Techneau, 05/02/07
MAY 2007

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Ceramic membranes – Case related protocol for optimal operational conditions to treat filter backwash water

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Quality Assurance
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Deliverable number
D 2.3.3.5.a

This report is: **PU** = Public.

Summary

Waterworks using surface water for drinking water production often include treatment steps for particle removal and increase of hardness by conventional filtration technologies. The backwash water of these filters contains the particle load of the raw water including added flocculants. Innovative methods for the treatment of these backwash waters are required to allow an environmentally friendly disposal.

Inorganic membranes, such as ceramic membranes, have several useful properties such as their resistance to mechanical, chemical and thermal stress, high porosity and a hydrophilic surface. Within this project research was conducted to implement inorganic membranes for treatment of backwash waters. A pilot plant was developed to pick up various inorganic membrane elements, such as different cut-offs and channel diameters in cross-flow and dead-end operation. The pilot plant was operated in a waterworks with real backwash water.

High loaded backwash waters (e.g. turbidity up to 560 NTU, aluminium concentration up to 256 mg/L) were treated with inorganic membranes in dead-end and cross-flow mode. Micro- and ultrafiltration membranes made from Al_2O_3 or SiC were used. Results indicated that the membranes were efficient to improve the backwash water quality. Among the membrane types tested SiC and Al_2O_3 membranes tend to show a similar fouling behaviour.

The current working stage indicates, that the treatment of residuals by inorganic membranes seems to be possible. However, further investigations are necessary especially to examine the influence of backwash water composition, long term behaviour and cost-benefit ratio in comparison with organic membranes.

Contents

1 Introduction

Inorganic membranes are resistant to mechanical, chemical and thermal stress. They have a high porosity and a hydrophilic surface. These properties may open new fields for applications in water treatment, such as the treatment of residuals from drinking water production or the direct treatment of surface waters.

Currently, inorganic membranes are not used in public water supply, despite of some pilot plants in Japan or the United States. Recent pilot scale examinations with a certain new developed ceramic membrane used for direct treatment of surface water indicated, that these membranes seem to be already cost efficient compared to the other conventional treatment technologies in drinking water treatment (LERCH et al., 2005).

Waterworks using surface water for drinking water production often include treatment steps for particle removal and increase of hardness by conventional filtration technologies. The backwash water of these filters contains the particle load of the raw water including added flocculants. A treatment of these backwash waters is required to allow an environmentally friendly disposal.

Objective of this project was to gain operational experience with ceramic membranes in pilot scale for treatment of backwash water from conventional rapid filters. While a number of ongoing research in the field of drinking water is applying Al_2O_3 membranes of one Asian producer this study includes ceramic membranes produced in Europe only. This includes also a test of a prototype membrane module made from SiC.

2 Ceramic membranes

Inorganic membranes are produced from materials like aluminia, zirconia, titania or silicon carbide. Pore sizes in the range from 0.005 µm to about 1 µm are available. However, most of the ceramic membranes intended for use in the field of water treatment are microfiltration membranes.

There are two types of modules available, where the flow direction is IN-OUT: element and monolith. Element type modules include several ceramic elements, each with a relatively small surface. The membrane elements are arranged in subdivided stainless steel housings according to Fig. 2.1. Monolith type modules consist of a ceramic body with various flow channels and therefore a relatively high surface area. An example is shown in Fig. 2.2. Both module types are expected to have their advantages. The monolith type offers a high membrane area in a compact volume with a reasonable price. The element types are assumed to be very resistant with fewer problems by channel blocking during long time operation. A third type, ceramic flat multi-duct plate membranes, for OUT-IN filtration direction is being tested in small communities for waste water treatment (Fig. 2.3). However, long time experiences under conditions in waterworks are not available for all types. At present, for water application producers from Japan and United States tend to manufacture monolith type modules. Element type modules and flat sheet membranes for OUT-IN filtration direction are produced in Europe.

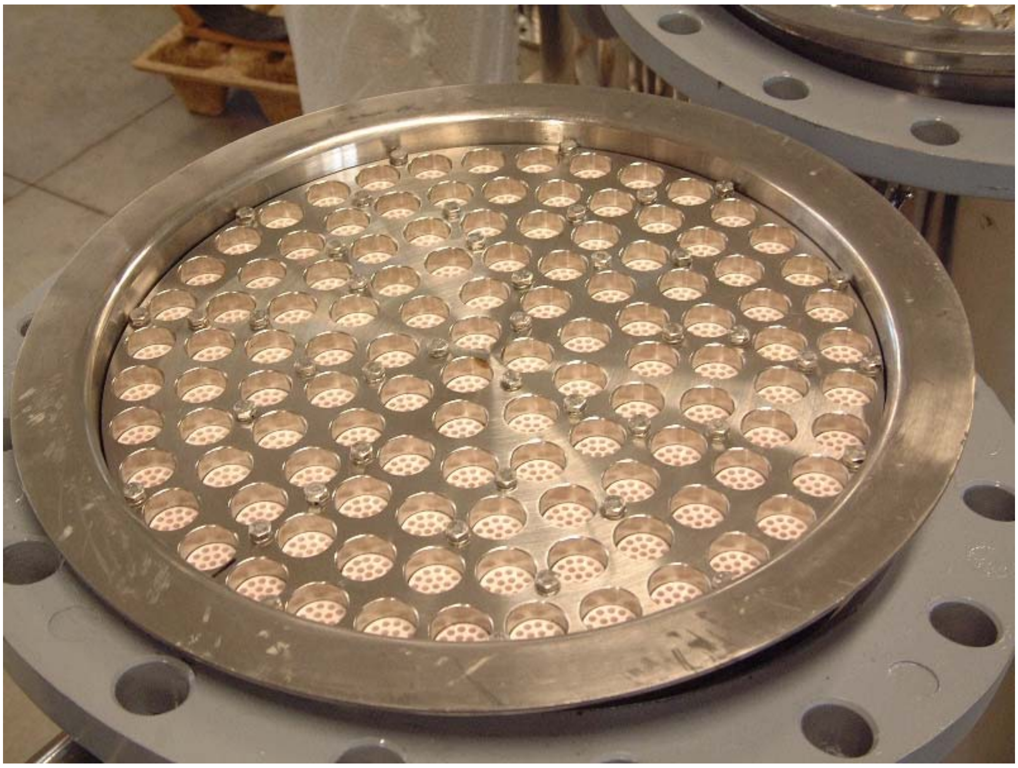

Fig. 2.1: Example for an element type ceramic membrane module (photo: Atech innovations GmbH)

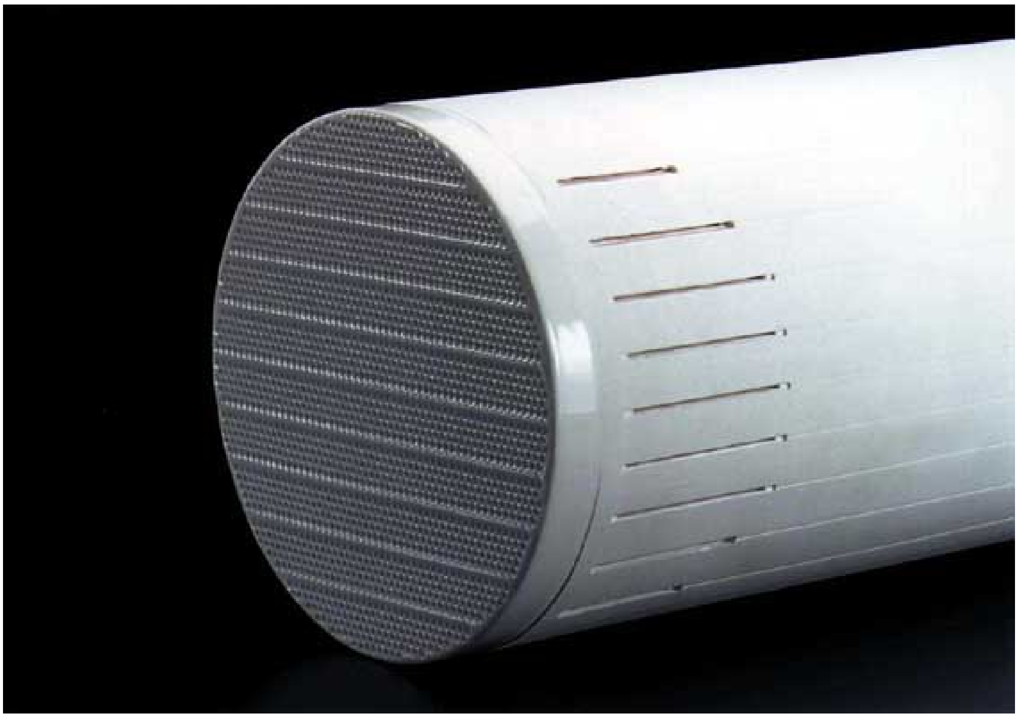

Fig. 2.2: Example for a monolith type ceramic membrane module 25 m² membrane area, 2.000 channels with 2.5 mm in diameter (photo: NGK)

Fig. 2.3: Example for flat sheet ceramic membrane modules for waste water treatment (photo: BUND, 2005)

Ceramic membranes are expected to have higher fluxes compared to organic membranes, due to their higher porosity and more hydrophilic surface. The resistance of ceramic membranes to mechanical, chemical and thermal stress allows a better recovery of membrane performance.

Despite of advantages of ceramic membranes some disadvantages have to be noted. Different thermal expansion of ceramic membrane and the module housing may cause problems with the sealing (MELIN and RAUTENBACH, 2003). Therefore, attention should be considered for choosing an appropriate gasket between the ceramic membrane and the housing. Ceramic membranes are brittle.

Ceramic membranes are much more expensive with respect to the membrane area compared to membranes produced from organic materials. As shown in Fig. 2.4 specific costs of ceramic membranes vary in a wide range, depending on module type and the pore size. Costs of organic membranes showed a sharp decrease in recent years leading to the assumption that a similar development for ceramic membranes may occur in the future. Moreover, higher fluxes for ceramic membranes will decrease the required membrane area for a given water flow. Longer membrane life time is another factor which may compensate the higher investment costs compared to organic membranes.

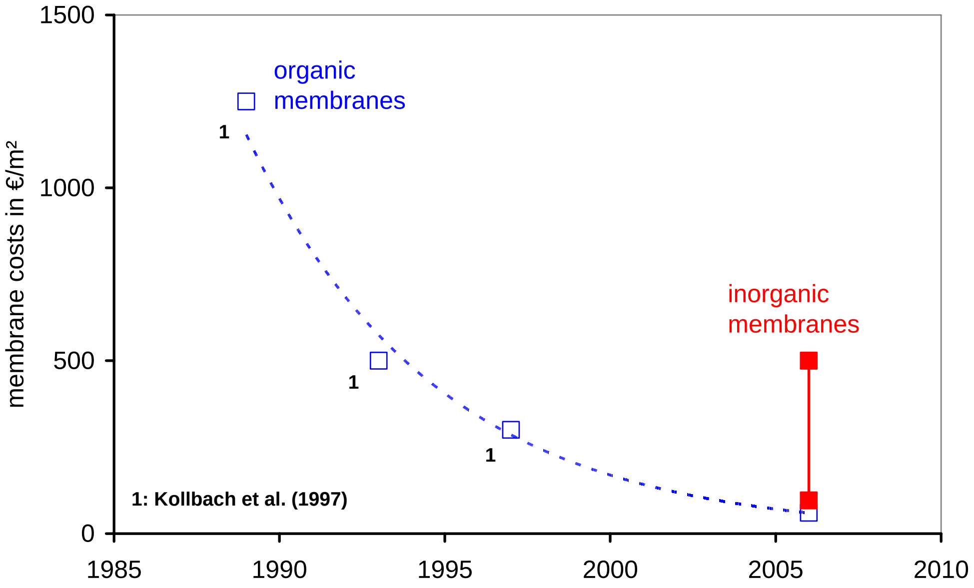

Fig. 2.4: Decrease of costs for organic membranes in the past and range of costs for inorganic membranes in 2006

3 Materials and methods

3.1 Pilot plant and ceramic membranes

Within the project a pilot plant for particle removal by ceramic membranes was developed in co-operation with membrane-engineering GmbH Salem, Germany. The pilot plant was designed to operate fully automated in cross-flow as well as in dead-end mode. Online sensors and data loggers were installed to monitor flow, pressure and temperature. Fig. 3.1 shows a photo of the pilot plant after installation in a waterworks.

Fig. 3.1: Pilot plant for ceramic membrane filtration (left to the right: storage tank, membrane housing, filtrate tank, visualized stored program control)

The construction of the pilot plant allowed the use of various ceramic membrane elements, such as different cut-offs and channel diameters. 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

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

Fig. 3.2: Ceramic membranes for pilot examinations (left Al_2O_3-membranes, right: SiC-membrane)

3.2 Analytical methods

Turbidity was measured according 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 Feed water

The pilot plant was installed in a waterworks using dam water as source water. Treatment steps in this waterworks include prefiltration, intermediate hardness increase in by-pass, ozonation, flocculation, rapid sand filtration followed by limestone filtration and disinfection. Backwash water from the rapid sand filtration step 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.

3.4 Operation of the pilot plant

Examinations started with pilot plant operation in cross-flow mode with the silicon carbide (SiC) membrane with a cross-flow velocity of 3.4 m/s. Transmembrane pressure was held constant at about 1.5 bar and the adequate flux decline was monitored. Backflush was conducted with filtrate and a flux of about 6.500 L/m²/h at 2.7 bar. Backflush frequency was 30 min. This resulted in a backwash volume of 20 % related to the produced filtrate flow. Concentrate was disposed every 3 hours leading to a concentrate flow of 11 % of the total filtrate flow.

Air flush on the raw water side of the membrane was conducted during water backwash to improve the membrane performance after a specific throughput of about 5 and 14 m^3 produced filtrate per m^2 membrane area. No chemical membrane cleaning was applied during operation in cross–flow mode, in which a specific throughput of 20 m^3/m^2 was achieved.

Dead-end operation was chosen to test the Al_2O_3 and SiC membrane respectively. Transmembrane pressure was held constant at about 2 bar and the decline of flux was monitored. Backflush frequency was 15 min. Backflush was executed with filtrate at fluxes up to 9.000 $L/m^2/h$ at 3 bar and supported by air flush with about 3 m/s. Backflush volume was between 6.6 and 12.8 % of the filtrate production.

Feed water was circulated by pumping in order to avoid sedimentation in the feed tank as described in the previous chapter. This resulted in an increase of the temperature up to 31.5 °C. Temperature effect was considered during interpretation of membrane resistances.

3.5 Determination of the membrane resistance

Total membrane resistance (R_{tot}) was computed according to

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

with:
TMP: trans membrane pressure
J: flux
η: dynamic viscosity of water as function of temperature

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

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

The resistance of the fouling layer (R_{foul}) was estimated by subtraction of the total membrane resistances between end and start of the run (BAARS et al., 2005). 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 Cross-flow mode

Backwash water from rapid sand filters after a settling time of 0.5 hours was used as feed for the pilot plant. A 0.5 µm silicon carbide membrane module (SiC) was installed in the pilot plant.

Tab. 4.1 summarizes the arithmetic mean values for physical-chemical quality parameters. Column "backwash" represents the settled backwash water from a full scale filter. "Cross-flow" is identical with the feed concentration for the membrane. "Filtrate" is the effluent of the membrane. Backwash water is concentrated by the cross-flow with a ratio of about 1:3 to 1:4. Influent concentration of 132.7 mg/L aluminium was decreased to 0.13 in average. Although no removal of humic substances was expected by a 0.5 µm microfiltration membrane, TOC and associated parameters such as SAC, were deceased between 45 and 74 %. This behaviour may be explained by flocculation effects due to the high influent aluminium concentration. Mean turbidity of the settled backwash water was 51 NTU, of the concentrate about 197 NTU. Mean filtrate turbidity was 0.1 NTU.

Tab. 4.1:Average quality parameters for examinations using a 0.5 µm SiC-membrane in cross-flow

		backwash	cross-flow	filtrate
aluminium	mg/L	38.0	132.7	0.13
calcium	mg/L	15.9	21.5	15.5
iron	mg/L	0.6	2.1	<0.01
manganese	mg/L	0.192	0.523	0.061
zinc	mg/L	0.080	0.290	0.030
nickel	mg/L	0.053	0.120	0.014
SAC(254 nm)	1/m	5.3	6.4	3.5
SAC(436 nm)	1/m	0.7	0.3	0.1
TOC	mg/L	4.7	8.3	2.2
dry matter	g/m^3	185.3	610.8	-
turbidity	NTU	51.3	197.4	0.1

To determine the concentration of particulate matter in the filtrate particles in the size range between 1 and 100 µm were counted. An internal target value for particle counts in drinking water was defined to 100 particles/mL. Fig. 4.1 shows the particle counts measured after a specific throughput of 0.3 m^3/m^2 representing a nearly virgin membrane. The influent turbidity during this starting phase was 132 NTU. During filtration phases particle counts were below the detection limit of the particle counter. However, particle counts increased to 145..186 particles/mL immediately after backflush. Fig. 4.2 indicates that a preloaded membrane, in this example after a throughput of 20 m^3/m^2, removes particles more efficiently. This may be attributed to an additional filter effect of the fouling layer.

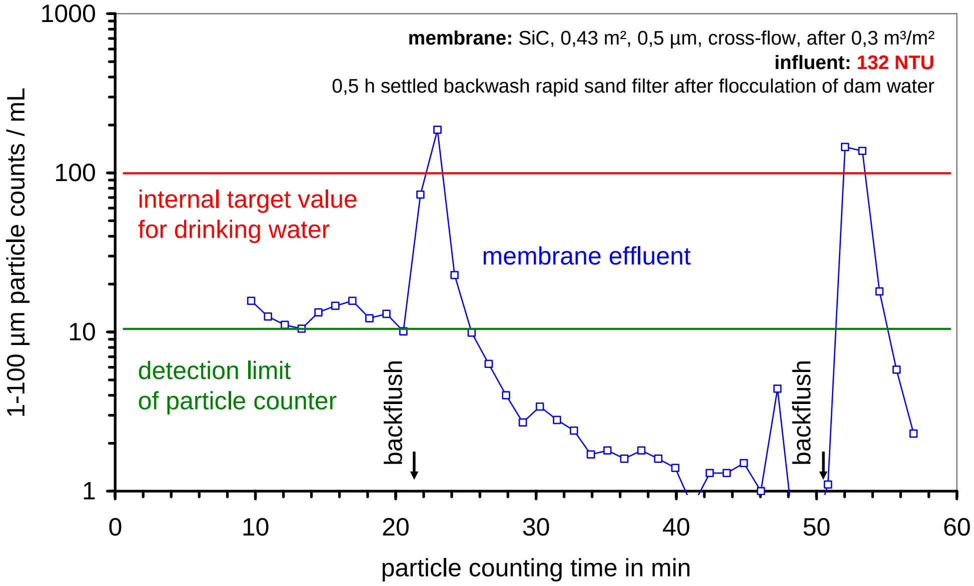

Fig. 4.1: Particle counts in the filtrate of the 0.5 µm SiC-membrane after a specific throughput of 0.3 m^3/m^2

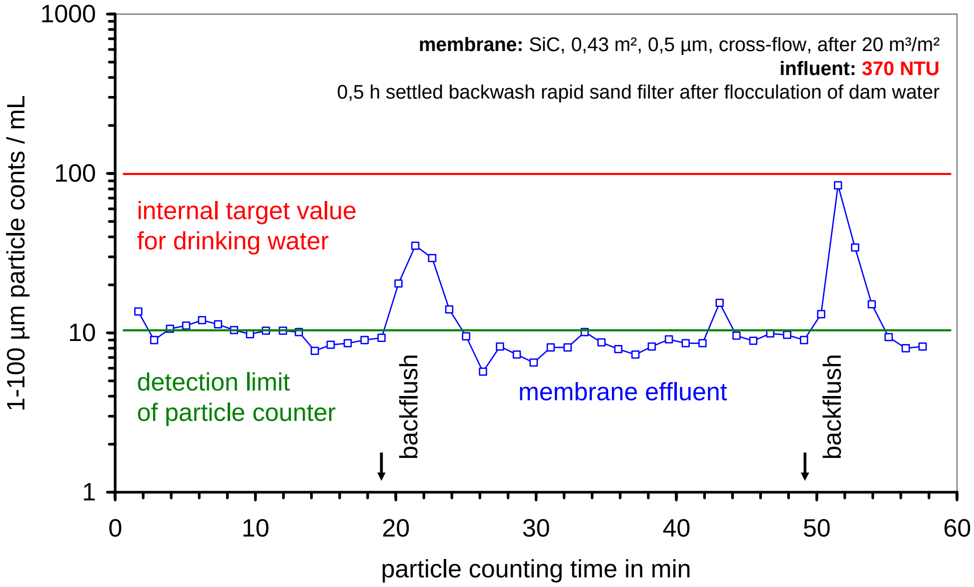

Fig. 4.2: Particle counts in the filtrate of the 0.5 µm SiC-membrane after a specific throughput of 20 m^3/m^2

Fig. 4.3 shows the increase of total membrane resistance in dependence on specific throughput. During the run average fluxes ranged between 102 and 280 $L/m^2/h$. Transmembrane pressure was held constant at 1.5 bar. Temperatures increased during the run from 9.8 to 31.5 °C due to the cross-flow. Temperature effect is considered in total membrane resistance through the dynamic viscosity of the water. Flux > 100 $L/m^2/h$ lead to a steep increase of total membrane resistance. A lower flux of about 100 $L/m^2/h$ caused a better operational behaviour. After 16 m^3/m^2 constant conditions were achieved in which shear forces of the cross-flow prevented a further increase of the total membrane resistance. Within the examination period restoration of membrane capacity was conducted by water backflush and air flushing without any dosage of chemicals. For a nearly virgin membrane corresponding to a throughput of 2.5 m^3/m^2 backflush alone was efficient to decrease the membrane resistance. However, after a throughput of 5 m^3/m^2 water backflush alone caused only a slight decrease of membrane resistance. Additional air flush was able to decrease membrane resistance to $1*10^{12}$ 1/m. This is comparable with the virgin membrane. After filtration of 13 m^3/m^2 water air flushing lost its efficiency too and increased the membrane resistance to $4*10^{12}$ 1/m. Energy consumption without energy recovery was estimated to about 5 kWh/m^3, which is regarded as too high for applications in water treatment.

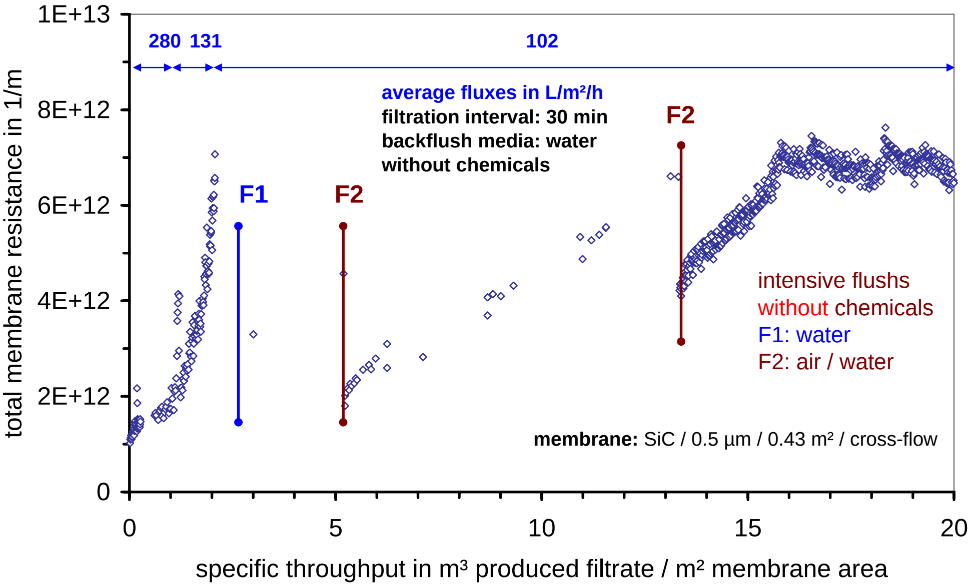

Fig. 4.3: Increase of total membrane resistance in dependence on specific throughput

4.2 Dead-end mode

4.2.1 *Feed water*

Examinations in dead-end mode were conducted with backwash water from a central basin of the waterworks. In this basin backwash waters from all filtration steps of the waterworks are being collected as a mixture. The operator of the waterworks managed nearly comparable conditions in this basin during sampling the feed water for the pilot plant.

Backwash water from this basin without settling was used as feed for the pilot plant.

4.2.2 *Membranes*

Four different membranes were installed in the pilot plant for these examinations:

- 0.5 µm SiC (microfiltration)
- 0.2 µm Al_2O_3 with 7 channels (microfiltration)
- 0.2 µm Al_2O_3 with 19 channels (microfiltration)
- 0.05 µm Al_2O_3 with 7 channels (ultrafiltration)

Further characteristics of the membranes may be found in chapter 3.1.

4.2.3 *Water quality*

Physical-chemical quality parameters were measured in feed and in filtrate for the membranes tested. Already a visual comparison between feed and filtrate showed a high efficiency of the membrane treatment (Fig. 4.4).

Fig. 4.4: Samples of feed (right) and filtrate (left) of the SiC-membrane

Tab. 4.2 to 4.5 summarize analytical results. The different feed concentrations during the examinations make a comparison between the membranes more difficult. However, this represents the situation in the practice of water treatment.

Tab. 4.2:Quality parameters for examinations using a 0.5 µm SiC-membrane in dead-end

		feed		filtrate	
spec. Throughput	**m^3/m^2**	**0.1**	**0.14**	**0.1**	**0.14**
Aluminium	mg/L	39	124	0.3	0.11
Calcium	mg/L	87	88.8	26.6	28.6
Iron	mg/L	2.64	4.36	<0.01	<0.01
Manganese	mg/L	4.68	5.9	0.011	0.18
Nickel	mg/L	0.006	0.009	<0.001	<0.001
Zinc	mg/L	0.36	0.62	<0.02	0.03
SAC (254 nm)	1/m	7.4	11	4.3	6.6
SAC (436 nm)	1/m	0.3	0.5	<0.1	0.2
TOC	mg/L	27.2	77	2.4	4
DOC	mg/L	6.6	9.1	2.3	3.9
Dry matter	g/m^3	584	756	-	-
Turbidity	NTU	340	258	0.01	0.01

Tab. 4.3:Quality parameters for examinations using a 0.2 µm Al_2O_3-membrane with 7 channels in dead-end

		feed				filtrate		
spec. throughput	**m^3/m^2**	**0.9**	**3.8**	**0.8**	**4.4**	**0.9**	**0.8**	**4.4**
Aluminium	mg/L	100	87.5	125	87.5	0.80	1.48	0.58
Iron	mg/L	4.35	3.37	4.89	2.94	0.02	0.03	0.03
Manganese	mg/L	6.35	4.36	6.60	3.78	0.340	0.046	0.030
SAC (254 nm)	1/m	5.8	6.7	9.9	7.3	5.5	9.7	6.8
DOC	mg/L	6.1	5.9	7.0	4.2	3.4	5.1	4.1
Turbidity	NTU	144	180	310	258	0.03	0.02	0.02

Tab. 4.4:Quality parameters for examinations using a 0.2 µm Al_2O_3-membrane with 19 channels in dead-end

		feed		filtrate	
spec. throughput	**m^3/m^2**	**0.64**	**3.94**	**0.64**	**3.94**
aluminium	mg/L	109	127	0.41	1.27
Iron	mg/L	4.22	4.85	0.01	0.02
manganese	mg/L	6.42	6.84	-	-
SAC (254 nm)	1/m	5.4	8.0	4.5	9.2
DOC	mg/L	3.9	5.6	3.0	5.4
Turbidity	NTU	138	148	0.02	0.01

Tab. 4.5:Quality parameters for examinations using a 0.05 µm Al_2O_3-membrane with 7 channels in dead-end

		feed	filtrate
spec. throughput	**m^3/m^2**	**0.26**	**0.26**
aluminium	mg/L	256	1.35
iron	mg/L	9.87	0.06
manganese	mg/L	15.1	0.087
SAC (254 nm)	1/m	9.4	3.3
DOC	mg/L	6.8	2.0
turbidity	NTU	560	0.02

These analytical results allow drawing of the following conclusions:

- SiC membrane filtrate showed lower aluminium concentrations compared to the Al_2O_3 membranes at similar feed concentrations
- SiC and Al_2O_3 microfiltration membranes as well as the Al_2O_3 ultrafiltration membrane produced filtrates with comparable iron and manganese concentrations
- SiC and Al_2O_3 microfiltration membranes showed similar SAC(254 nm) and DOC concentrations in the filtrate
- Al_2O_3 ultrafiltration membrane showed a better decrease of SAC(254 nm) and DOC compared to Al_2O_3 microfiltration
- Al_2O_3 microfiltration membranes with 7 and 19 channels produced comparable filtrate qualities

For the parameters determined and the waters tested no differences of practical relevance were found between the SiC and Al_2O_3 microfiltration membranes, although the SiC membrane is characterized by a cut-off of 0.5 µm and the Al_2O_3 membrane by a cut-off of 0.2 µm.

4.2.4 Operational experience

The membranes were operated with a filtration interval of 15 minutes. Backwash of membranes was conducted with filtrate and supported simultaneously by a forward flush with air. No chemicals were added during backwash.

Fig. 4.5 to 4.8 show the specific throughput and the corresponding total membrane resistances as well as the permeability normalized at 20°C. To compare the operational behaviour of the different membranes, the examinations were performed up to a specific throughput of 4 m^3/m^2.

The 0.05 µm Al_2O_3 (Fig. 4.5), 0.2 µm Al_2O_3/19 channel (Fig. 4.6) and the SiC (Fig. 4.7) membranes showed only a very slight increase of the total membrane resistance during the examination period. The total membrane resistance was somewhat higher for the SiC membrane.

An unexpected sharp increase of the total membrane resistance after a specific throughput of about 3 m^3/m^2 was found for the 0.2 µm Al_2O_3/7 channel (Fig. 4.8). This pattern was confirmed by a second run. The reason is still unknown and is thought to be originated in the experimental setup. Further examinations are necessary to clarify this effect.

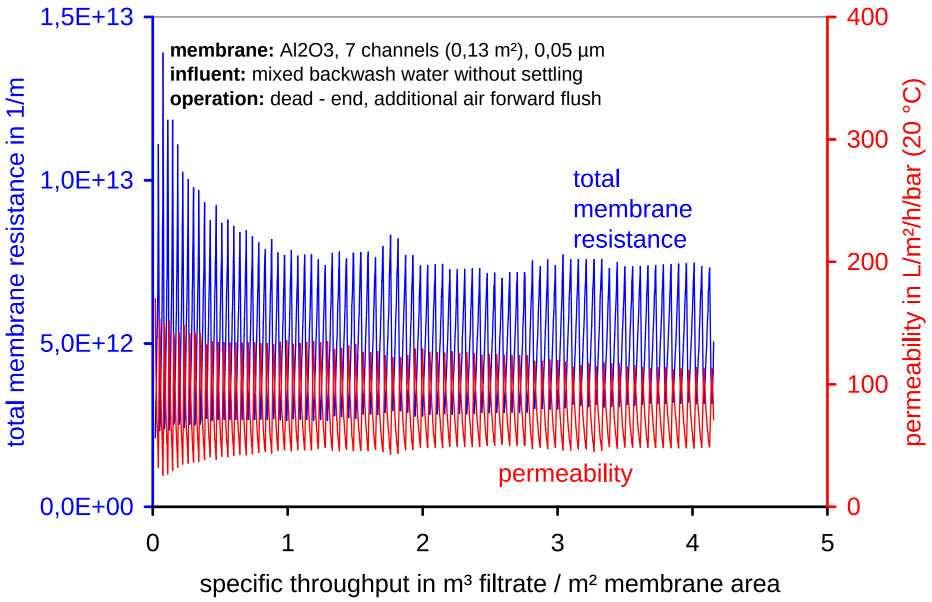

Fig. 4.5: Total membrane resistance and permeability in dependence on specific throughput for a 0.05 µm Al_2O_3 – membrane

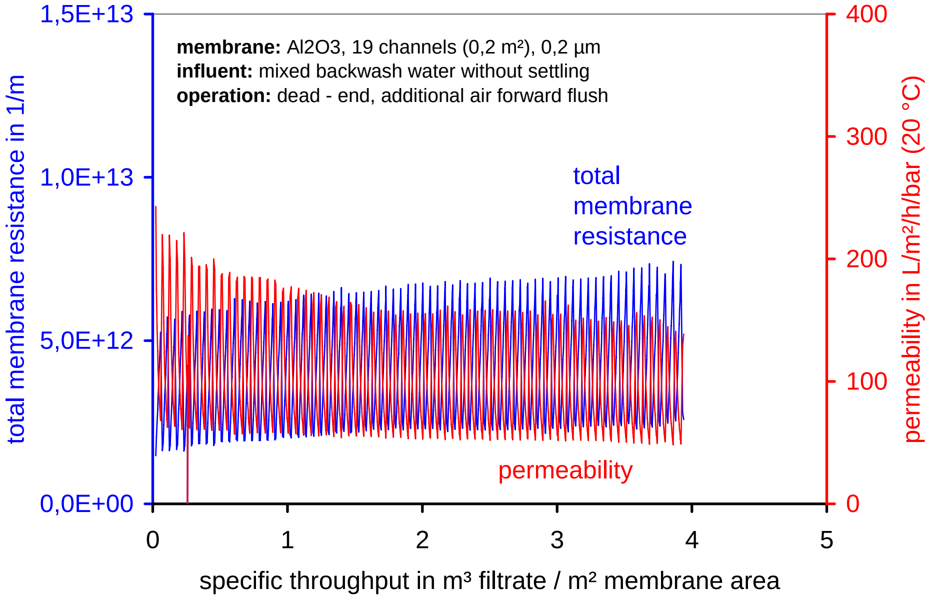

Fig. 4.6: Total membrane resistance and permeability in dependence on specific throughput for a 0.2 µm Al_2O_3/19 channel – membrane

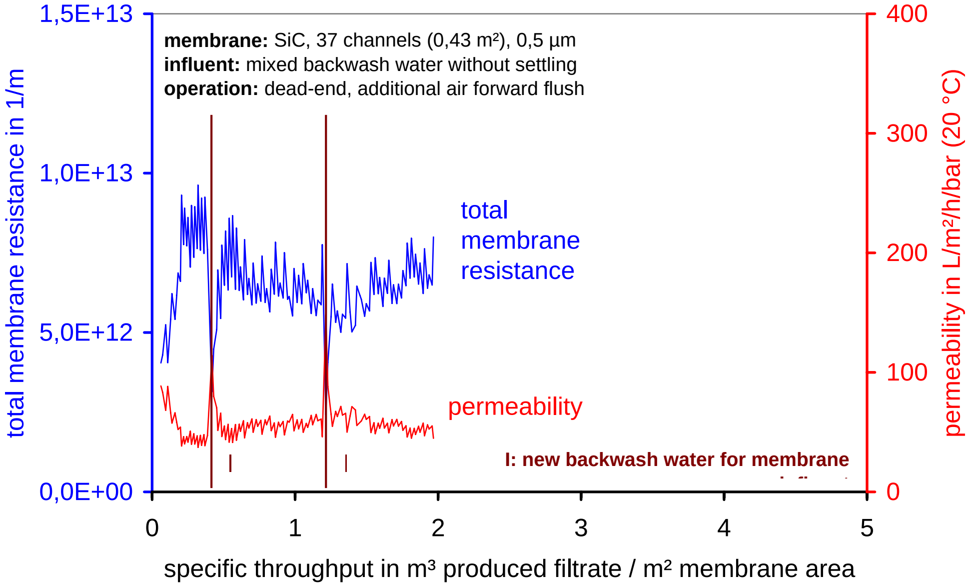

Fig. 4.7: Total membrane resistance and permeability in dependence on specific throughput for the 0.5 µm SiC – membrane

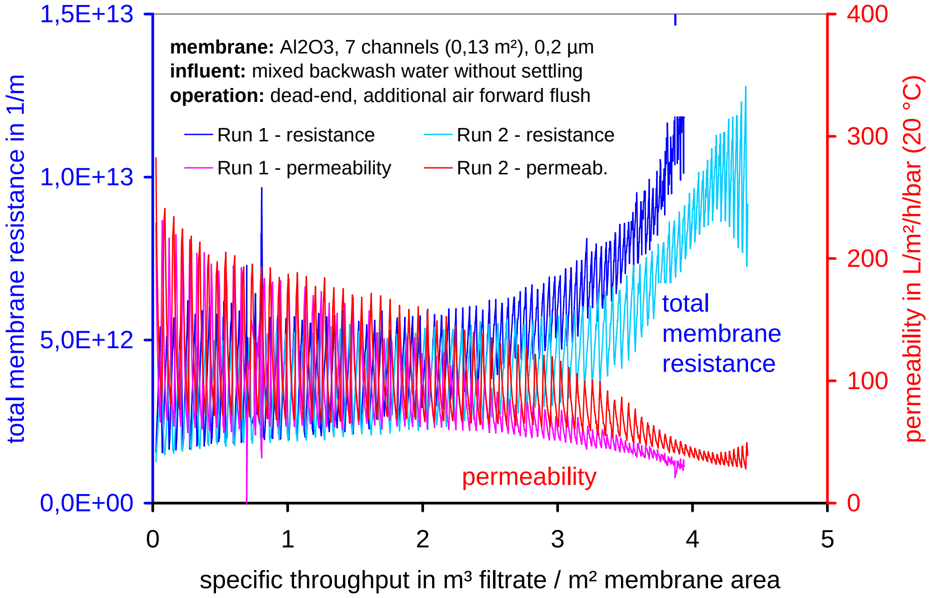

Fig. 4.8: Total membrane resistance and permeability in dependence on specific throughput for a 0.2 µm Al_2O_3/7 channel – membrane including verification run

To allow a better comparison between the membranes, their resistances and permeabilities were determined at a specific throughput of 2 m³/m².

Fig. 4.9 includes the total membrane resistance as well as the resistance of the fouling layer. Resistances were computed according to chapter 3.5. As expected the resistances of the Al_2O_3-microfiltration membranes are similar.

The resistance of the Al_2O_3-ultrafiltration membrane itself is higher in relation to the microfiltration membrane due to the smaller cut-off. Results also indicate that ultrafiltration membranes seem to be more resistant against fouling in contrast to the microfiltration membranes. For the water examined the differences in the Al_2O_3-membrane resistances between the membranes tested are considered to be not relevant for practical purposes.

The SiC-membrane showed the highest total membrane resistances and therefore the lowest permeability in this comparison. The resistance of the fouling layer was comparable with those of the Al_2O_3-membranes. This indicates that fouling occurs in the same extent on SiC as well as on Al_2O_3-membranes.

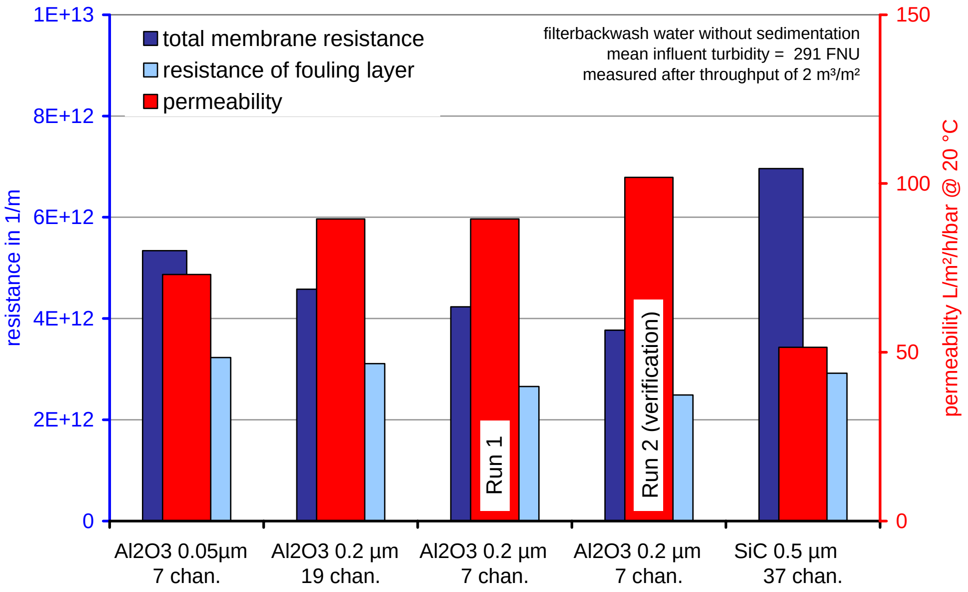

Fig. 4.9: Comparison of membranes concerning their resistances and permeability determined after a specific throughput of 2 m³/m²

5 Conclusion

Existing waterworks for surface water treatment are using conventional treatment steps such as a combination of flocculation and rapid sand filtration for particle removal or a limestone filtration for increase of hardness. The volume of backwash water from rapid filters often range between 2 and 7 % of the drinking water produced and contain the particle load of the raw water including the flocculants. Innovative methods for treatment of these backwash waters allow an environmentally friendly disposal. This is in accordance with environmental regulations such as the European Water Framework Directive.

The study focused on the application of micro- and ultrafiltration membranes made from SiC as well as from Al_2O_3 for particle removal from filter backwash water. Pilot scale examinations with these membranes were conducted using filter backwash water of a full scale surface water treatment plant.

Cross-flow filtration with the inorganic membranes resulted in good operational behaviour even for treatment of high loaded backwash water. However, energy consumption for cross-flow mode was considered as too high in relation to the achieved filtrate flow. For the water as well as the operational setup tested, cross-flow filtration with ceramic membranes was not economical. Dead-end filtration indicates that a stable operation should be possible even using a feed of not presettled backwash water.

Among the membranes tested, the SiC made membrane showed a somewhat higher total membrane resistance compared to Al_2O_3 membranes. Therefore, the SiC-membrane tested has a similar cost-benefit ratio if their purchase price is lower compared to Al_2O_3 membranes tested. The results are not qualified to generalize a difference between SiC and Al_2O_3 membranes, because membrane materials are only on criteria among others with influence on membrane performance.

Al_2O_3 ultrafiltration membranes showed only a slightly higher total membrane resistance compared to microfiltration membranes, even the removal efficiency is better.

No differences between SiC and Al_2O_3 microfiltration membranes were found concerning the removal of particulate matter.

The intermediate results showed that inorganic membranes may make full scale applications not implausible. Further research is necessary to investigate open questions including the influence of the feed water type, long term intervals for chemical cleaning of the membrane and the cost-benefit ratios compared to organic membranes.

6 Acknowledgements

This research was conducted by subsidy of the European Union. The authors wish to thank the Zweckverband Wasserversorgung Kleine Kinzig, in Alpirsbach-Reinerzau, Germany, for their extensive support during installation and operation of the pilot plant.

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