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Water Filtration Applications Using Porous Silicon Carbide Membranes

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Abstract: The use of ceramic membranes for microfiltration has gained increasing attention in the water treatment realm. Silicon carbide (SiC) is of particular interest due to its chemical resistance over the whole pH range, its inertness to chemical cleaning, its high temperature stability and its low fouling behavior, making the material especially suitable for treating hot, corrosive wastewater. Saint-Gobain Ceramic Materials, a leading company in making both dense and porous SiC products, manufactures SiC filters with SiC membranes of various pore sizes. Depending on the application, dead-end and cross-flow SiC filter configurations are available. Dead-end filters have been successfully employed for filtration of groundwater. In combination with a flocculation process developed by Gruppo Zilio, Saint-Gobain SiC membranes were found to efficiently remove arsenic from flocculated water. Dead-end filters can also be employed in swimming pool water filtration where they enable a smaller footprint, lower operating costs, significantly reduced chlorine usage and improved water quality compared to the traditional sand filter system. Cross-flow filters are generally used for treating water with high solid loadings, and Saint-Gobain has successfully treated produced water from actual oil wells in the field. Significant reduction of turbidity as well as of solid, bacteria and oil content has been demonstrated.

Key words: Water, filtration, membrane, silicon carbide, SiC, ceramic.

1. Introduction

Contamination of groundwater with heavy metals, chemicals etc., as well as overall scarcity of water are leading to an increasing need for efficient treatment methods to produce pure, drinkable water even in remote areas. One of the technologies of focus is water filtration where the water is filtered through a porous membrane material. Depending on the particle size of the membrane material, different contaminants can be removed from the water (Table 1).

Reverse Osmosis (RO)	Nano-filtration (NF)	Ultra-filtration (UF)	Micro-filtration (MF)	Macro-filtration
Below 0.5 nm	0.5 to 1.5 nm	1 to 100 nm	0.1 to 10 µm	Above 3 µm
Ions & salts	Molecular-level particles	Nanoparticles	Micro- to macro-particles	Macro-particles
Salts (desalination), metal ions…	Pesticides, herbicides, Mg, Ca, sugar, viruses…	Latex, viruses, pigments, proteins…	Bacteria, blood cells, emulsified oil, mineral and organic particles…	Sand, silt, mineral particles…

Table 1. Classification of filtration technologies based on particle size (Komolikov and Blaginina, 2002).

Typical membrane materials include polymeric, ceramic oxide or silicon carbide (SiC) membranes. Saint-Gobain manufactures recrystallized silicon carbide (R-SiC) filters with R-SiC membranes of controlled pore size for the microfiltration (MF) range (Stobbe and Hack, 2010). Compared to other membrane materials, R-SiC membranes exhibit high chemical resistance, high temperature stability, low fouling behavior (Hofs et al, 2011) and high filtration area.

In most applications, during filtration, a filter cake builds up on the membrane, increasing the backpressure of the filter and contributing to filtration of even finer particles. To remove the filter cake, backflushing with air or water is often required in certain intervals. An important advantage of R-SiC membrane filters is their ability to be cleaned even under extreme chemical conditions (e.g. at pH 0.5 and pH 13.5). After such cleaning the filters are practically in “as delivered” state. If the filtration system design supports this, the filters can remain mounted in the system for the chemical cleaning and are ready for filtration immediately afterwards (CIP = “Clean In Place”). Due to the outstanding material properties of silicon carbide, the chemical cleaning can be repeated as often as required to ensure a long service time.

As shown in the following sections, Saint-Gobain R-SiC membranes have been demonstrated to effectively clean water from various sources: (i) groundwater containing arsenic, (ii) municipal swimming pool water, (iii) produced water from oil and gas exploration.

2. Saint-Gobain SiC membranes

The Saint-Gobain SiC ceramic membrane filters consist completely of re-crystallized silicon carbide. This material was developed to resist extreme mechanical, thermal and chemical stress.

The carrier material is extruded to form monolithic honeycombs. The material exhibits a very high open porosity beyond 40 % and a multitude of big pores in the range of 5-10 micron pore size (Fig. 1). This guarantees an excellent permeability for the filtrate. Fired at temperatures beyond 2000 °C, the carrier reaches its final mechanical and chemical robustness.

The multi-layer membrane on top of the carrier fully consists of re-crystallized silicon carbide as well, and serves as a functional layer in the filtration process. The membrane is deposited as a slurry on the carrier substrate and then sintered. A wide range of pore sizes (200 to 2000 nm) can be achieved, by adjusting the slurry composition and the sintering conditions (Fig. 1).

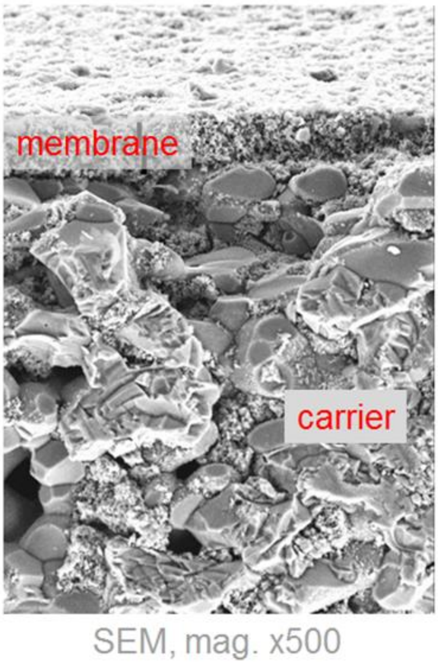

Figure 1. Cross-sectional view of Saint-Gobain SiC filter: coarse-grain carrier structure with fine-grain membrane layer.

Every channel is alternately plugged at the inlet or outlet side (Fig. 2, left). The water enters at the inlet channels and is forced through the porous wall and thus is filtered by the membrane layer. The clean filtrate leaves through the outlet channels, while the filtered particles deposit in the inlet channels. If required, the dead-end filter monoliths may be provided with a mounting flange consisting of stainless steel or PVC to facilitate the assembly into the filter housing (Fig. 2, right).

In addition to dead-end filters, Saint-Gobain also manufactures tubular cross-flow filters which are especially interesting for filtration of water with high solid loadings, e.g. industrial wastewater or produced water from oil and gas exploration (Bakshi et al, 2015),(Kuhn et al, 2015).

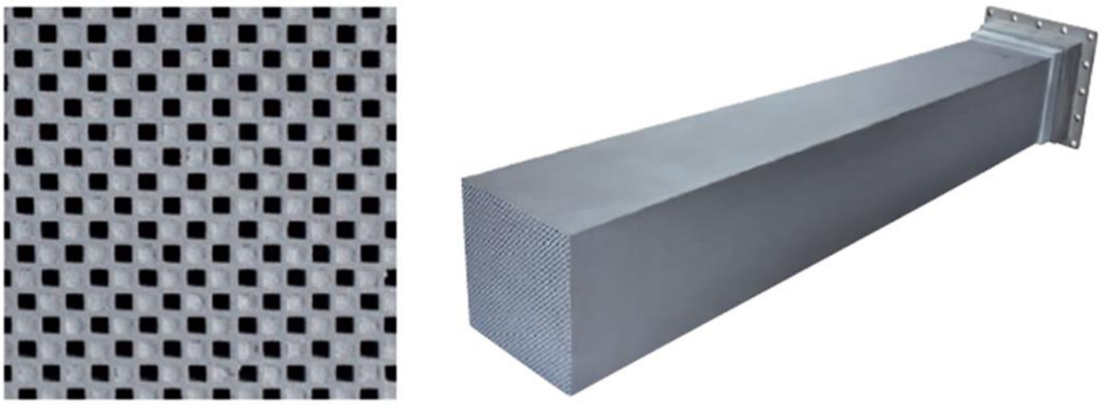

Figure 2. Honey-comb filter with alternately closed channels for dead-end filtration (left); Saint-Gobain SiC dead-end filter with flange (right). Size is 1000 mm long and cross section is 149 mm by 149 mm.

3. Applications

3.1 Drinking water

One application of porous silicon carbide filters for drinking water is the removal of inorganic contaminants, such as arsenic. For this process, the silicon carbide ceramic filter is combined with a chemical pre-treatment step to oxidize and flocculate/precipitate the contaminants. Depending on the pre-treatment conditions, several contaminants can be removed in a single filtration step, making this method much more efficient than removal of each contaminant separately with a specialized absorbent. The resulting filtrate has a Silt Density Index (SDI) that is low enough for use in Reverse Osmosis (RO) equipment.
One of the main advantages of using dead-end filters for drinking water applications, in contrast to cross-flow filters, is the lower water consumption. During filtration mode, all water is filtered, so there is no water loss. During the backwash step, only 20 to 30 liters of water are required for an 11 m^2 filter module and have to be drained to remove the accumulated flocculants. Depending on the backwash interval and flow rate per filter module, this water loss for cleaning equals only about 1% of the filtered water.
A field test was conducted in collaboration with Gruppo Zilio in March 2015 at a site in Serbia to demonstrate the efficiency of using Saint-Gobain SiC filters to remove arsenic from groundwater. The location is known to have higher than desirable arsenic levels in the drinking water supply. A pilot system with a silicon carbide dead-end filter with a

filtration area of 11 m² and a membrane pore size of 500 nm was used. The system was operated at different backwash (BW) intervals and corresponding trans-membrane pressures (TMP) to find the optimum operating conditions. Sodium oxychloride (NaOCl) was used as oxidizing agent while ferric chloride (FeCl3) was used as flocculating/precipitating agent. An average flux of 550 L/(m²*h) (or LMH) was achieved for a TMP of 0.5 bar and a backwash frequency of every 10 minutes (Fig. 3). When increasing the backwash interval to 20 minutes, an average flux rate of 500 LMH was achieved for a TMP of 0.7 bar (Fig. 4). The flux rate and TMP were constant during the 7h test cycle.

It is worth noting that all along the tests, the backwash efficiency was constant with systematic recovering of the initial flux rate of 600 LMH. This result indicates minimal irreversible fouling.

The chemical analysis of the feed and permeate water is shown in Table 2. The arsenic content was reduced by 98% from 99 µg/L to 2 µg/L, proving the efficiency of the system. The high iron content in the feed water was due to the flocculants dosing, which were completely removed by the filter.

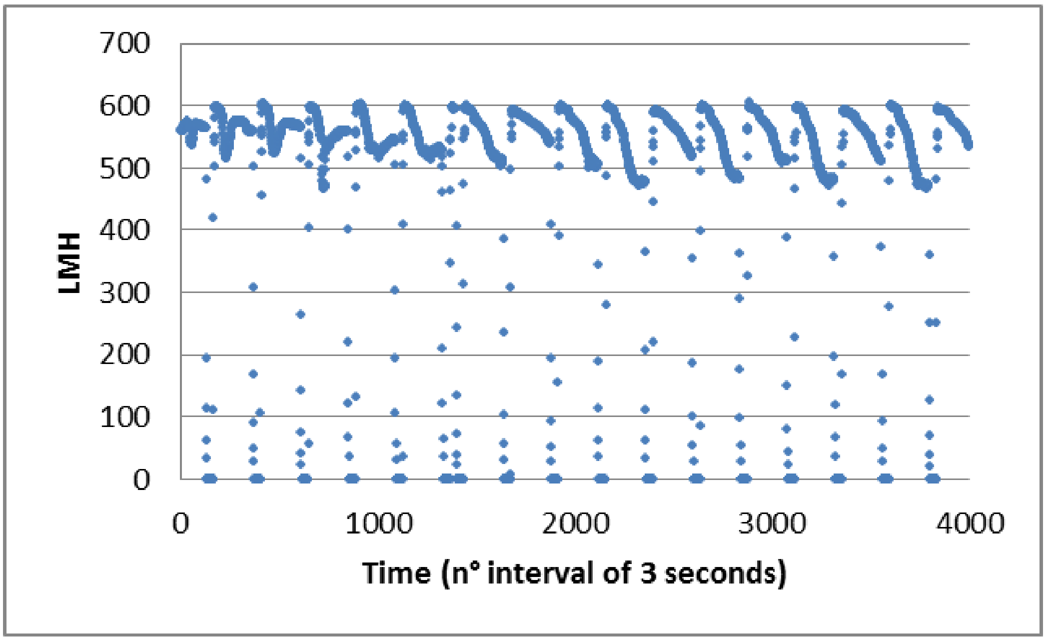

Figure 3. Permeate flux in LMH at 10 min backwash interval with 0.5 bar TMP.

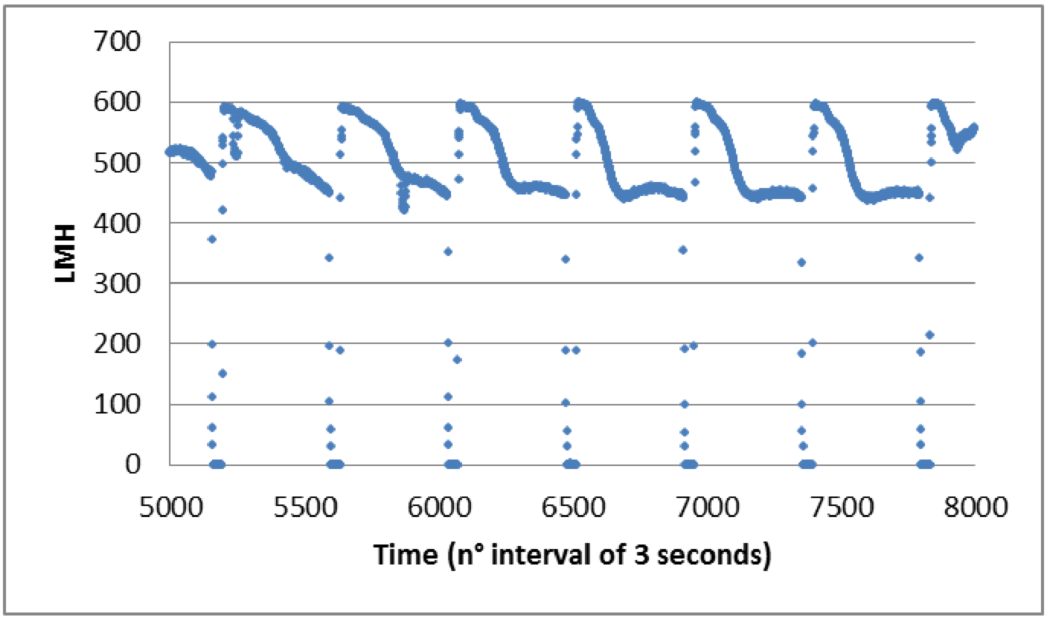

Figure 4. Permeate flux in LMH at 20 min backwash interval with 0.7 bar TMP.

Component		Feed	Permeate
Phosphate	mg/L	<10,0	<10,0
Ammonia	mg/L	1,34	<0,05
pH		7,9	7,8
Redox potential	mV	225	239
Arsenic	µg/L	99	2
Boron	µg/L	1125	1110
Iron	µg/L	316	<40
Manganese	µg/L	<20	<20
Sodium	mg/L	264	272

Table 2. Chemical analysis of feed and permeate water.

3.2 Swimming pools

The SiC dead-end filters are used for pool water filtration in public swimming pools (Fig. 5) (Neufert et al, 2013). The pool water is collected from the pool spill channel and pumped through the membrane elements. A pore size of 250 nm ensures that particles including all bacteria are removed from the water. The filtrate is de-aired and then treated with UV-light to destroy remaining organic components including viruses. The clean water is finally chlorinated (to a lower level than in pools with traditional filters) and pumped back into the pool.

Figure 5. Filtration system using Saint-Gobain SiC dead-end filters in a public swimming pool in Germany.

3.3 Produced water

Cross-flow Saint-Gobain SiC filters with 250 and 1000 nm membrane pore sizes were used to filter produced water from both conventional and unconventional (fracking) oil and gas exploration (Bakshi et al, 2015),(Kuhn et al, 2015). In combination with flocculation/precipitation and pH pre-treatment, the filters enabled removal of bacteria, suspended solids (turbidity), oil and scale-forming ions at overall a much smaller footprint than typical water treatment systems currently used in the produced water field. Additionally, less chemicals, such as biocides, are needed to obtain similar water quality of the filtrate.

4. Conclusions

Saint-Gobain SiC membrane filters – when combined with an adapted pre-treatment step – have been demonstrated to effectively remove contaminants and pollutants and provide clean, filtered water. In comparison to other microfiltration membrane materials, R-SiC membrane technology promises to be a more stable process for treatment of drinking water for removal of arsenic as well as other pollutants, with very good backwash efficiency, minimal drop in flow rate over the filtration time, higher flux and good filtration efficiency.

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