High purity products by crystallisation

Dr Dirk Verdoes and **Dr Jean-Marie Bassett** of **TNO Science & Industry** introduce the TNO Hydraulic Wash Column

Crystallisation from a melt or solution has the potential to yield a product with a very high purity in a single equilibrium step. Pure crystals have to be separated from the impure mother liquor, which is usually done by standard solid-liquid separation techniques like filtration or centrifugation. For high purity products, additional washing is required to remove residual mother liquor from the crystal cake.

An attractive alternative, however, is to use a wash column, which combines continuous solid-liquid separation with efficient counter-current washing using very little or no wash liquid. The hydraulic wash column (HWC) developed by TNO combines a high washing efficiency with a high specific production capacity.

To take full advantage of the HWC, the crystals should have reasonable filtration properties, the viscosity of the mother liquor should not be too high and, in a melt crystallisation application, the product should be stable at its melting temperature. A rule of thumb for all HWC applications is that a mean particle size of 100 µm will usually be sufficient when the liquid has a viscosity comparable to that of water (1 mPas).

The first and oldest application area for the HWC is suspension-based melt crystallisation, which is a powerful technique for the purification of organic chemicals and metals. In general, pure crystals will be formed when an impure melt is cooled in a controlled way, because most impurities with a deviating shape and/or size will not fit into the very regular crystal lattice and will therefore be excluded from the crystals.

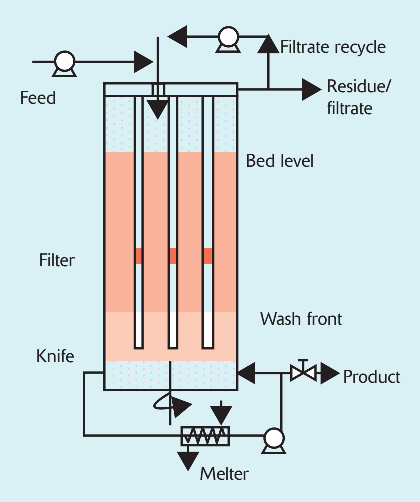


Figure 1 - TNO HWC in a melt crystallisation application

An HWC can be used for the separation of the pure crystals from the impure mother liquor. Melt crystallisation usually has a higher selectivity than distillation and extraction. The high selectivity, the low energy consumption and the absence of solvents make melt crystallisation a perfect example of a 'green' production process, while it also fulfils the increasing demand for high-purity products in industry.

Eutectic freeze crystallisation (EFC) can be seen as a special form of melt crystallisation. In an EFC process, an aqueous stream with dissolved salts is cooled to the eutectic temperature and both salt and ice crystals are formed. Their yield is controlled via the cold withdrawn from the crystalliser and they can be separated easily in a settler due to the difference in density.

An HWC is used to separate the ice crystals from the mother liquor. This is important for the EFC process, because minimising the amount of mother liquor in the washed ice will maximise the overall yield of the process. In addition, an efficient ice-mother liquor separation improves the purity of the water, which increases the possibility of re-using the water in the process or reducing the treatment costs in case the water needs to be disposed of.

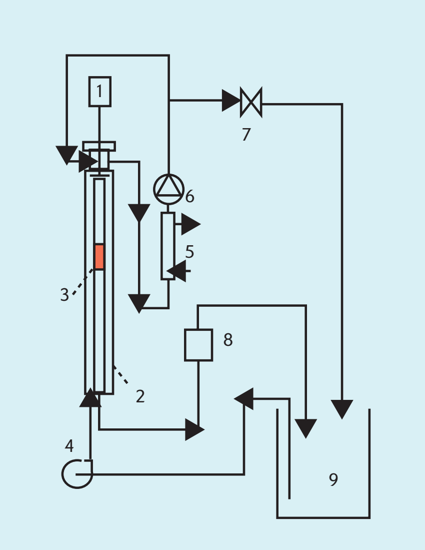
A third application for the HWC is to transfer solids in a very efficient way from one solvent to another. The operating principle of this 'solvent switch' differs in some aspects from melt crystallisation or EFC. In this case, the HWC product is a suspension instead of a melt.

This application is interesting when high product purity and/or low wash liquid consumption is required. Real world examples include the purification of carnallite ($KMgCl_3.6H_2O$), KCl and NaCl crystals using counter-current washing in an HWC. Other potential applications in this field are the separation of polymer particles from organic solvents (for instance, in emulsion polymerisation), continuous adsorption/ion exchange and the recovery of heterogeneous catalysts.

Principle of operation

An HWC is a continuous filtration apparatus, which simultaneously washes the filtered particles. Figure 1 shows the layout of the HWC in a melt crystallisation application.

In melt crystallisation, a suspension of pure crystals is formed by the controlled cooling of an impure feed in a crystalliser. This suspension is pumped into the HWC and the mother liquor escapes via filters, which are placed in separate filter tubes distributed uniformly over the cross-section of the HWC. The filters retain the crystals and a packed bed of crystals is built up. This is transported downwards by means of hydraulic pressure, which is built up above the packed bed. The pressure can be adjusted by means of the filtrate recycle.



Note: 1 - Scraper & motor, 2 - HWC, 3 - Filter tube with filter, 4 - Feed pump, 5 - Melter, 6 - Melt circulation pump, 7 - Product control valve, 8 - Back pressure regulator, 9 - Buffer tank with ice suspension (feed)

Figure 2 - HWC for washing ice in an EFC process

At the bottom of the HWC, the crystals are cut off by a scraper knife, suspended in wash liquid circulating pure melt and melted externally. The main portion of this melt is taken off as product via the product control valve, which also ensures that the melting circuit at the bottom of the HWC is kept pressurised. The pressure causes the wash liquid to flow upwards into the bottom part of the downward-moving crystal bed.

This efficient counter-current washing action prevents impure mother liquor from reaching the pure product. The wash liquid does not leave the HWC but re-crystallises on the cold crystal bed, thereby producing the so-called wash front, which marks steep gradients in concentration, temperature and porosity.

In steady state operation, three zones can be detected in the HWC. The first, at the top of the column, contains the suspension as produced in the crystalliser, eventually somewhat diluted by the filtrate recirculation. The central zone consists of a packed bed of crystals, which are still in contact with impure liquid. The bottom zone between the wash front and the scraper knife consists of crystals in contact with pure melt and is virtually free of impurities. Typical solids concentrations in these zones are 25%, 50% and 60%, respectively.

Figure 2 shows a typical test installation of an HWC for the washing of ice originating from an EFC process. This HWC is turned upside-down from the HWC for a melt crystallisation application, so that the crystal bed can be maintained in position when the HWC is stopped. The feed is at the top for suspensions with organic crystals - which are heavier than the mother liquor - and at the bottom for suspensions with ice crystals, which are lighter than mother liquor.

Another difference between melt crystallisation and EFC is the absence of a filtrate recirculation pump in the EFC installation. The reasons for this is that the solids content and the feed flow, which determine the transport velocity of the bed, can be controlled easily by means of the concentration of ice crystal content in the feed suspension in the buffer tank.

Figure 3 shows the HWC for a solvent switch application, in which a solid is transferred from one liquid into another without melting the product. The layout of the HWC itself is identical to the HWC for melt crystallisation.

In a solvent switch application, the product is not molten and consequently the melting circuit is absent. Instead, the crystals are mixed with another solvent/wash liquid below the rotating scraper knife. The two pumps at the bottom of the solvent switch HWC are adjusted so that wash liquid flows upwards through the bed towards the filters.

In the example shown, the product suspension is separated into crystals and wash liquid, which is recycled in the process after adding make-up water to compensate for the wash liquid losses.

In addition, the counter-current washing of the downwards-moving crystal bed should displace the impure mother liquor but in this case the wash liquid will leave the HWC through the filters together with the impure mother liquor, as the wash liquid will usually not re-crystallise on the crystal bed.

Consequently, the wash front will always be positioned at the filters, whereas the wash front in melt crystallisation and EFC applications is controlled somewhere between the filters and the scraper knife. Another intrinsic difference for a solvent switch application is that the HWC product is taken off as a suspension and not as a melt, as is the case in melt crystallisation and EFC.

Results

The purification potential of the HWC for the crystallisation of organic chemicals from the melt is illustrated by a feasibility study for the separation of para-xylene from a simulated industrial feed, which contained ortho-xylene, ethylbenzene and toluene as impurities.

A 70-litre mixed suspension/mixed product removal crystalliser with indirect cooling using a scraped surface heat exchanger was used for the crystallisation. The product suspension was fed to a 15 cm diameter HWC with six filter tubes and a glass column wall. Sudan Red dye was added to the feed in order to visualise the separation process, which made it easy to recognise the three aforementioned zones

Table 1 - Impurity concentrations in the product (P) & mother liquor (ML) & related kd for the separation of a simulated industrial para-xylene mixture using a combined suspension melt crystallisation-HWC process

Impurity	[Impurity] in P (wt%)	[Impurity] in ML (wt%)	k_d (-)
Ortho-xylene	0.002	2.0	0.001
Ethylbenzene	0.001	1.5	0.0007
Toluene	0.115	5.3	0.02
Total impurities	0.07	10.8	0.006

Table 1 shows the compositions of the HWC product and the mother liquor from which the crystal were grown. The corresponding distribution coefficient (k_d), which is the ratio between the impurity concentrations in the product and the mother liquor, is also given. This shows that the combination of suspension melt crystallisation with the HWC is very efficient, achieving ≥99.9% removal of o-xylene and ethylbenzene.

For toluene, which is known to form solid solutions with para-xylene, the purification is less good but still considerable (98%). Technical feasibility studies with a variety of other organic chemicals reveal that a kd of ≤0.01 is a typical order of magnitude for the separation and purification efficiency of eutectic impurities in a melt crystallisation process in which a HWC is used for the solid-liquid separation.

TNO executed numerous HWC experiments with para-xylene. A robust and reliable operation of the HWC could be demonstrated in a continuous run of 150 hours. High specific production capacities of 5-20 tonnes/hour/m^2 of HWC could be achieved for para-xylene, which shows the HWC's potential as a compact solid-liquid separator in large-scale applications.

The HWC also has a broad turn-down ratio. The extreme example of this feature is that a 15 cm diameter HWC operating at a production capacity of 100 kg/hour could be restarted without any problem after an intentional stop of fours hours. This shows how easily it can adapt to upstream or downstream problems in the process.

The potential of the HWC for separating ice in EFC processes is illustrated by the results obtained for a highly concentrated $MgSO_4$ off-gas scrubbing liquid. The aim of the EFC process was to recover epsomite ($MgSO_4.7H_2O$) and clean water.

An 8 cm diameter HWC with one filter tube and a PVC wall was used to separate the ice from the mother liquor. The salt crystals were separated completely from the ice suspension fed to the HWC, which contained ±6 wt% ice. The feed and wash pressures of the HWC were 3.8 and 2.8 bar respectively.

Figure 4 shows the product flow and the in-line measured conductivity of the produced water, which is a good indication of product purity. At about 16 hours 30 minutes, the product conductivity crosses the bottom horizontal line, which marks the maximum allowed conductivity for Dutch drinking water (1,250 μS/cm). It decreased further to 250 μS/cm at the end of the experiment.

AAS analyses revealed that the product only contained 0.032 g/litre of Mg^{2+}, compared to 27.7 in the mother liquor. This corresponds to a distribution coefficient of 0.0012, implying that 99.88% of the Mg^{2+} was removed in the EFC-HWC process. The result for the EFC-$MgSO_4$ system agrees well with the typical purification results for the HWC in melt crystallisation processes for organic chemicals.

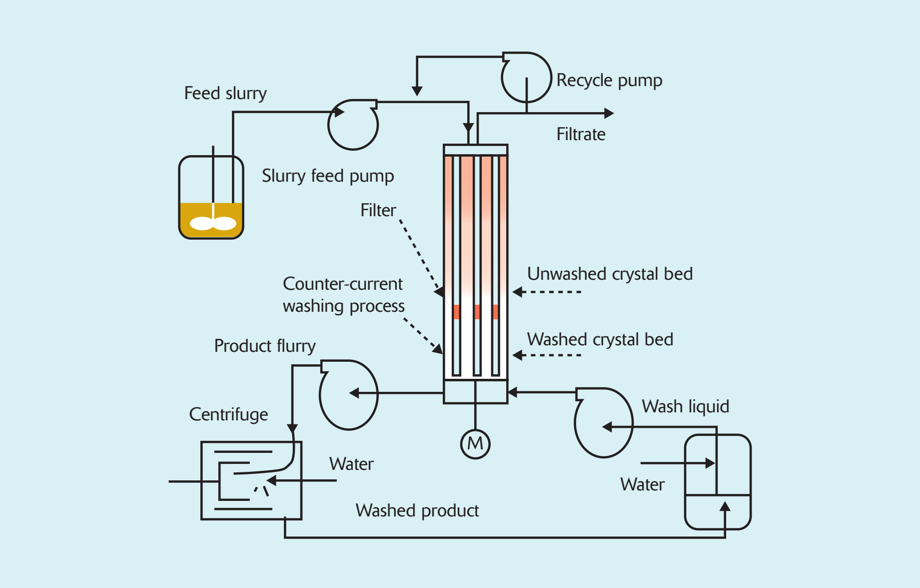


Figure 3 - Layout of TNO HWC in a solvent switch application

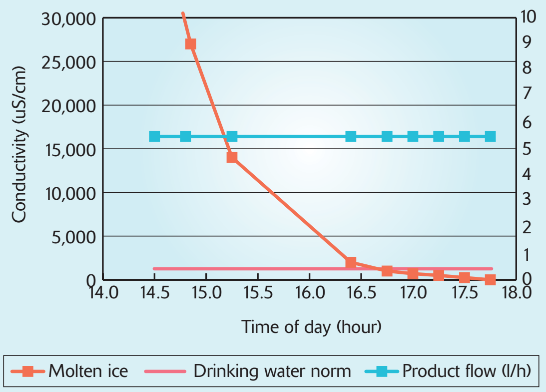


Figure 4 - Conductivity of the HWC product (i.e. molten washed ice) as a function of time in an EFC experiment with an industrial $MgSO_4$-feed.

The result for ice is remarkable. Different behaviour would have been expected because ice has a higher specific volume than water, which means that recrystallisation at the wash front is accompanied by a reduction in the pore volume in the bed. By contrast, almost all organics shrink when they solidify. The different characteristics of ice could have made the washing of a bed of ice in an HWC more difficult but this clearly did not occur in the experiments.

A 6 cm diameter HWC with one filter tube was used for the washing of NaCl. The hollow filter tubes above the filter were made of steel and had a diameter of 2 cm. The filters with a pore size of about 250 µm are 4 cm high and they were positioned 15-30 cm above the scraper knife. Below the filters, massive Teflon filter tube extensions were used so as not to disturb the packing of the bed. The wall of the HWC was made of glass.

The tests were done with a NaCl suspension consisting of crystals with a mean size of 500 µm in a saturated, SO_4^{2-}-containing NaCl solution. SO_4^{2-} can poison the cathodes during the electrolytic production of Cl_2 and the aim of the tests was to investigate whether the HWC could reduce the SO_4^{2-} content in the suspension.

The wash liquid was a SO_4^{2-}-free saturated NaCl solution. Tracers were used to measure the wash efficiency and the wash liquid consumption: Li^+ for the NaCl feed suspension and ethanol for the wash liquid.

Figure 5 plots the wash efficiency, which is equal to SO_4^{2-} removal versus the wash liquid flow rate. The wash efficiency is defined as $\{[SO_4^{2-}]ml - \{[SO_4^{2-}]pr\}/[SO_4^{2-}]ml$, where $[SO_4^{2-}]ml$ and $[SO_4^{2-}]pr$ are the SO_4^{2-}-concentrations in the mother liquor and the liquid part of the product suspension of the HWC respectively. The wash liquid flow rate is expressed as a relative quantity: a flow rate of 1 wt% means 1 kg wash liquid per 100 kg of washed crystals.

A very high wash efficiency (≥99% removal) has already been attained with only 1 wt% of wash liquid. This result shows again that the counter-current washing in the HWC is very efficient in removing the impurities dissolved in the mother liquor. It agrees well with the removal of 99-99.9% of the eutectic impurities for the HWC in suspension melt crystallisation and EFC applications. The measured specific production capacity was 21.2 tonnes of washed NaCl crystals/hour for a HWC with a cross-sectional surface area of $1 m^2$.

This example demonstrates that the HWC can transfer solids efficiently from one solvent into another. This can, for instance, create added value via a higher product purity or save costs in the recovery of the wash liquid or the original solvent by minimising the flow of wash liquid.

Scale-up strategy

The production capacity of the HWC depends linearly on the cross-sectional surface area. During scale up, the diameter of the HWC and the number of filter tubes are increased, such that each filter tube is surrounded by a filtration area in the order of 30-60 cm^2. The filter tubes are distributed uniformly over the cross-section and the height of the HWC will be 0.75-1.5 metres.

When the diameter of the HWC is increased from 8 to 15 cm, the number of filter tubes increases from one to three or six and the production capacity increases from 25 to 100 kg/hour. The corresponding filtration areas are ± 50 cm^2 for the 8 cm HWC to 30-60 cm^2 for the 15 cm HWC. The filtration properties of the crystals are also important for the production capacity.

In general, filtration becomes easier when the crystals are larger and/or when the crystal size distribution is narrower. Cubic and spherical particles are preferred to needles or plates but an HWC can also be operated with these shapes of particles.

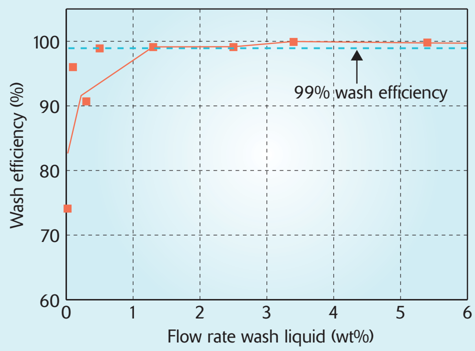
Based on this scale-up strategy, TNO built a skid-mounted pilot plant with a 55 cm diameter HWC that has a design production capacity of 1- 4.5 tonnes/hour (*pictured right*). The cross-sectional area of the HWC is ± 0.25 m^2, the height is ± 1.5 m and it contains ± 50 filter tubes. The corresponding filtration area is 50 cm^2/tube.

The HWC can be equipped with or without a scraper knife and it contains several inlet ports for the feed. The skid is suited for melt crystallisation and EFC applications. It can be operated at between -15˚C and +80˚C and for pressures up to 10 bar.

The skid was tested in a confidential melt crystallisation application at the site of a client. The HWC was started up successfully on the first day and after one week the pilot plant successfully passed a plant acceptance test, which required 72 hours of continuous running without significant safety or mechanical problems. The HWC-55 could run stably and reliably overnight without any operator assistance.

The client tested the HWC-55 pilot plant was tested under various operating conditions, establishing that a stable production capacity of 2.5 tonnes/hour could easily be attained. The corresponding operating conditions of the HWC were: feed and wash pressures of 3 and 1.5 bar respectively, the feed side bed 30 cm above the filters, the wash front 10 cm above the scraper knife and a ΔT over the wash front of 7-8˚C. These relatively mild conditions indicate that higher production capacities will be feasible.

In the test, a stable and high product purity of 99.94 wt% was demonstrated for a mother liquor containing 15 wt% impurities. The corresponding distribution coefficient is 0.004, which agrees well with the typical distribution coefficients measured in smaller HWCs. The HWC product was significantly better than the product in the existing industrial process, in which the crystals are separated with a centrifuge, followed by a washing step for the centrifuge cake with a portion of pure molten product.



Note: The impurity to be removed was SO_4^{2-} and the applied wash liquid was a saturated NaCl solution

Figure 5 - Results for the washing of NaCl in a HWC.

During the pilot plant tests, the robustness, reliability and flexibility of the HWC-55 were successfully demonstrated in a continuous and uninterrupted test run of three weeks in which all key performance criteria defined by the client in terms of product purity, production capacity, maximum loss of product to filtrate and mechanical/operational reliability and stability were met.

The response of the HWC-55 to an intentional process interruption of 30 minutes, like a blockage of the feed, was tested. It easily re-established operation without having to melt the column contents. These very successful tests prove the validity of the scale-up strategy for the HWC.

Conclusion

The HWC is a versatile and efficient solid-liquid separation device. It can be used for the purification of (organic) chemicals in melt crystallisation, for the purification of the ice/water in EFC processes and for a solvent switch in which solids are transferred efficiently from one solvent into another.

Efficient solid-liquid separation in combination with the counter-current washing in an HWC usually results in very high product purities in one process step. Typically the product of the HWC contains 100-1,000 times fewer impurities than the mother liquor from which the crystals or solids were separated.

The successful tests with a skid mounted pilot plant containing a 55 cm diameter HWC prove that this device can be scaled up by increasing the diameter and the number of filter tubes in such a way that the filtration area around each filter tube is kept constant at typical values of 30-60 cm^2. The tests further proved that the specific production capacity and the high purification efficiency can be maintained during scale-up.

Skid mounted pilot plant with a 55 cm diameter HWC for on-site demonstrations

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