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Ceramic membrane applications for spent filter backwash water treatment

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Summary

Application of low pressure membranes in public drinking water supply for particle removal has been rapidly increased in recent years. Among numerous innovations in this sector ceramic membranes are attracting an increasing interest. Due to their resistance, porosity and hydrophilic surface ceramic membranes may enter the field of drinking water treatment in the future.

In this study various ceramic membranes, different in pore size and membrane material, were applied in pilot scale to remove dissolved and organic matter from different backwash water types of a full scale water treatment plant. The ambition was to consider conditions typical for waterworks and to keep dosages of chemicals during membrane filtration as low as possible.

Results of the study showed, that treatment of spent backwash water may be applied in water treatment. A comparison of different ceramic membranes implies that total membrane resistance was more influenced by backwash water composition and by operation than by membrane type for the waters tested. Life cycle cost estimations indicate, that even element type ceramic membranes are still more expensive but not so far from costs of treatment by polymeric membranes. Therefore, introduction of ceramic membranes for water treatment under cost-aspects could be not impossible in medium-term.

Contents

1 Introduction

Low pressure membranes for particle removal got an increasing importance in public drinking water supply in recent years. Today, membranes made from organic materials such as PVDF or PES will be applied in full scale plants in waterworks. Ceramic membranes are made from inorganic materials such as alum oxide or silicon carbide. They are established in industrial applications, e.g. for recovery of catalytic converters since a couple of years. However, ceramic membranes are not applied in public drinking water supply in Europe today. The first construction stage of a 51,900 m^3/day drinking water utility, containing a ceramic microfiltration step, went into operation in Japan end of 2006 (NGK, 2006).

Ceramic membranes are considered as resistant to mechanical, chemical and thermal stress anticipating a long membrane life time. Further advantages include their high porosity and hydrophilic surface which allow higher fluxes compared to organic membranes. These properties may open various fields for applications in water treatment, such as the treatment of residuals from drinking water production or the direct treatment of surface waters.

Environmental aspects are very important for the drinking water community and for the acceptance of treatment technologies. The ambition is to keep dosages of chemicals during water treatment as low as possible. Relatively little is known for the operation of ceramic membranes under restricted use of chemicals. Therefore, objective of this project was to examine different ceramic membrane materials, pore sizes and feed waters with limited use of chemicals for treatment of backwash waters from a full scale water treatment plant.

Existing waterworks treating surface water for drinking water production often use flocculation and filtration by conventional dual media filters for particle removal. The backwash water of these filters contains the particle load of the raw water including added flocculants at relatively small flow rates. High particle loads in small flows may lead to an improved cost/benefit-ratio for ceramic membranes. A further treatment of residuals may support an environmentally friendly water treatment, too. For that reason ceramic membranes were applied for filtration of spent backwash waters in this study.

While a number of ongoing research in the field of drinking water is applying Al_2O_3 membranes of one Asian manufacturer this study includes ceramic membranes produced in Europe only. This includes also a test of prototype microfiltration membrane modules made from silicon carbide (SiC).

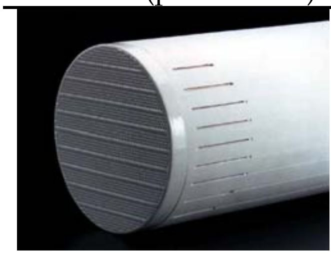
2 Ceramic membranes

2.1 Characteristics

Advantages of ceramic membranes include higher fluxes, due to their higher porosity and more hydrophilic surface, compared to organic membranes. The resistance of ceramic membranes against mechanical, chemical and thermal stress allows a better recovery of membrane performance. Disadvantages contain sealing problems, due to the different thermal expansion of ceramic membrane and module housing (Melin and Rautenbach, 2003). Brittleness of ceramic membranes requires a careful handling.

Ceramic membranes are available with IN-OUT and OUT-IN flow directions. IN-OUT membranes are produced as monolith or element type, OUT-IN membranes as flat sheet type. Module types are summarized in table 2.1.

Tab. 2.1:Overview of ceramic membranes

Monolith type	Element type	Flat sheet type
IN-OUT (pressurized)	IN-OUT (pressurized)	OUT-IN (submerged)
 photo: NGK	 photo: Atech innovations GmbH	 photo: membrane-engineering
0.1 µm Al_2O_3	Different pore sizes and materials, e.g. > 0.1 µm SiC, Al_2O_3 < 0.1 µm ZrO_2, TiO_2	Different pore sizes and materials, e.g. > 0.1 µm Al_2O_3 < 0.1 µm ZrO_2, TiO_2
15 or 25 m² membrane area/module	e.g. < 30 m² membrane area/module	e.g. < 2 m² membrane area/module

Monolith type modules consist of a ceramic body with a high number (e.g. 2,000) of flow channels, leading to relatively high membrane areas per module of 15 and 25 m². One module fills one housing and is arranged vertically in full scale. Pore sizes within the microfiltration membrane range are available for this module type. The monolith type offers a high membrane area in a compact volume with a reasonable price.

Element type modules include several ceramic elements, each with a relatively small surface of about 0.1 to 0.2 m². The membrane elements are arranged in subdivided stainless steel housings resulting in total membrane areas per module of about 20 to 30 m². Pore sizes are covering micro-, ultra- and nanofiltration applications. Element type modules and flat sheet membranes for OUT-IN filtration direction are produced in Europe.

Ceramic flat sheet membranes are under investigation for OUT-IN filtration direction for applications in small communities to treat waste water. Micro-, ultra- and nanofiltration membranes are produced for this membrane type.

Raw materials used for ceramic membrane production are characterized among other things by their different isoelectric point (IEP). pH-values below IEP will lead to a positive charge of material. pH-values above IEP initiate a negative charge. Natural waters used for drinking water production show pH-values between 6.5 and 8 in general. As can be concluded from Tab. 2.2 during filtration of natural waters pure Al_2O_3-membranes will be charged positively while pure SiC-membranes have a negative charge. Different charges of membranes may cause different fouling on membrane surface. It should be considered that membranes are composed from different raw materials and burnt at high temperatures. IEP of the membrane can be therefore different from those of the raw materials.

Tab. 2.2:Isoelectric points of various ceramic membrane raw materials

Raw material	IEP	Reference
Al_2O_3	8.3 .. 9.8	Piwonski (2005) Gunko (1999)
SiC	2.7	Piwonski (2005)
TiO_2	6	Gunko (1999)
ZrO_2	7.5	Omatete (1991)

Ceramic membranes are more expensive with respect to the membrane area compared to membranes produced from polymeric materials. Moreover, prices of ceramic membranes depend on module type and pore size. E.g. monolith type membranes may be three to five times cheaper compared to element type membranes.

2.2 Literature review

Some research has been done on applications of ceramic membranes on drinking water treatment in recent years. Hagen (1996) compared silicon carbide membranes with polymeric membranes for particle removal of preflocculated and prefiltered dam water in pilot scale. Matsui et al. (2003), Yonekawa (2004), Matsushita et al. (2005) examined a hybrid system of flocculation followed by aluminium oxide microfiltration membranes with nominal pore sizes between 0.1 and 1.0 µm for virus removal. Lerch et al. (2005), Wessels (2006) and Heijman (2007) used flocculation followed by a 0.1 µm aluminium oxide membrane filtration for treatment of river water in pilot scale.

Results of these studies correspond well. Ceramic microfiltration membranes showed high permeabilities up to 500 L/m²/h/bar under certain operation conditions. However, relatively high flocculant dosages up to 3.5 mg/L Al, pH-adjustment of feed and chemical enhanced back wash were required. Decreasing dosages for pretreatment lead to declined fluxes. Virus removal with the combination of flocculant and MF-membrane was in the range between 1 and 6 log, dependent on pore size, flocculant dosage and operational conditions.

3 Materials and methods

3.1 Pilot plant and ceramic membranes

A pilot plant with ceramic membranes was operated in a waterworks using dam water as source water. Treatment steps in this waterworks include prefiltration with granular media, intermediate hardness increase in by-pass, ozonation, flocculation, rapid sand filtration followed by limestone filtration and disinfection.

Backwash water from prefiltration, rapid sand filtration and limestone filtration steps was collected during the full scale backwash process in 1 m^3 containers as feed of the pilot plant. To avoid sedimentation of the backwash water within the container and to maintain a constant feed quality a circular flow by a pump was installed.

The pilot plant was operated in dead-end mode. Transmembrane pressure was held constant at about 2 bar and decline of flux was monitored online. Membranes were backflushed with filtrate and air every 15 to 30 min. Details of operation were described previously (Mueller et al., 2007).

Membranes which were used in the examinations are characterized by Tab. 3.1 and Fig. 3.2.

Tab. 3.1: Ceramic membrane module for pilot examinations

pore size	**µm**	**0.2**		**0.05**		**0.5**
carrier material		a-Al_2O_3		a-Al_2O_3		SiC
membrane material		a-Al_2O_3		TiO_2		SiC
number of channels		7	19	7	19	37
channel diameter	mm	6	3.3	6	3.3	3.4
membrane area of test module	m^2	0.13	0.2	0.13	0.2	0.43

3.2 Analytical methods

Turbidity was measured according to DIN EN 27027 (90°, 880 nm) with an online turbidimeter (type Ultraturb, Hach Lange GmbH, Duesseldorf, Germany). Particle counts in the size range 1-100 µm were measured by an online counter (type Abakus mobil fluid, Markus Klotz GmbH, Bad Liebenzell, Germany). Aluminium, iron and manganese were analyzed according to DIN EN ISO 11885-E22. TOC and SAC at 254 nm were measured in conformity to DIN-EN 1484-H3 and DIN 38404-3-C3, respectively.

3.3 Evaluation of membrane resistance

Total membrane resistance (R_{tot} in m^{-1}) was computed according to Baars et al. (2005):

$$R_{tot} = \frac{TMP}{J * \eta}$$

with:

TMP:	transmembrane pressure in Pa
J:	flux in m/s
η:	dynamic viscosity of water as function of temperature in Pa * s

To allow a better comparison of results the runtime was replaced by the specific throughput (Q_{spec} in m^3/m^2), which is defined by produced filtrate volume ($V_{filtrate}$ in m^3) divided by the membrane area of the module ($A_{membrane}$ in m^2).

$$Q_{spec} = \frac{V_{filtrate}}{A_{membrane}}$$

The resistance of the fouling layer (R_{foul} in m^{-1}) was estimated by subtraction of the total membrane resistances between end and start of the run (Roorda and van der Graaf, 2000). The end of the run was defined as the time where a chemical cleaning of the membrane is required.

$$R_{foul} = R_{tot(Q_{spec}=t)} - R_{tot(Q_{spec}=0)}$$

4 Results and discussion

4.1 Influence of membrane type

Membranes tested were compared concerning the increase of membrane resistance during chemical free operation for one backwash water type, collected from full scale filters. Al_2O_3-microfiltration membranes showed comparable total membrane resistances and resistances of fouling layers according to Fig. 4.1.

Channel diameter had no influence on operational behavior. This indicates that distribution of air within the pilot plant during backflush processes was balanced. The total membrane resistance of Al_2O_3-ultrafiltration membrane is somewhat higher in relation to the microfiltration membrane due to the smaller cut-off of the ultrafiltration membrane. The Al_2O_3-ultrafiltration membrane had about the same resistance of fouling layer compared to the Al_2O_3-microfiltration membranes.

The SiC microfiltration membrane showed the highest total membrane resistances in this comparison. This effect is assumed to be influenced by a changed composition of the feed water during this run as a result of a changed operation of the full scale plant and sampling from full scale tanks respectively. Further research will be conducted to compare fouling behavior of SiC and Al_2O_3 membranes.

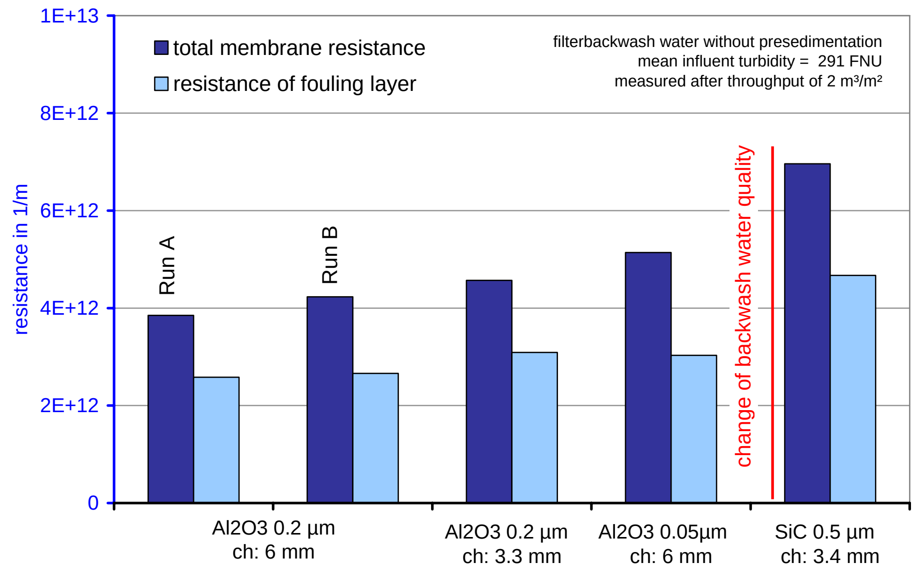


Fig. 4.1: Influence of membrane material and pore size on membrane and fouling layer resistance during dead-end operation

4.2 Influence of feed type

Previous results showed a considerable influence of backwash water quality on total membrane resistance. To get more knowledge on this issue, a given membrane was operated with different backwash waters collected from various full scale treatment steps of the waterworks. The examinations were run with 0.5 µm SiC-membrane and three backwash water types. Type 1 is backwash water from dual media filtration step, filtering untreated dam water. Type 2 is backwash water from the second dual media filtration step, filtering flocculated and ozonated dam water. Type 3 is backwash water from a limestone filtration step.

As can be seen from Fig. 4.2, membrane resistances during filtration of these backwash waters are quite different. Lowest resistance was found for filtration of limestone backwash water. Even within the same backwash water type the composition may be extremely different, due to the changes of operation of the full scale water treatment plant. It is obvious, that changes in composition of membrane feed will influence the total membrane resistance.

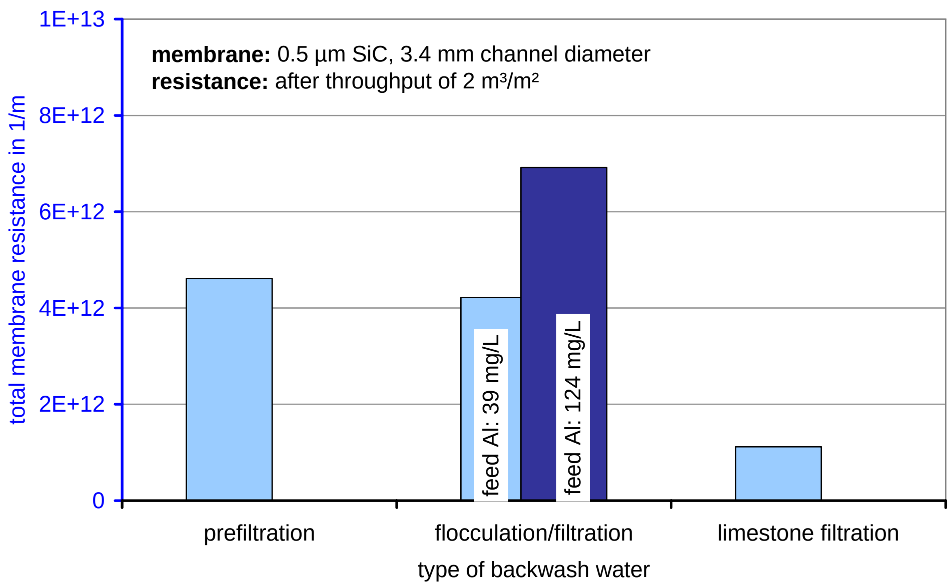


Fig. 4.2: Influence of backwash water type on membrane resistance during dead-end operation

Results imply that total membrane resistance was more influenced by backwash water type and operation than to membrane type for the waters tested. Plant optimization is therefore not limited to changing the membrane type.

Total membrane resistance during membrane filtration of backwash water from dual media filter was compared to membrane filtration of source water of the dual media filter. That means that dam water which was filtered by the rapid sand filter was also treated by membrane filtration. Fig. 4.3 shows for filtration of dam water a rapid increase of total membrane resistance, whereas for filtration of backwash water the total membrane resistance remains approximately constant under the same operation conditions.

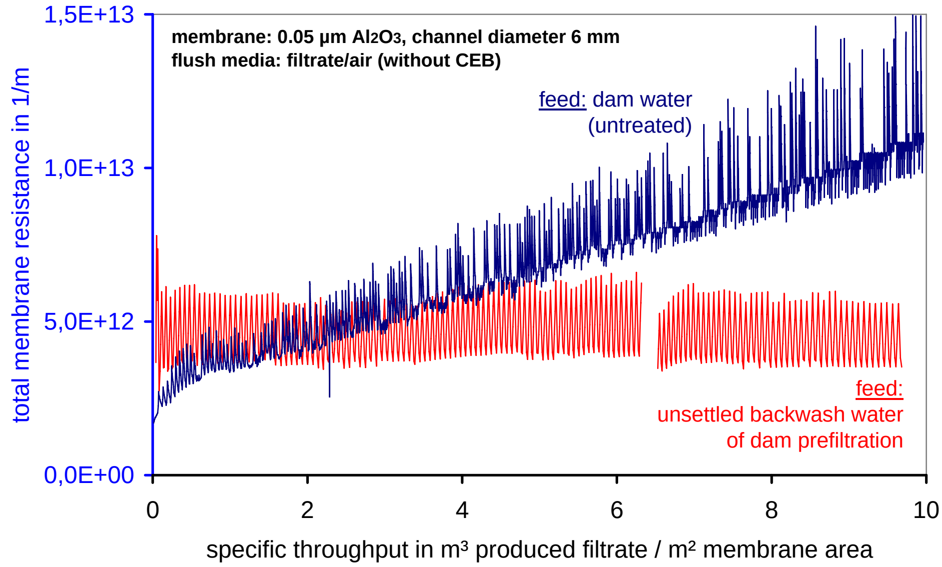


Fig. 4.3: Total membrane resistances of a ceramic membrane operated with untreated dam water (feed of a conventional dual media filter) and with the unsettled backwash water from this filter

That means filtration of backwash water from a sand filter was more efficient than filtration of the feed of the sand filter. This could be due to the higher particle load of backwash water, which formed a secondary layer on the membranes surface. This secondary layer causing fouling of the membranes is thought to be removed by flushing.

4.3 Cleaning of ceramic membranes

The cleaning procedure for the ceramic membranes was kept unchanged during this study. Therefore, the influence of feed water quality and membrane type on the efficiency of the chemical cleaning process can be determined. Cleaning solutions were:

(1) Alkaline at pH 12-13 with 3 mg/L Chlorine
(2) Acidic at pH 2 with a commercial membrane cleaner containing nitric and phosphoric acid

The applied cleaning process can be described as follows: Cleaning solutions were periodically pressed through the membrane during a soaking period of one hour. Chlorine dosages were kept considerably lower compared to typically applied concentrations to minimize formation of xenobiotic by-products which might complicate the discharge of spent cleaning solutions.

Chemical cleaning procedure was followed by an additional soaking of the membrane in alkaline environment for about one week in some cases. This was necessary to restore membrane capacity.

Efficiency of cleaning process was measured with finished (drinking) water. This clean water permeability was measured before and after each cleaning step.

Efficiency of cleaning process was dependent on cleaning agent and membrane type. According to Fig. 4.4 alkaline cleaning was more efficient compared to acidic cleaning for backwash water of the rapid filter.

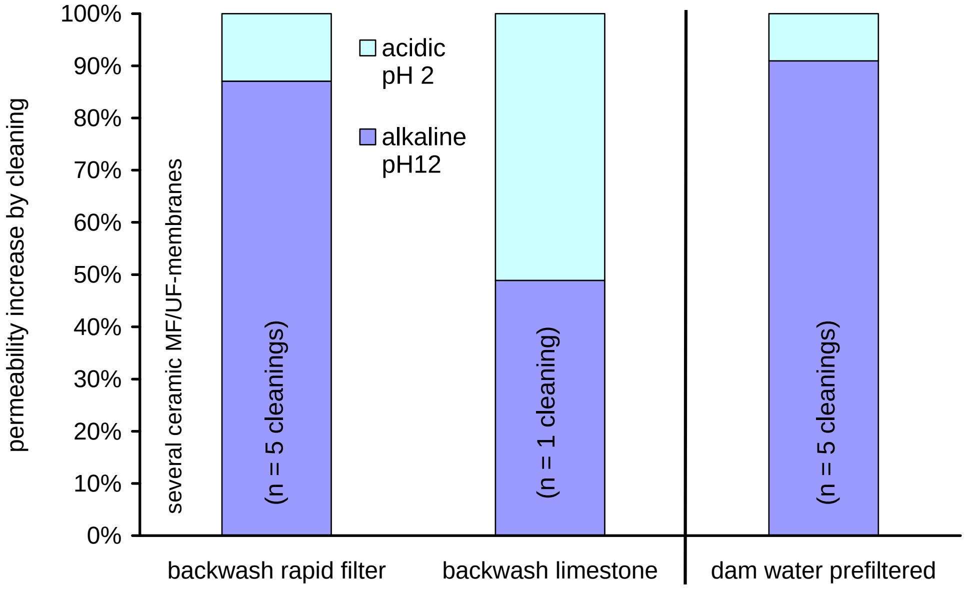


Fig. 4.4: Influence of acidic and alkaline cleaning on restoration of membrane permeability (100 % is equivalent with total effect of one cleaning process)

This correlates with the efficiency of cleaning of membranes preloaded with the feed of rapid filters. These behaviours were expected because dam water contains elevated concentrations of humic substances. It is well known, that alkaline cleaning is effective to remove organic foulants from the membrane. However, for membranes preloaded with backwash water of limestone filtration acidic cleaning showed nearly the same efficiency as alkaline cleaning.

For the backwash waters tested microfiltration membranes could be cleaned more effectively than ultrafiltration membranes. Fig. 4.5 summarizes the clean water permeability of the 0.2 µm Al_2O_3-membrane cleaned in 5 pilot runs. Efficiency of cleaning fluctuated between 40 and 80 % compared to clean water permeability of virgin membrane. Fluctuation is thought to be due to changes in composition of feed water resulting in different fouling layers on the membranes surface.

Ultrafiltration membranes were cleaned by the same procedure, which was applied for microfiltration membranes. According to Fig. 4.6 this process was considerably less efficient compared to the results for microfiltration membranes. Only about 40 % of the permeability of virgin membrane was restored by cleaning procedure. To achieve primary permeability additional soaking was required as described before.

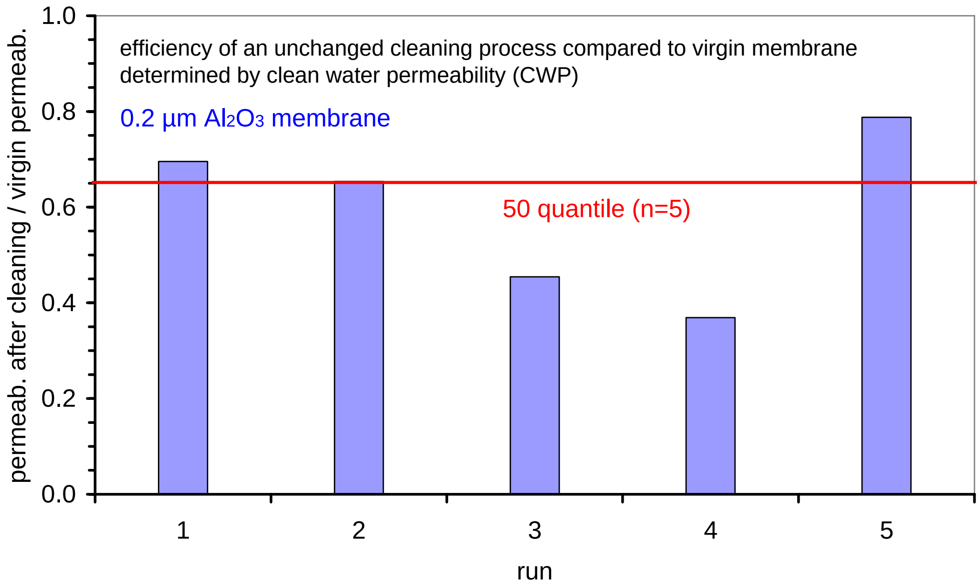


Fig. 4.5: Effect of an unchanged cleaning procedure on reconstitution of permeability for microfiltration membranes (1.0 is equivalent with virgin membrane)

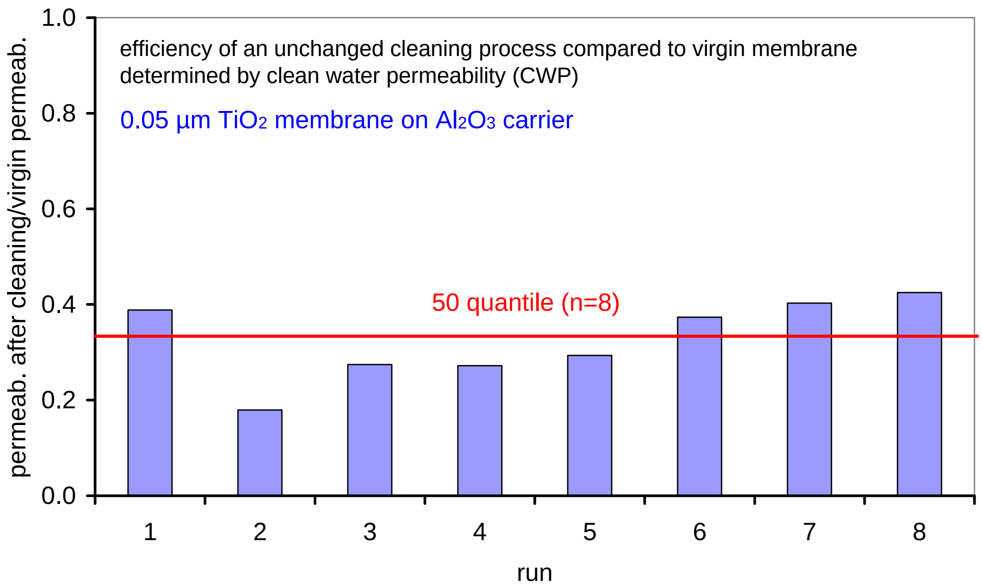


Fig. 4.6: Effect of an unchanged cleaning procedure on reconstitution of permeability for ultrafiltration membranes (1.0 is equivalent with virgin membrane)

Cleaning processes for ceramic membranes should be adopted to both, feed water quality and membrane type. Cleaning ceramic ultrafiltration membranes was somewhat more complex compared to microfiltration membranes.

4.4 Cost considerations

Life cycle costs were determined to compare costs of ceramic and organic membranes for backwash water treatment. Cost considerations base on a maximum plant capacity of 100 m^3/h for spent backwash water filtration. Site specific assumptions are summarized in Tab. 4.1.

Tab. 4.1: Site specific assumptions for life cycle cost estimation for backwash water filtration by ceramic and organic membranes

membrane		organic	ceramic
Q_{feed}	m^3/h	100	
	m^3/a	425,000	
Average operation time	h/d	approx. 12	
membrane backwash water	m^3/a	43,000	21,000
membrane life time	a	7	20
raw water tax	€/m^3	0.051	

Feed water flows were chosen under consideration of an increasing backwash frequency of conventional rapid filters during declined raw water quality leading to an increase of backwash water. Recovery was supposed to be 5 % for ceramic and 10 % for organic membranes. For ceramic membranes a life span of 20 years was assumed. It is still not clear, whether membrane producers will issue a guarantee for this time and how the guarantee will be collateralised. Raw water tax which must be paid for raw water intake in this case can be partly saved by backwash water recycling and was considered, therefore.

Not listed parameters such as energy consumption, demand for chemicals, man power, maintenance costs (except membrane replacement) or service contract were assumed to be comparable for both ceramic and organic membranes. Amortization and debt was calculated with a life span for filtration plant (except membrane) of 15 years and an interest rate of 5 %. Membrane area per module sizes was assumed to be 50 m^2 for organic and 28 m^2 for ceramic membranes. Element type ceramic membrane price was assumed to be 500 €/m^2 which is about ten times the prize of organic membranes.

Fig. 4.7 shows the annual life cycle costs (LCC) for a ceramic membrane filtration plant in dependence of flux and membrane costs including housings. LCC declines with decreasing membrane costs or increasing flux as expected. Under the assumptions made break even for LCC of organic and ceramic membranes was estimated either for a ceramic membrane price of about 240 €/m² at a flux of 71 L/m²/h or 360 €/m² at a flux of 110 L/m²/h. LCC for a ceramic membrane plant would be about 30 % higher than for a plant with organic membranes for the case considered, in which ceramic membrane costs were estimated with 500 €/m² and organic membranes with 50 €/m². That means the relatively high purchase price for ceramic membrane was partly compensated.

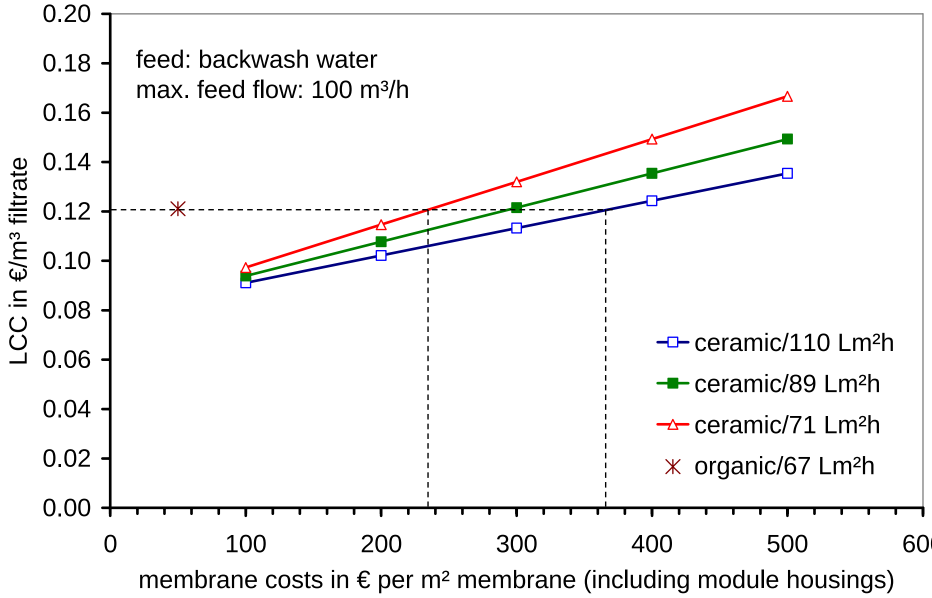


Fig. 4.7: Example for life cycle costs for spent backwash water filtration with ceramic membranes compared to organic membranes

Additional costs may result to discharge the backflush water of the membrane plant, which were not included in this LCC-cost evaluation.

Other sources (Koetzle, 2006) have summarized costs for backwash water treatment with organic membranes in six cases. LCC moved from 0.14 to 0.62 €/m³ excluding costs for discharge of membrane backflush water. The lower costs determined in this study may come from savings of raw water tax, due to recycling of backwash water and reuse the filtrate as raw water.

Ceramic membranes will be more competitive if prices decline or membranes will allow more elevated fluxes. This life cycle cost estimation indicates, that even element type ceramic membranes are still more expensive but not so far from costs of treatment by organic membranes. Therefore, introduction of ceramic membranes for water treatment under cost-aspects could be not impossible in medium-term, especially if the more cost-efficient monolith module type is applied.

5 Conclusion

Ceramic membranes are products with a long history in industrial applications and might get increasing importance in drinking water treatment, too. Current examinations are focusing on a replacement of organic by ceramic membranes. However, a better identification of advantages of ceramic membranes which make them more applicable for drinking water utilities would be desirable and is therefore a task of further research. This includes a comparison of different ceramic membranes with measures to influence water quality regarding to their cost/benefit-ratios.

Resistance of ceramic membranes would allow extreme chemical cleaning procedures. However, chemical cleaning must be balanced in accordance with an environmentally friendly process. Physical cleaning methods such as ultrasound cleaning may be also applicable for ceramic membranes. Developing appropriate technologies in accordance with module structures may be another task of future investigations.

The study implied that influence of backwash water composition and operation was stronger than the influence of various ceramic membranes tested. Plant optimization is therefore not limited on changing the membrane type.

6 Acknowledgements

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