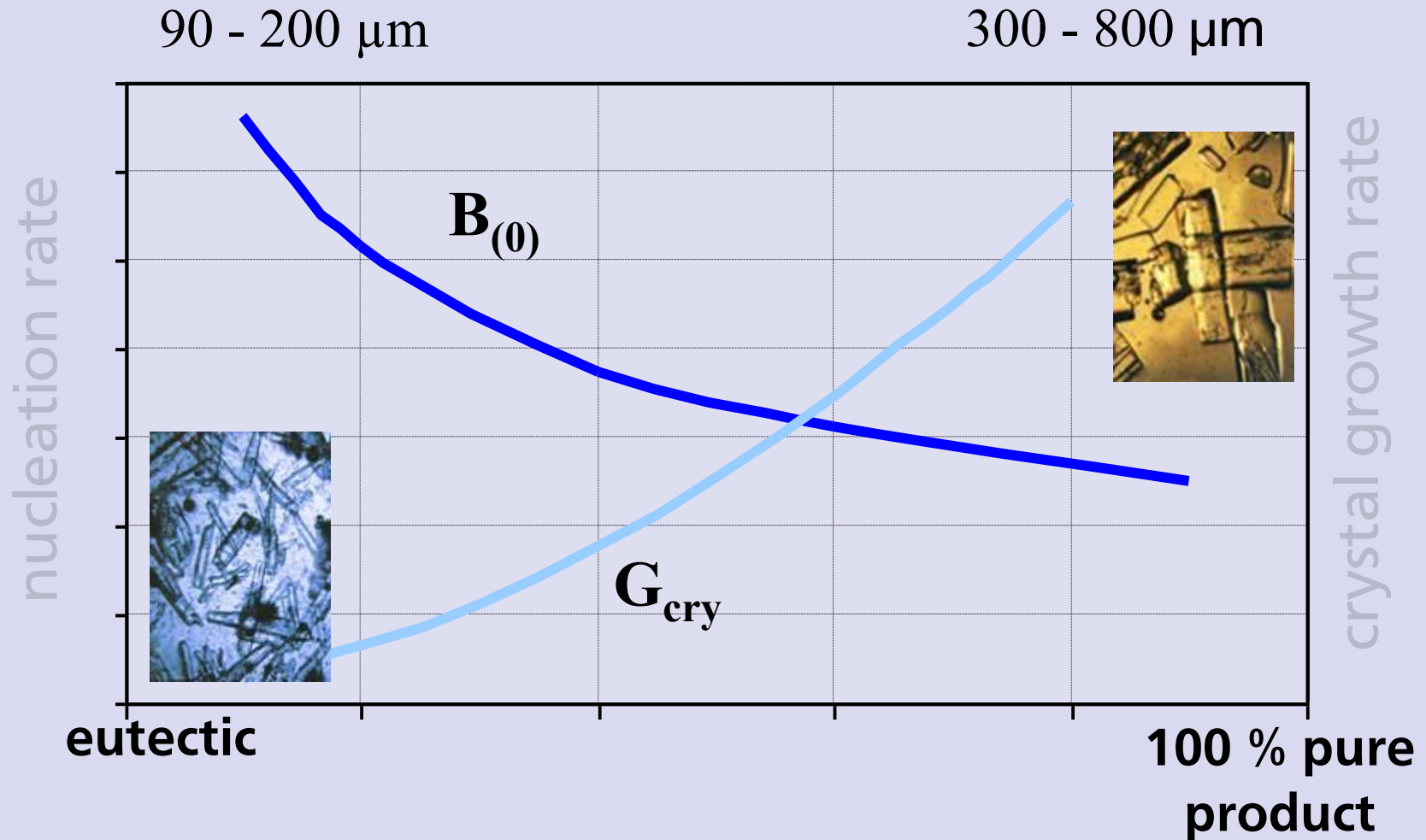


-  Simple Eutectic with no SS
-  Azeotropic system with SS
-  Congruently melting intermediate, no SS
-  Eutectic system with SS
-  Incongruently melting compound, no SS
-  Complete SS



Over 80% of binary organic mixtures are Eutectic systems

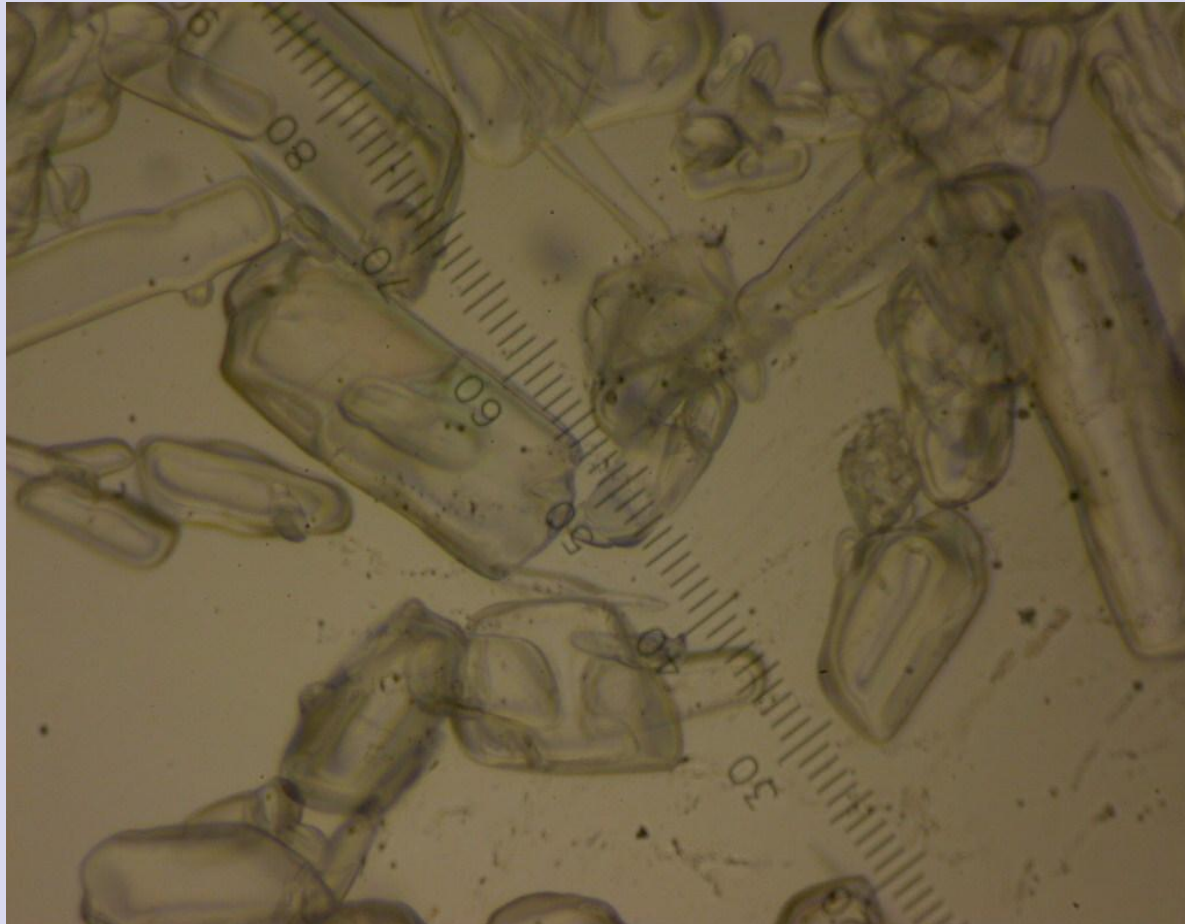




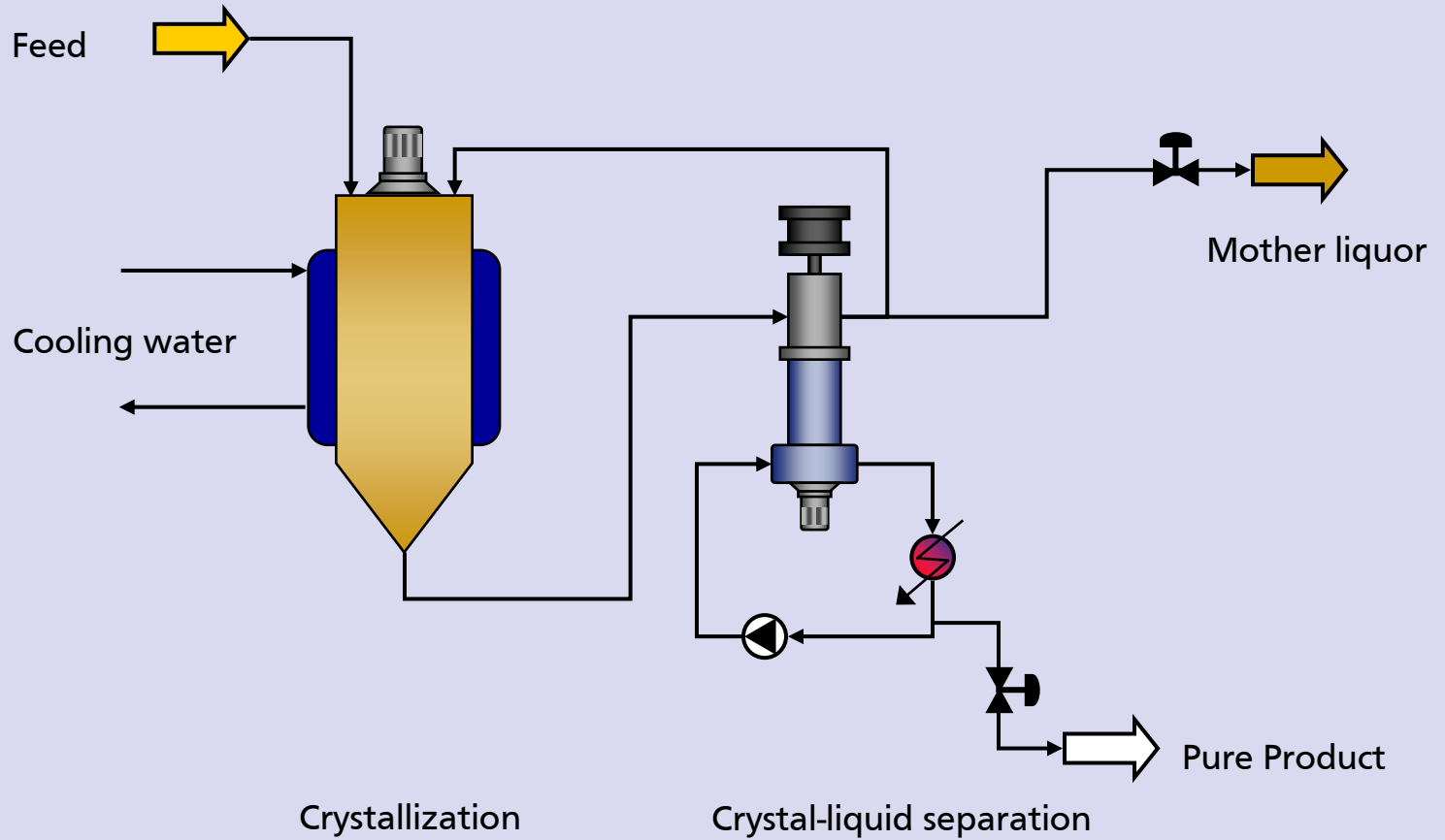
Arkenbout: "Melt Crystallization Technology"; © Technomic Publishing Company, Inc.; 1995

König et al: "Influence of impurities on Nucleation and growth rates of organic melts"; Chem. Eng. Technol. 25 (2002) 2;

© Wiley-VCH Verlag GmbH, D-69469 Weinheim, 2002



p-DCB crystals in mother liquor



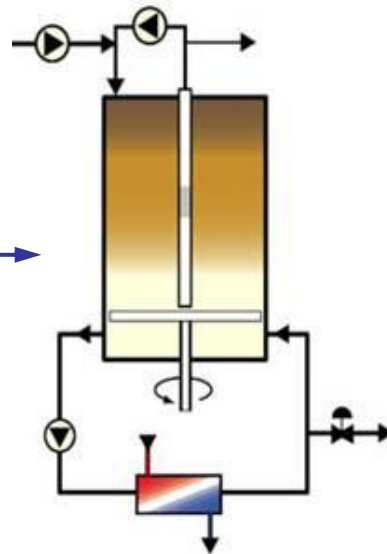
Wash columns

Commercially available systems

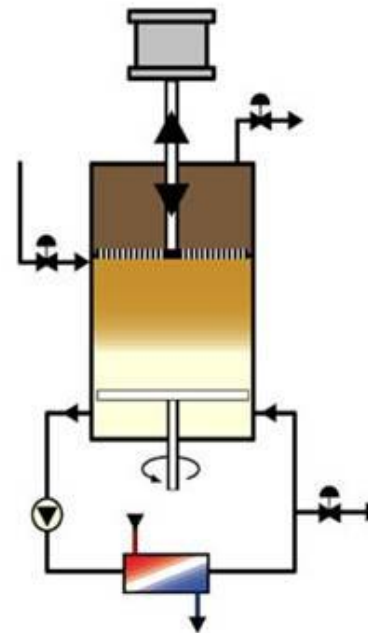
Ø 30 cm
Ø 60 cm
Ø 120 cm
50 worldwide

Ø 6 cm
Ø 30 cm
Ø 60 cm
Ø 90 cm
67 worldwide

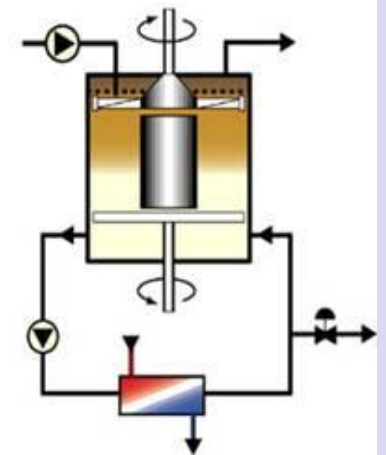
Ø 6 cm
Ø 8 cm
Ø 15 cm
Ø 30 cm
Ø 55 cm
7 worldwide



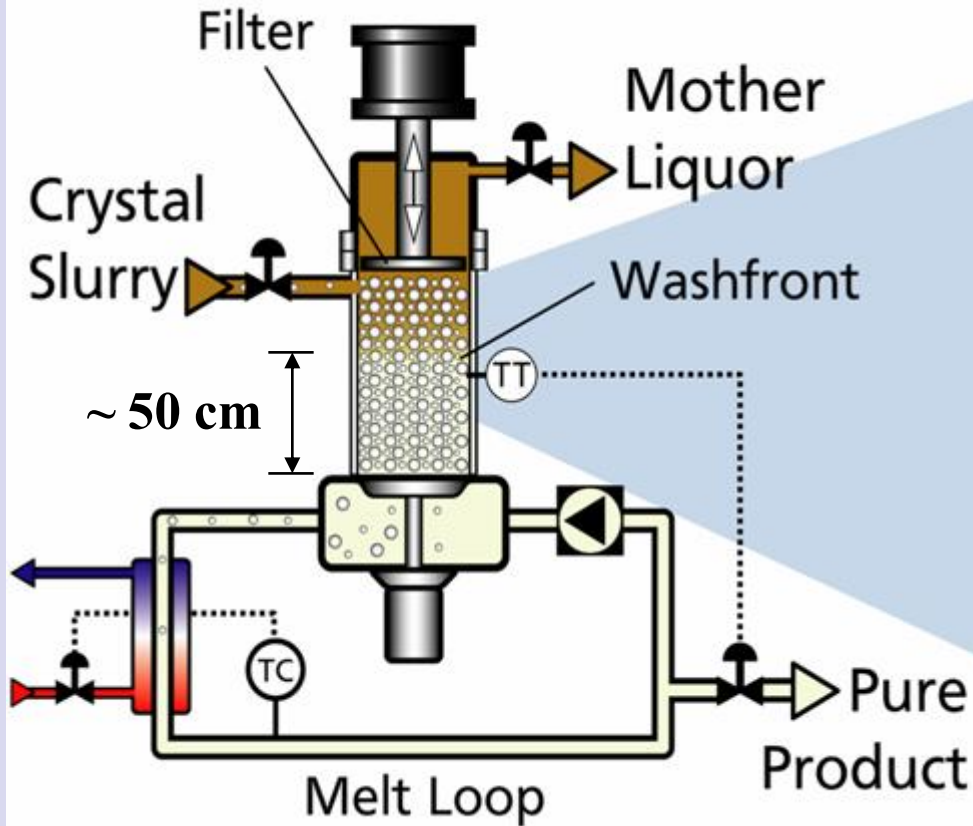
Hydraulic Transport



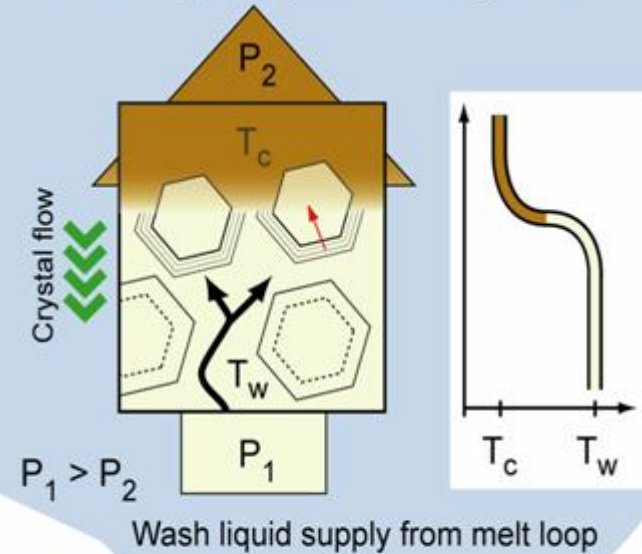
Mechanical Transport
Piston type



Mechanical Transport
Screw type

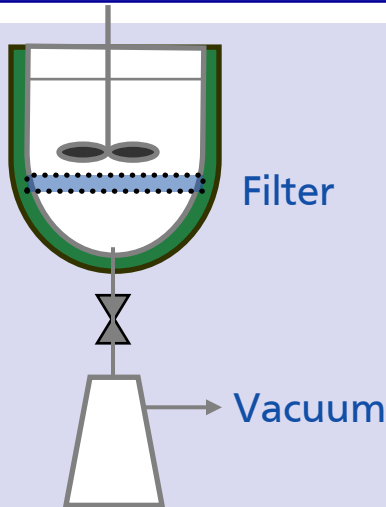


Crystallization provides the heat required to warm up the crystals from T_c to T_w



1. Ultra high purity by high selectivity
 - Crystallization is extremely selective
 - Wash column effectively separates impurity rich mother liquor from pure crystals
2. Low energy consumption
 - Product is crystallized only once
 - Heat of evaporation is two to four times higher as heat of fusion
 - Continuous operation
3. Low temperature level
 - Temperature sensitive products (polymerisation, (acrylic acid, MDI), instability)
 - Components with close boiling points which require large amount of trays in distillation (xylenes, di-chlorobenzenes)
 - azeotropic mixtures (acrylic acid (with acetic acid/ propionic acid) or HCL-water)
4. No need for solvents, thus no need for solvent recovery or waste by-products
5. No gas phase in the process (leakages, reactions)
6. Proven Technology
 - 30+ years of experience, ~70 plants installed worldwide

100 ml
jacketed
crystallizer



MDI crystals batch experiment
Average size ~ 700 μm

Small scale batch crystallization

Objective:

Investigate size, shape, hardness, filterability and purity

Results:

Feed = 90 wt% MDI

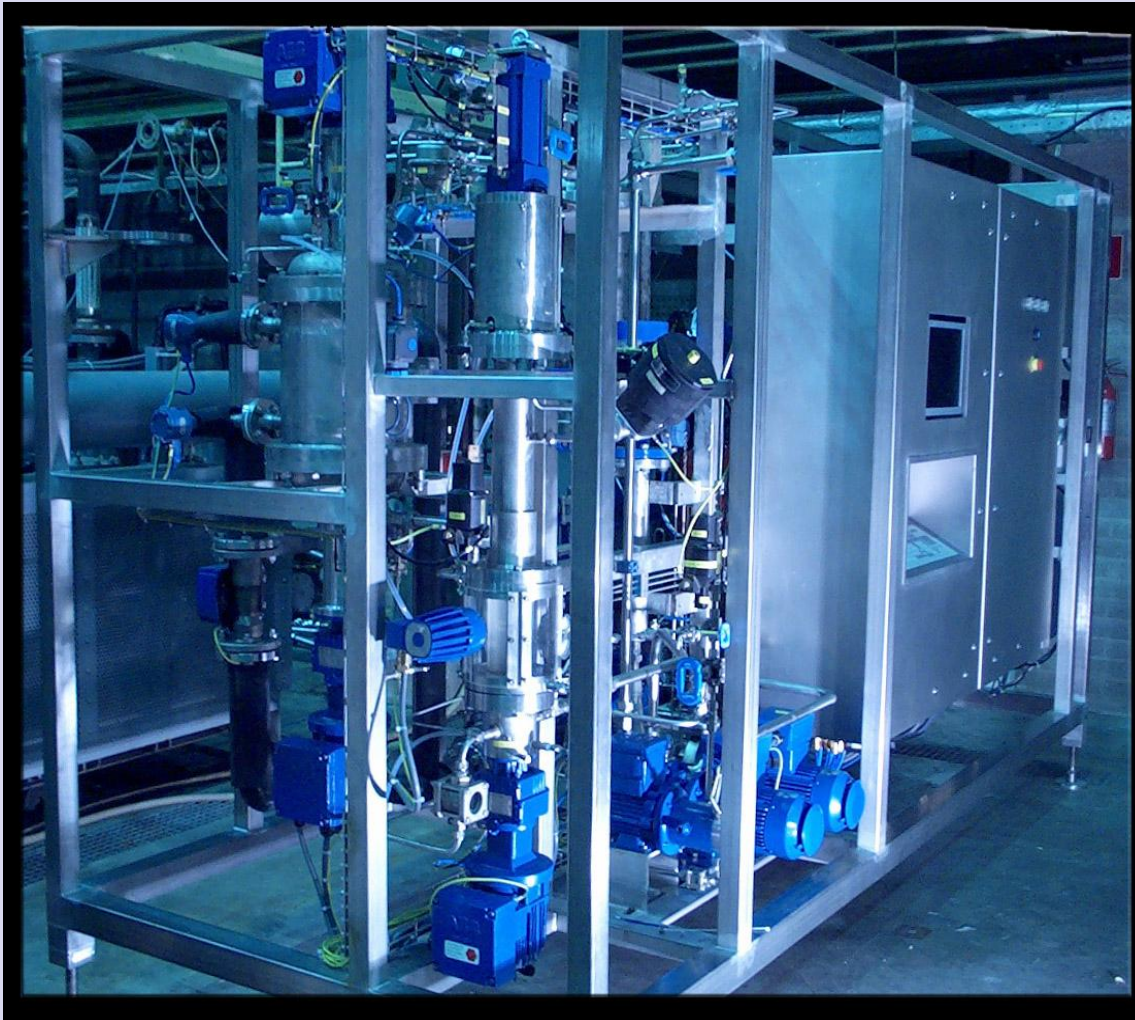
Mother liquor = 88.5 wt% MDI

Crystals (unwashed) = 99.03 wt% MDI

Distribution coefficient = 0.093



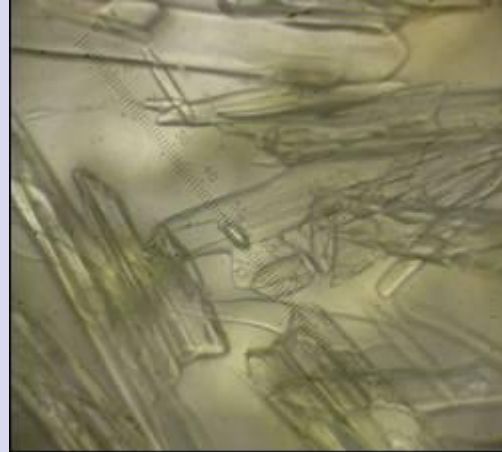
Benzoic acid crystals batch experiment, average size $\sim 1500 \mu\text{m}$



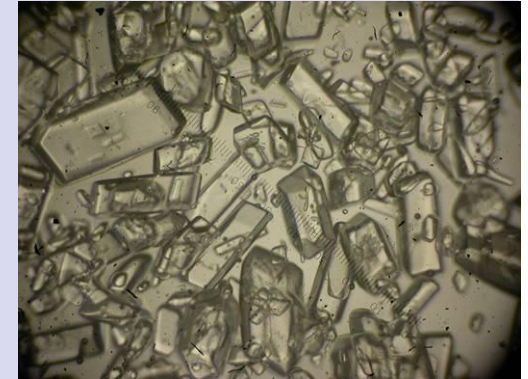
1. Nominal capacity 5 to 15 kg/hr
2. Self-contained process skid incl. control
3. Local installation completed in one day
4. Explosion proof design to ATEX 94/9/EC



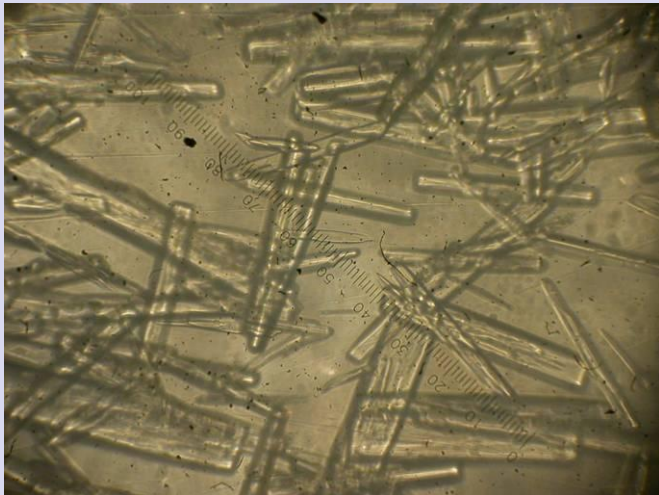
p-DCB crystals



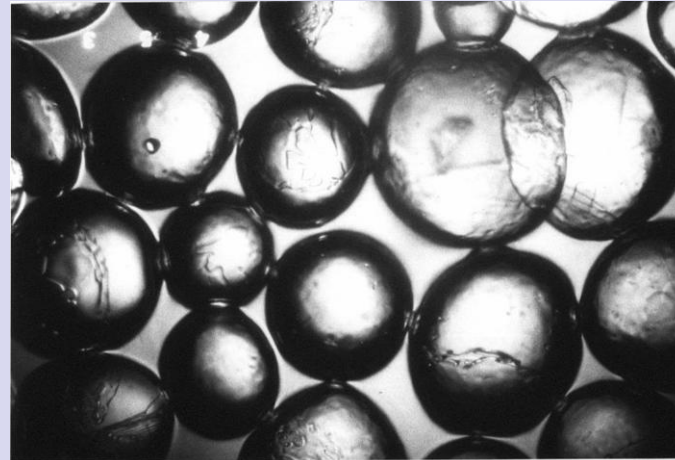
Phosphoric acid crystals



Para-xylene crystals



Crystals of lactic acid derivative



Water crystals in hazardous effluent

P-Xylene

Melt Crystallization Plant

The unique suspension crystallization process is licensed for p-Xylene as part of an Alliance with Stone & Webster and UOP in conjunction with their PX-Plus™ and HySorb™ technologies

Niro PT



Enichem S.A.,
Italy



P-Xylene

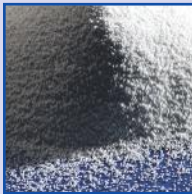
Melt Crystallization Plant

The unique suspension crystallization process is licensed for p-Xylene as part of an Alliance with Stone & Webster and UOP in conjunction with their PX-Plus™ and HySorb™ technologies

Niro PT



Enichem S.A.,
Italy



P-Xylene

Melt Crystallization Plant

The unique suspension crystallization process is licensed for p-Xylene as part of an Alliance with Stone & Webster and UOP in conjunction with their PX-Plus™ and HySorb™ technologies

Niro PT



Confidential

Fine chemical application

Melt Crystallization Plant

Capacity: 7 MT/day
Impurities: < 20 ppm

Niro PT



Confidential,
Asia

p-Dichlorobenzene

Melt Crystallization Plant

The Niro technology can be applied to a wide variety of bulk and fine chemicals

Niro PT



confidential,
Europe

Ethyl lactate

Melt Crystallization Plant

Niro PT

Ethyl lactate is considered an environmentally friendly solvent used in the electronics industry where high purities are required.



confidential,
Europe

"Discovery consists of seeing
what everybody has seen and
thinking what nobody has
thought."

— *Albert Szent-Györgyi (1893)*

