Filtration by Means of Ceramic Membranes - Practical Examples from the Chemical and Food Industries

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1 Introduction

Ceramic membranes based on aluminum oxide are an operationally reliable filter medium - in particular under extreme conditions - with an excellent chemical, thermal and mechanical strength that is matched by almost no other material. Consequently, membranes made by atech are primarily used when polymer membranes are no longer able to meet the requirements. Moreover, due to their high separation potential, membrane processes are considered an alternative option that in many cases is superior to traditional processes. For example, it is partly possible to specifically design the separating effect/property of membranes to suit specific applications. They are able under certain circumstances to separate desired or undesired substances/substance groups.

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Traditionally, ceramic membranes have been used in waste water engineering. Meanwhile, they are applied in all areas where media need to be filtered, such as in recycling processes in the chemical industry, for cell separation in biotechnology or for fruit-juice filtration in the food industry. This document describes several examples from the chemical and food industries where ceramic membranes can make the most of their advantages as compared to products from competitors and where filtration processes are superior to other separation processes.

2 Ceramic membranes

The ceramic membranes made by atech (Fig. 1) are tubular composite membranes on an open porous carrier tube made of high-purity α-aluminum oxide. This tube is optimized for maximum water permeability and high mechanical stability (bursting strength >100 bar) and is coated on its inner side with a ceramic membrane. Then, it is subjected to a sintering process to form a monolithic combination.

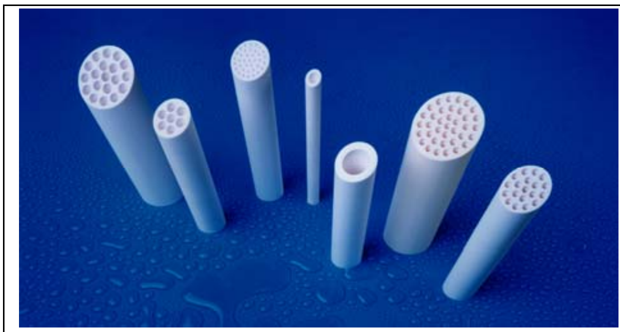

Figure 1. Ceramic membranes made by atech in single-channel and multi-channel design.

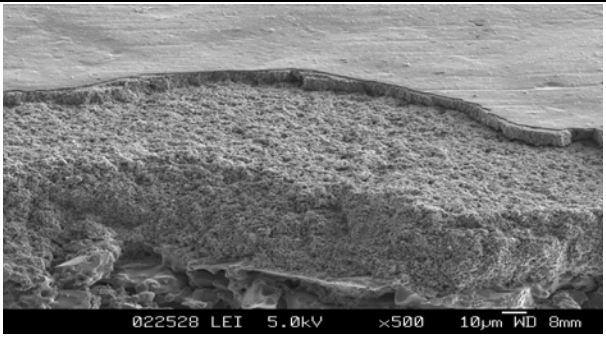

Figure 2. Scanning electron microscope image of the multi-layer membrane applied to the porous carrier material

Depending on the pore size of the membrane, one or more layers of decreasing pore radii are applied and sintered (Fig. 2). During filtration by means of ceramic membranes made by atech the medium to be filtered flows through the channels of the membrane carrier. All particles whose size exceeds the pore radius of the membrane are retained. The particles / molecules build up in the concentrate. The filtrate permeates through the pores and – depending on the procedure – is subjected to subsequent process stages.

Figure 3. The ceramic membranes are arranged in parallel in pressure casings to form modules.

Aluminum oxide membranes are available for micro-filtration and ultrafiltration either in single-channel or in multi-channel design with channel diameters between 2 and 16 mm. Their main characteristics are:

- pressure resistance, possibility of backflushing,
- permanent resistance to concentrated, hot acids and caustic solutions,
- high temperature resistance, sterilisable by steam,
- abrasion resistance,
- high flux, and
- resistance to oxidation and solvents.

The ceramic membranes are arranged in parallel in pressure casings to form modules (Fig. 3). These pressure casings are produced from different types of stainless steel, coated steel or plastic, as required by the application.

3 Effluent Treatment

3.1 Effluent from the production of isopropyl alcohol/ethyl alcohol

3.1.1 Background

During the production of isopropyl alcohol/ethyl alcohol by chemical synthesis propylene is cracked with ethylene, with H_3PO_4 acting as a catalyst. Soda lye is added to the mixture generated during this process. As a result, the mixture reacts on the phosphoric acid, forming sodium phosphate. This is followed by distillation to retrieve the alcohol. The mixture remaining in the bottom of the distillation column, the effluent (Tables 1 and 2), is mainly composed of Na_3PO_4, water, and long-chain hydrocarbons (fusel oils) produced by the cracking process, and of alcohol residues.

Effluent quantity	45 m³/h
Conductivity	500-1300 µS/cm
Oil content	50–100 mg/l
Phosphate content	250–500 mg/l
pH-value	10–11

Table 1. Composition of effluent from the production of ethyl alcohol

Effluent quantity	20 m³/h
Conductivity	25-50 µS/cm
Oil content	5–50 mg/l
Phosphate content	30–50 mg/l
pH-value	7–8

Table 2. Composition of effluent from the production of isopropyl alcohol

Previously, this effluent of 1,560 m³/d was treated mainly by means of a gravity separator and subsequent disposal. Due to the constantly rising costs for the disposal of effluent in recent years and in order to save on resources for reasons of environmental protection the operating company decided to have a system developed where water recycling is used to achieve closed water cycles.

3.1.2 Requirements

The most important requirement to be fulfilled by the recycling system was economic efficiency combined with short payback periods because the up-front and the operating costs had to be balanced by savings on the fee levied for the discharge of effluents. Finally, it was decided to rely on membrane applications in order to meet the requirements, and pilot tests were conducted for months.

The process technology that was finally selected consists of an ultrafiltration stage using multi-channel ceramic membranes made by atech, two reverse osmosis units with spiral-wound modules, and one ion exchanger. The operating company decided to utilize ceramic membranes because they permit to lead the effluent mixture directly to the ultrafiltration unit at a temperature of 80-90 °C. In addition, ceramic membranes are operationally extremely reliable, even with variations in media supply.

3.1.3 Process description

When leaving the distillation process, the effluent has a maximum temperature of 95 °C and is fed directly to the working tank of the double-line ultrafiltration unit (56.4 m² per line) (Table 3) [1]. Ultrafiltration removes the oil-containing constituents and micro-particles from the effluent and concentrates them. Membranes are used for separation because most of the hydrocarbon compounds are emulsified, membranes being best suited for such a separation process. Due to the high temperatures ceramic membranes are the only technology that can be used. The oils separated during the concentration cycle are fed to a calming area where they are separated in working tanks by means of a skimmer. Then, they are recycled to the in-house combustion plant for energy generation. The sludge is extracted from the bottom of the working tank.

Filtering surface	2 x 56,4 m²
Operating mode	continuous
VCF	approx. 22
spec. permeate output	> 500 l/hm²

Table 3. Performance characteristics of the ultrafiltration unit

Design	double-line
Permeate output	approx. 62 m³/h
Temperature	approx. 40 °C
pH-value	8–10
Operating pressure	20–25 bar

Table 4. Performance characteristics of the first stage of reverse osmosis

"Ultrafiltration removes the oil-containing constituents and micro-particles from the effluent and concentrates them."

The filtrate from the ultrafiltration stage is mainly composed of sodium phosphate and water. After passing through a heat recovery unit (heating of process water) it is led at a temperature of 38 °C to the first stage of reverse osmosis where phosphates are separated (Table 4). The permeate resulting from this stage has a conductivity of 30-60 µS/cm and is used directly for the in-house production of de-ionized water.

The retentate from the first stage of reverse osmosis contains approximately 500-1,000 mg/l of phosphates which are transformed to H_3PO_4 in the (double-line) strong-acid ion exchanger arranged downstream (Na ions are exchanged by H ions). The approximate throughput per regeneration cycle is 40 m³/h. The second stage of reverse osmosis is of single-line design. The phosphoric acid has a concentration of approx. 0.1-0.2 % and is led to the second stage of reverse osmosis where the concentration factor is increased to approx. 5-7 %. The permeate resulting from this stage is recycled back upstream of the first stage of reverse osmosis to be used for the production of de-ionized water.

3.1.4 Results

The process technology as described above mainly uses membrane processes and permits to achieve an almost closed cycle of process water and to use the resulting filtrates / permeates for the production of de-ionized water or to use the concentrates for power generation. The recycling rate is more than 90 %, which corresponds to approximate savings in fresh water/effluent of 60 m³/h.

There are additional savings, such as:

- The conductivity of the permeates in the supply line to the de-ionized water unit is approx. 30-60 µS/cm, compared to 400-600 µS/cm for groundwater that had exclusively been used previously. This increase in quality will have a beneficial effect on the service life of the ion exchangers of the de-ionized water unit.
- Combustion of the concentrates from ultrafiltration can be used to produce energy.
- Phosphoric acid can partly be re-used in the cracking process. Research is currently under way to find out if high-pressure reverse osmosis will further increase concentration levels so that the possibilities to utilize the acid would be increased as well.

Based on total capital expenditure (depreciation and interest) and taking into account the operational costs for maintenance, replacement of membranes, energy, membrane cleaner etc. the costs amount to approx. EUR 0.90 per m³, and the payback period for the entire plant is less than two years.

3.1.5 Analysis

The requirements of the operating company to achieve an economically efficient recycling system could be achieved. No additional savings on production of de-ionized water, energy generation and acid consumption were included in the computation of profitability because the plant was to be funded entirely from savings on the fee levied for the discharge of effluents.

Ultrafiltration as a pre-treatment stage for all subsequent process stages is of critical importance because in case of plant failure all treatment stages downstream will be affected as well. Operational reliability for this part of the plant is achieved due to the ceramic membranes made by atech which work reliably even if the composition of media varies. The higher up-front costs for ceramic membranes as compared to polymer membranes are made up by the high specific permeate output (> 500 l/hm²) resulting partly from the high temperature. Usually, polymer membranes can not be used at such a temperature level which means that the medium would have to be cooled first.

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The facts outlined above clearly show that despite their higher up-front costs ceramic membranes can be utilized for the treatment of large volumes of effluent in a technically and economically efficient way.

3.1.6 Outlook

Strict regulations for the protection of the environment and requirements to close water cycles will continue to drive industries such as the chemical, paper or textile industries etc. to consider appropriate action and implement appropriate systems. Membrane technology can provide a suitable means to achieve such goals because it relies on physical separating principles and, therefore, its level of environmental acceptability is particularly high. This also includes ceramic membranes because their technical features such as thermal and chemical resistance and their several years of service life makes them an efficient option for selected applications for the treatment of large volumes of effluent.

3.2 Treatment of laundry effluents

In a major laundry, a filtration unit working with ceramic membranes was installed, having a total filtering surface of 56.4 m². This unit filters 100 m³ of washing water per day and

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achieves a recycling rate of approx. 80% with a power consumption of 4 kWh/m³. In many cases, it is more economical for laundries to treat effluent in-house and thus to save on fresh water and detergents than to pay fees for the disposal of effluents (including fees for heavily polluted effluent). The following example involves a laundry for industrial clothes where heavily soiled working apparel is washed. Washing water and detergents are recycled in a two-stage installation comprising microfiltration and nanofiltration.

Figure 4. Microfiltration unit with a capacity of 20m³/h to separate softeners during the production of flat film (source: Amafilter GmbH).

The first process step (microfiltration) removes all emulsified and suspended contaminants. The membrane pipe modules are specifically designed adjusted to match the medium that is to be filtered. The medium is separated in the modules into a clear filtrate flow and a concentrate flow where all contaminants are concentrated with only a small remaining quantity that must be disposed of. The clear filtrate still contains detergent elements that have not been utilised and can thus be re-used for prewashing and main washing. For the rinsing cycles the filtrate from microfiltration is further processed in a second stage (nanofiltration) in order to remove detergents still present and part of salts.

3.3 Separation of softeners during the production of flat film

During the production of film for safety glass approx. 10m³/h of cooling water arise as effluent that is polluted with softeners. The requirements regarding the quality of fresh water prevented a re-use of this "effluent" containing softeners for recycling without further treatment. Ceramic membranes made by atech can be used to clean the effluent to a degree which makes it suitable for re-use, resulting in considerable savings on fresh water.

The effluent has a temperature of 30°C and is composed of different softeners in the form of droplets, mainly based on acrylic. Its pH value is 7. The results of preliminary studies conducted at the Aachen University of Applied Sciences (Fachhochschule) using an ozonization unit and a coalescence separator were not satisfactory; polymer membranes were irreversibly blocked up by the softeners. Only filtration by ceramic microfiltration membranes yielded promising results in the pilot test: With a permeate output of more than 90% they achieved an almost complete retention of the softeners used. After cleaning the membranes chemically the initial value of the water was achieved again.

Subsequently, a large-scale plant built by Amafilter Deutschland GmbH (Fig. 4) was put into operation and has meanwhile operated since 1999 trouble free and without requiring an exchange of membranes. The quality of its filtrates continues to fully comply with the requirements. Its permeate output is between 95 and 97%. In addition, the number of off-specification batches resulting from variations in water quality was significantly reduced. As a result of considerable improvements in the process a second microfiltration unit with twice the capacity of the first one was put into operation in 2000.

4 Filtration by Means of Ceramic Membranes in the Food Industry

4.1 Production of color concentrate from black carrots

In the food industry, color concentrate from beetroot is increasingly replaced by color concentrate from black carrots because the

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latter is cheaper and less sensitive to treatment at high temperatures. The average sugar content of black carrots is 9 Brix and is increased in the evaporator to a maximum of 70 Brix. This results in a concentration degree of 7.8, and the color intensity achieved in the concentrate varies with the initial color intensity of the vegetables. This initial color intensity can vary considerably.

If a certain color intensity (standardization) or a higher color concentration in the product is to be achieved an appropriate flexibility in the evaporator is required to make up for variations in the initial color. It is possible to preselect a sugar content of, for example, 4.5 Brix by means of sugar separation with color loss reduced to the lowest extent possible using ceramic ultrafiltration membranes. As a result, the color concentration in the evaporator can be doubled. Membrane filtration upstream of evaporation can reduce the sugar content so that the required high color concentration can be achieved in the end product even if the initial juices are less intense in color (color in the retentate, sugar in the filtrate) while the loss of color is minimized.

4.2 Polishing filtration of citrus fruit juices

The use of ceramic membranes in a plant operated by Unipektin for polishing filtration of citrus fruit juices having a throughput of up to 10 m³/h yields a product whose clarity is considerably higher than that achieved by a filtration process using traditional technology. Polymer membranes are rather unsuited for this kind of application. One reason is that essential oils from the skin enter the juice during the treatment of lemons. These oils are prone to damage and, in the long term, destroy polymer membranes. Therefore, if polymer membranes were used, an additional process step would be necessary before starting filtration to extract all or part of the oil from the juice.

Ceramic membranes are resistant to essential oils and, additionally, provide a very high separation effect. This advantage enables them to also retain proteins which might cause undesired secondary cloudiness. The positive features of ceramic membranes are also useful in the so-called peel wash procedure. This is a second pressing stage, followed by washing out, during which juice is extracted from the fruit flesh left on the shell halves. During peel washing, many essential oils and bitter principles pass into the juice which requires a still more intense cleaning and filtering procedure.

4.3 Ceramic membranes used for the production of glucose from sorghum

4.3.1 Task description

As a result of the ever increasing demand for sugar, especially in less developed countries, more and more facilities to produce saccharose and other types of sugar are built in these countries [4]. These facilities not only provide the possibility to extract saccharose from sugar beets and sugar cane but also allow for the production of to produce glucose from starchy plants. Various plants are used as raw material, for example potatoes, rice, corn or – as is done in a Nigerian glucose production plant – sorghum. In the Nigerian facilities glucose syrup is produced which is later used for ice cream, confectionery, bakeries, jam and fruit juices. Large quantities are consumed for the enzymatic production of alcohol.

4.3.2 Background

The Nigerian company uses sorghum as source for starch to produce glucose because sorghum is easily available and has a low price. The resulting glucose syrup has a dextrose equivalent value (DE, percentage of reducing sugars in the dry matter, calculated as glucose) of 42 DE. Glucose syrup with a DE value of 42 is very popular because it can be concentrated to up to 84 Brix without crystallizing out while forming an auto-sterile solution. The production plant discussed here does not follow the traditional procedure to first obtain the starch, refine it and then process it into glucose. Instead, a direct procedure is used. Here, the starch contained in the sorghum grains is transformed 'directly' into glucose.

"Here, the starch contained in the sorghum grains is transformed 'directly' into glucose."

4.3.3 Production of sugar syrup

The grains are washed and crushed in a hammer mill. The resulting product is then subjected to sieve classification. For a short time, attempts were made to use a disk mill. However, it quickly turned out that this type of mill did neither achieve a satisfactory crushing quality nor sufficient reproducibility. Water is added to the resulting flour and the starch is liquefied by means of thermoresistant amylase at a temperature of 50–90 °C. Then, an enzyme cocktail is added to achieve saccharification to a DE value of 42. When this transformation has been completed the content of solid matter in the glucose syrup is 15 to 17 %. The syrup also contains proteins, fat, colorants (mainly of a phenolic nature), and fibrous material.

4.3.4 Processing

The raw product that resulted from the saccharification process was led through belt filters to remove the remaining husk material and coarse contaminating particles, followed by a pre-evaporation and a centrifugation stage. After centrifuging, complete evaporation took place where the product was concentrated to approx. 80 Brix. The separation performance achieved with the technical means available on site was inadequate. As a result, syrup quality was relatively poor and product losses were high. The task was to improve the separation performance and to reduce the product losses by means of membrane technology.

The existing belt filter stage was maintained, however, belt usage was optimized. Pre-filtration is now immediately followed by microfiltration in ceramic membranes operated on plants from Unipektin in order to completely remove unwanted substances, pre-evaporation, ion exchange / adsorption and complete evaporation to a content of solid matter of approximately 80 %.

4.3.4.1 Filtration

During filtration, fibrous material, fats, starch and most proteins are removed. Basically, filtration is a two-stage process: a rough pre-filtration stage, followed by full filtration in a filtration plant equipped with ceramic membranes. This plant uses tubular multi-channel microfiltration membranes and operates under the so-called cross-flow principle. This means that a mixture to be screened is led crosswise to the membrane surface at a high speed (3-5 m/sec.) in order to minimize the formation of a gel layer.

Gel layers often build up during traditional filtration processes and result in a constant reduction of the flow rate up to the point where the filter must be exchanged. Cross-flow filtration, in contrast, means that the thickness of the gel layer is greatly reduced due to the speed of flow. This results in high specific filtration performance. In addition, the ceramic membrane is backflushed at regular intervals from the filtrate side so that the covering layer is "lifted". The "lifted" layer is then carried away by the flow occurring during the backflush pulse. In this way the filtering performance is continuously maintained at a high level.

"The flow occurring during the backflush pulse carries away the 'lifted' layer so that the filtering performance is continuously maintained at a high level."

Filtration takes place at temperatures between 75 and 80 °C and at an average pressure across the membrane of 2.0 bar. As is customary for membrane filtration installations, a combined filtration and diafiltration procedure is used to maximize output. Filtering the glucose solution is far more difficult than filtering a glucose syrup produced from starch that has been isolated in a preceding stage. The glucose solution has a significantly higher content of non-sugar substances such as fats and proteins. This means that the membrane and the control system must meet high quality requirements in order to achieve a constant performance of the installation. In addition, special cleaning methods must be developed to ensure that the plant works constantly without causing unprofitable costs for cleaning agents.

4.3.4.2 Pre-evaporation/ion exchange/adsorption

Filtration is followed by a pre-evaporation stage. In this stage, the mixture is concentrated from 15-17 Brix to approx. 25 Brix. This pre-evaporation stage has been included upstream of the ion exchanger because effects such as Maillard reactions occur during inspissation, resulting in increased coloring. It is therefore preferable to actively intensify these reactions and then to remove the resulting products in the ion exchanger.

As has been noted above, after completion of the first concentration stage the syrup is led into ion exchangers and adsorbers for demineralization and decoloring. In addition, unwanted flavoring and odorous substances are removed. The components are arranged in the following order: cation exchanger, adsorber, anion exchanger. This order may not be varied. The performance of adsorbers is higher when pH values are low. Therefore, the cation exchanger reducing the pH value must be arranged upstream of the adsorber. This stage is followed by gradual evaporation until a Brix value of 80 to 82 is achieved, i.e. a concentration which allows for low-cost transportation and easy storage of the glucose syrup.

The permeate produced in the membrane unit is free from sedimentary material and has a dark color. In the membrane unit which has a filtering surface of 65.8 m² the glucose juice having a temperature of approx. 75-80 °C is filtered by batches and the concentration of the sedimentary material is increased (VCF: 10-12). The filtrate output is 150,000 l/d (7,500 l/h) at about 15 Brix.

4.3.5 Conclusions / Outlook

An improvement of glucose syrup quality was achieved in that the filtrate does not contain any sedimentary material any more (reduction from > 1,000 to 0.5 Nemometric Turbidity Units). Combined with the other parts of process technology, the glucose now not only proved suitable for in-house manufacture of confectionery but could also be sold on to other parties. This, together with optimizing the belt filter process, resulted in an overall reduction of product losses by approximately 7%. Based on the plant output stated above (7,500 l/h at 15 Brix) this means that losses are reduced by approx. 113 kg of glucose/h.

Additional investigations were carried out in the field of filtration of hot glucose solutions. These investigations clearly showed that with higher saccharification ratios (DE 90) a much higher specific filtration output can be reached which means that it should be possible to process higher volume flows in a cost-efficient manner.

4.4 Pre-concentration of chicken protein

The usual method to produce granulates from chicken protein is evaporation, followed by spray drying. Using ceramic membranes for pre-concentration allows for energy savings in the following process stages and for improved product quality. During pre-concentration, water, sugar and mineral matter are removed with the filtrate from the chicken protein because the ceramic membrane does not retain these substances.

“The usual method to produce granulates from chicken protein is evaporation, followed by spray drying.”

The concentrate is largely free from sugar and is thus better suited for the following spray drying process because pre-concentration minimizes the unwanted browning reaction (Maillard reaction) resulting from the reaction of sugar and protein in the presence of heat. Therefore, higher-quality granulates are achieved. The ceramic membranes used in the filtering process are sterilisable by steam and,

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for a number of reasons such as hygienic issues, are preferable to polymeric membranes.

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