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Arsenic Removal Process for Drinking Water Production: Benefits of R-Sic Microfiltration Membranes

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Abstract: Health concerns linked to arsenic content in ground water are leading to an increasing need for treatment to produce pure, drinkable water. The flocculation process developed by Gruppo Zilio coupled with an ultra-/microfiltration (UF/MF) step demonstrates to be a very efficient process for arsenic removal from feed water. Polymeric, oxide and silicon carbide MF membrane materials have been investigated as potential candidates for the MF treatment step. Saint-Gobain manufactures recrystallized silicon carbide (R-SiC) dead-end filters with R-SiC membranes of controlled pore size for the MF range. Due to their chemical resistance, high temperature stability, low fouling behavior and high filtration area, R-SiC membranes were found to efficiently remove arsenic from flocculated water. In comparison to other MF membrane materials, R-SiC membrane technology in dead-end mode promises to be a more stable process with very good backwash efficiency, minimal drop in flow rate over the filtration time, higher flux and very good filtration efficiency.

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

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. This topic is particularly true about natural aquifer's contamination by arsenic (Fig. 1).

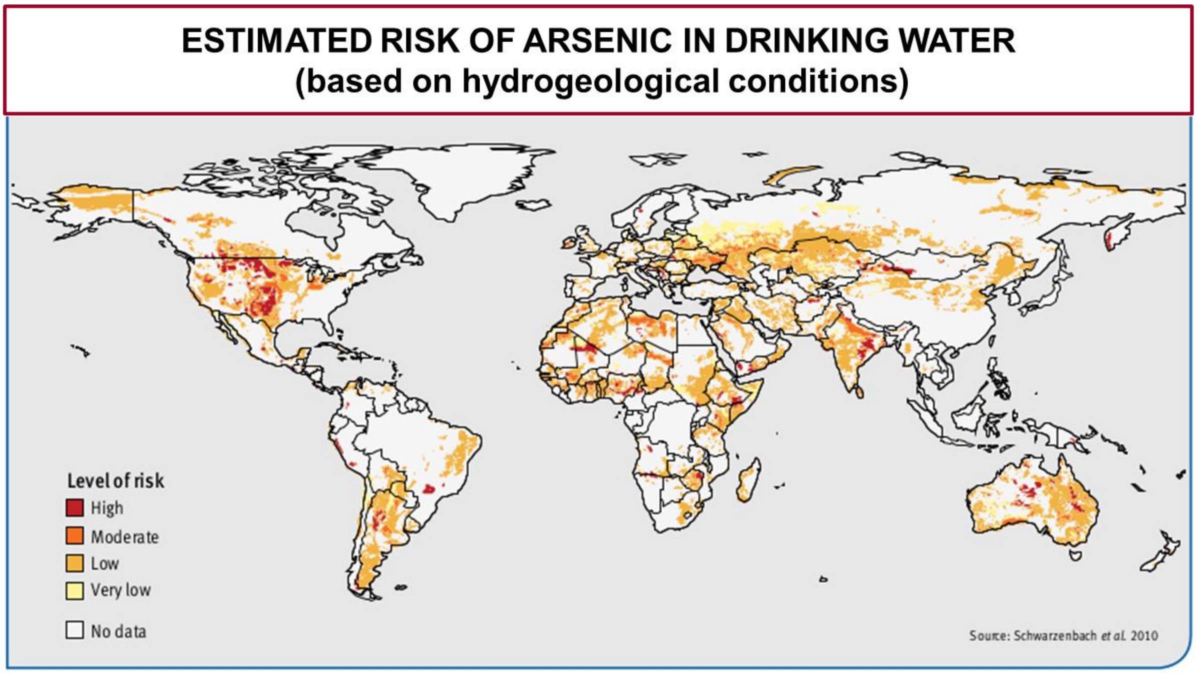

Figure 1: Estimated risk of Arsenic in drinking water over the world.

One of the technologies of focus is the water filtration whereby 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).

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

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…

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 dead-end membranes used into Zilio’s process have been demonstrated to effectively clean water from groundwater containing arsenic.

2. Zilio’s process

The process developed by Zilio consists of a silicon carbide ceramic filter 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 which completes Zilio’s process (Fig.2).

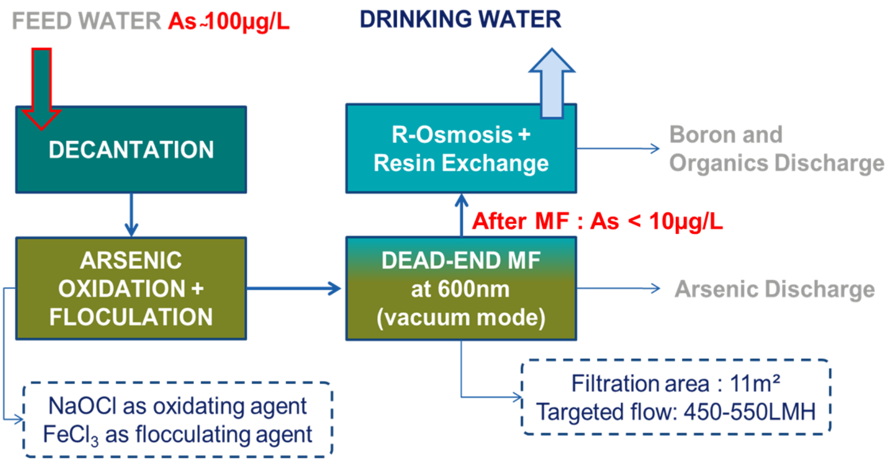

Figure 2: Zilio’s process for arsenic removal

3. Saint-Gobain SiC membranes

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

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. 3). 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 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. 3).

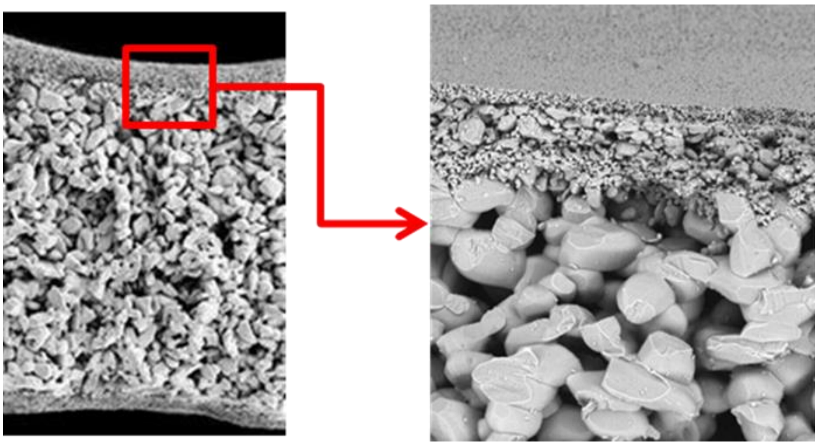

Figure 3: Cross-sectional view of Saint-Gobain SiC filter: coarse-grain carrier structure with fine-grain membrane layer.

Every channel is alternately plugged at the inlet or outlet side (Fig. 4, 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. 4, right).

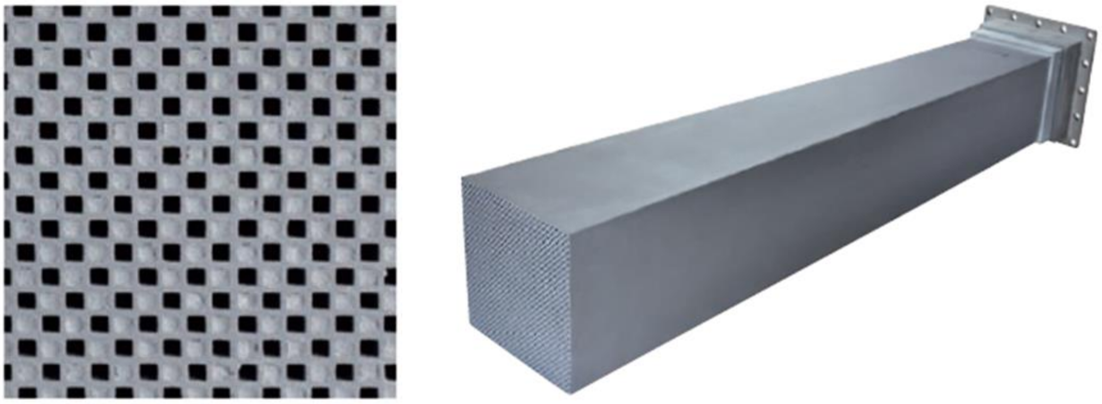

Figure 4: Honey-comb filter with alternately closed channels for dead-end filtration (left); Saint-Gobain SiC dead-end filter with flange (right). Size is 1000 mm long and cross section is 149 mm by 149 mm.

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).

4. Field test

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 m^2 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 ($FeCl_3$) was used as flocculating/precipitating agent. An average flux of 550 LMH was achieved for a TMP of 0.5 bar and a backwash frequency of every 10 minutes (Fig. 5). 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. 6). The flux rate and TMP were constant during the 4h 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 (OMS recommendation for drinkable water is Arsenic content below 10 µg/L). The high iron content in the feed water was due to the flocculants dosing, which were completely removed by the filter.

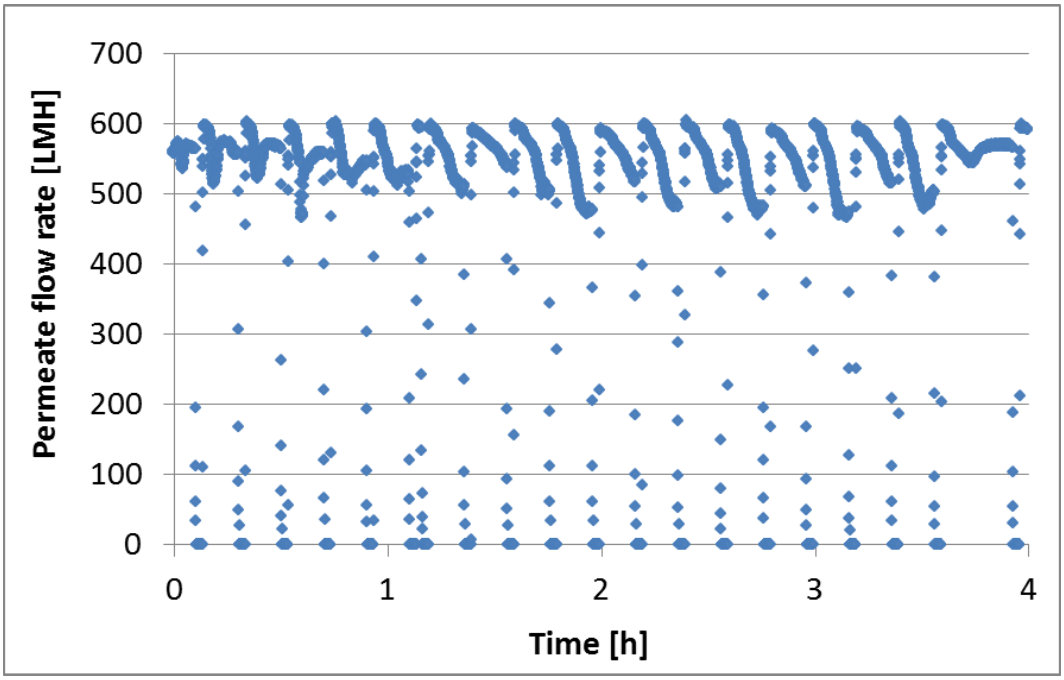

Figure 5: Permeate flux in LMH at 10 min backwash interval with 0.5 bar TMP.

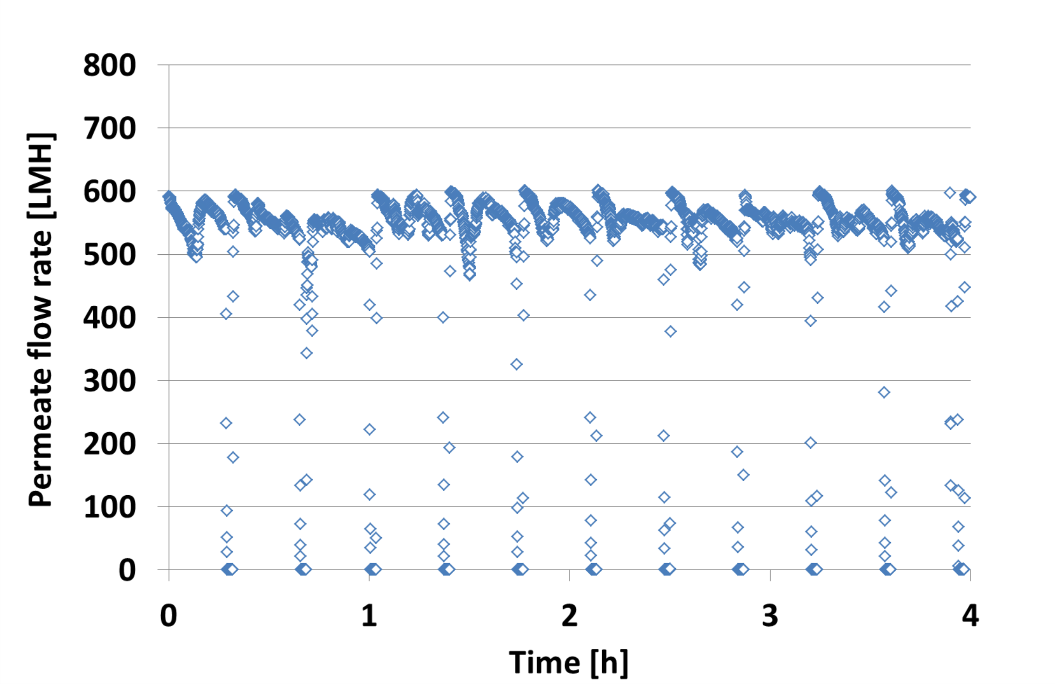

Figure 6: Permeate flux in LMH at 20 min backwash interval with 0.7 bar TMP.

Table 2. Chemical analysis of feed and permeate water.

Component	Units	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

In addition, two of the mains advantages of using dead-end filters for drinking water applications, in contrast to cross-flow filters, are:

- The lower water consumption:
  - During filtration step, all the 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. In comparison, the sedimentation process frequently used to treat arsenic of ground water consumes 4% to 5% of water.
- The lower energy consumption: no recirculation pump is required in dead-end mode. Only feed pump and backwash pumps are necessary. As a consequence the energy consumption in dead end mode is roughly 70% to 80% lower than in cross-flow configuration.

5. Lab test

Additional tests with stronger testing conditions were performed at lab scale with dead-end samples of 1.9 m^2 of filtration area. The considered testing conditions are given in Table 3 below and compared with field test conditions.

Table 3: test conditions used for lab and field tests

	Field test	Lab test
Average Flow [LMH]	500	600
Iron content into the feed water [mg/L]	18.6	50
Test duration [h]	4	24

Due to stronger flocculent content inside the feed water, the filtration time was fixed to 10 min.

The evolution of the permeability of the membrane was followed over time (Fig.7).

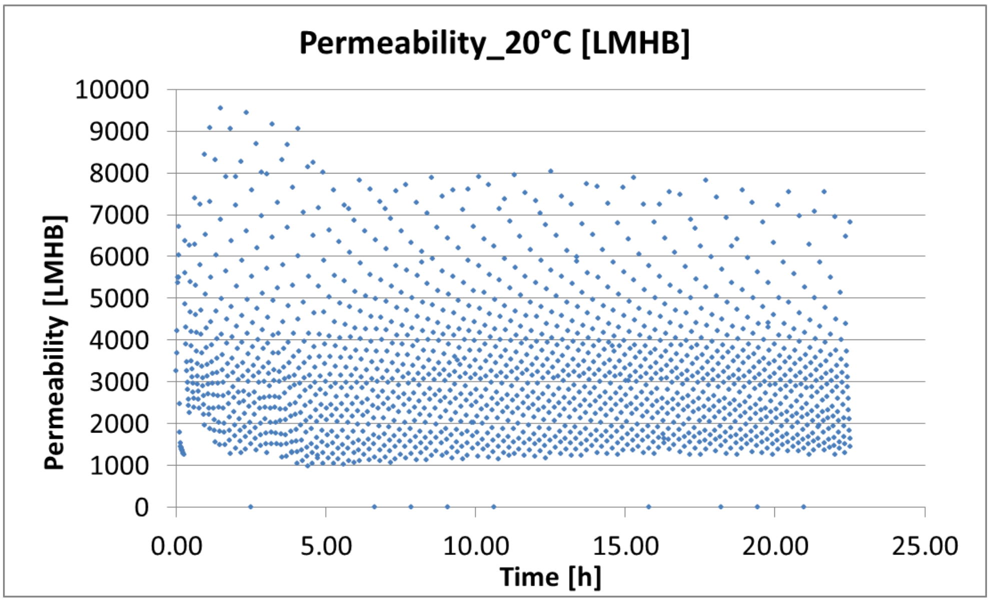

Figure 7: Permeability evolution over time

The permeability remains almost constant over the 24 h of testing. After each backwash, permeability starts at 8000 LMHB and decreases down to 1200 LMHB at the end of the filtration cycle. Corresponding flow rate and TMP over time are respectively given hereafter in Figures 8 and 9. The average permeate flow over the 24 h of testing is around 600 LMH. TMP is also nearly constant with a variation between 110 mbar at the beginning of the filtration cycle and 360 mbar just before backwash. As a reminder, the backwash pressure applied is at -300 mbar.

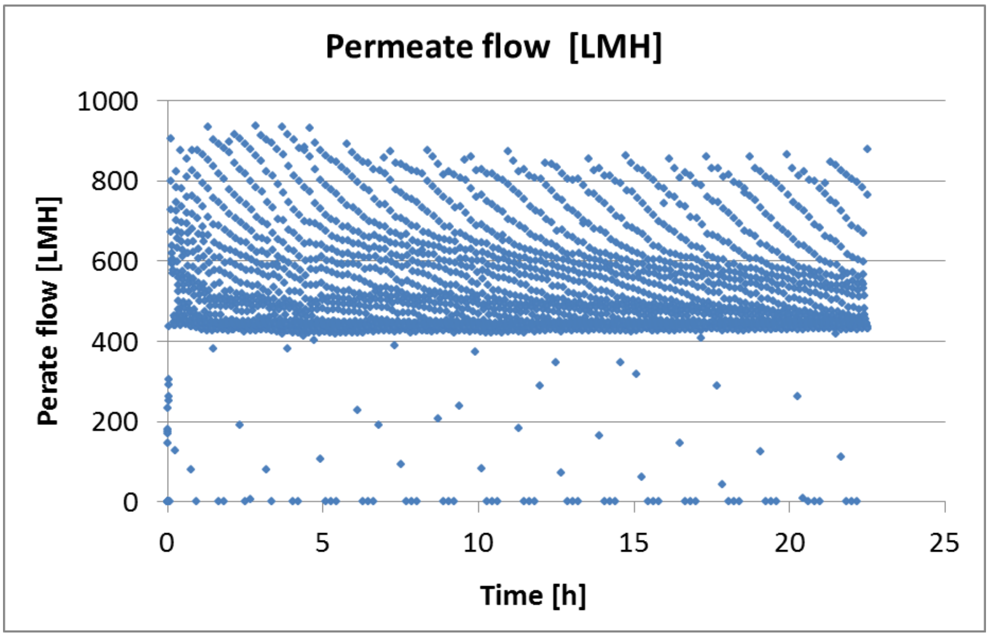

Figure 8: Flow rate evolution over time

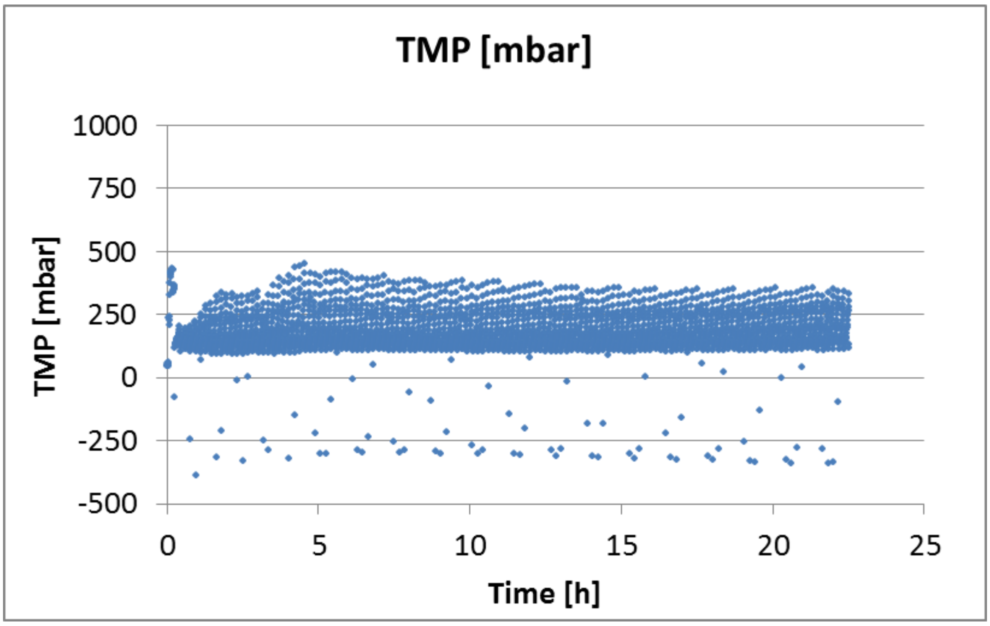

Figure 9: TMP evolution over time

In addition, qualitative analysis of the permeate was performed during the test. Turbidity was measured continuously using on-line turbidity sensors (Fig.10) and iron content was measured by sampling the permeate during the filtration cycles. The peaks of turbidity at 6-8 NTU correspond to the beginning of the filtration cycle, after a few seconds of filtration the turbidity decreases down to 1.5 NTU.

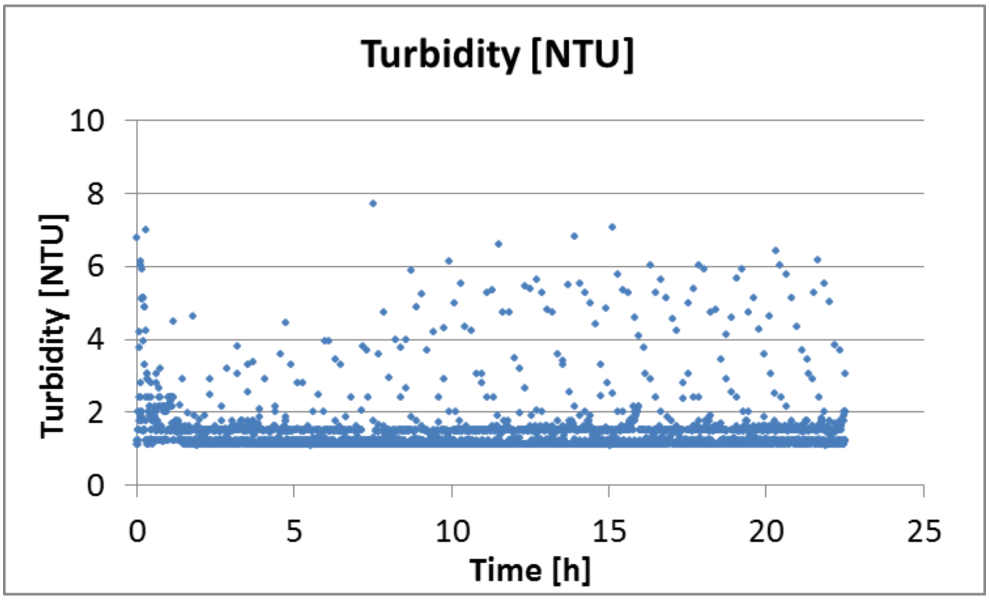

Figure 9: Typical turbidity evolution over the filtration cycle

The measurement of iron content in the permeate indicates a content of about 150 µg/L. Starting from 50 mg/L the iron removal efficiency is 99.7%.

6. Conclusions

During the field tests, the Saint-Gobain SiC membrane filters used in combination with Zilio's pre-treatment step were demonstrated to effectively remove arsenic from groundwater and provide clean, filtered water.

Subsequent lab tests under much more severe conditions (iron content almost three times higher and flow rate 20% higher than during field tests), the filtration properties of the Saint-Gobain dead end membrane were kept at the same level as the ones obtained on field.

In comparison to other microfiltration membrane materials, R-SiC membrane technology promises to be more robust for the removal of arsenic from drinking water, with very good backwash efficiency, minimal drop in flow rate over the filtration time, higher flux and good filtration efficiency.

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