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Reducing the ecological footprint of PVDF membrane storage

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ABSTRACT

The aim of the research is to develop a cost-effective and environmentally friendly membrane inspection method for over-stored PVDF membranes. It is generally accepted that PVDF-based fiber membranes are sensitive to dehydration during storage. The current practice to prevent this is that membranes stored beyond the planned period are returned to the manufacturer's site for costly re-impregnation, which like the original impregnation, delivers a glycerol-water solution to the pores. This is a costly process, as it is labor-intensive, needs high raw material consumption, and requires membrane cassettes to be transported over long distances. During the research our goal was to replace this, so we developed a new method to control the drying process. The method involves the in-situ sampling of membrane fibers from filters and transporting the samples to the manufacturer's laboratory. There we measured the membranes' performance with a custom-built permeability tester, and the data obtained here were compared with the values measured at the time of manufacturing and from this data we inferred to the condition of the fibers. After 5 y of storage no fiber property degradation was observed.

With this method, it's possible to save 98.78% of the normal storage extension cost. We also experienced a significant reduction in the environmental load, as the yearly transportation of the cassette can be eliminated, thus significantly reducing the CO_2 emissions associated with traveling, by 2,423,250 kg for the project under investigation.

Keywords: PVDF membrane; Membrane drying; Membrane permeability; CO_2 pollution

1. Introduction

Membrane technology has become the most important separation method in recent decades [1]. Polyvinylidene-difluoride (PVDF)-based filtration membranes are the main materials for ultrafiltration technologies. Developing their filtration ability, drying resistance and anti-fouling properties are important areas of membrane research that have significant economic value [2–7].

PVDF-based membrane products are widely used in the water treatment industry. PVDF has been applied to many applications, for example, membrane distillation, membrane contactor, and seawater desalination [8]. PVDF is a special, interesting, exceptionally porous plastic. It is applicable for filtering wastewaters having different characteristics due to its resistance to acids, hydrocarbons, solvents, oxidizing agents and temperatures. These features make this plastic to a superb raw material of micro-, ultra-, and nanofiltration sheet and fiber membranes, too [9–15]. Such filters are operating mainly at municipal and industrial water treatment plants and, with their 0.01–0.1 μm pore size, they can filter suspended solids, bacteria, viruses and colloid particles [16]. The essence of the filters is the membrane, which is a solid polymer with a porous structure. After the formation of the porous structure during polymerization, the pores are filled with a mixture of glycerol and water. This solution remains in place during the following steps of the filter production, helping to sustain the original structure. During production, membranes are arranged into modules and, for assessing their quality and performance, they are tested immersed.

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These processes leach out glycerol, so it is necessary for a final production step impregnate again the membranes with a glycerol-water mixture.

In our profit-focused world in any industry, there are only a few international companies which are working not only to maximize their revenue while shaping strategy, but also taking into consideration some other aspects such as sustainable market share and less burden to the environment.

Due to different reasons it's often happening that after signing the contract between the membrane producer and the final user, the manufacturer supplies the membranes to the site, but the cassettes won't be immersed immediately, and they are standing in a warehouse for years. Due to the nature of the membranes, after a certain time the water diffuses through the membrane wall. If they are kept in prolonged storage, the filters tend to dry out and this may lead to decreased performance. The filtering capacity of the product is declared in the contracts between producers and buyers, so compliance with this is a crucial question. An occasional deviation from that capacity may lead to customer dissatisfaction.

The aim of this work is to develop a new treating method for long-stored membranes prior to immersion in water treatment plants. This is of primary importance as financial savings and environmental burden reduction are assumed. In-situ sampling can be an effective and environmentally friendly method compare with the present membrane treatment protocol.

Present practice – namely, that it is necessary to re-impregnate the modules at the premises of the producer after 12 months of dry storage – guarantees with high probability for the producer that issues of drying out will not occur. However, this process is extremely costly for the buyer and causes high environmental impact, since, for each produced cassette, it is necessary to transport a box with 8 m^3 volume and 2 metric tons weight for many thousands of kilometers by means of air, sea or road transport. After that, disassembled membranes must be treated for additional storing by using hundreds of kilograms of glycerol-water solution.

The actual storage extension method doesn't differentiate, all overstored membranes have to be shipped back (Fig. 1). This is the reason why it causes redundant environmental load since it could happen that membranes in perfect condition with proper permeability values would be re-impregnated.

There is no literature regarding overstored membranes since each manufacturer works according to their own processes. We don't know previous publications on whether others store membranes for long periods, as this data is kept confidential and will not be published. Even if there are longer storages, this is the manufacturers' intellectual property, so they do not publish methods for extending it or correcting the membranes' drying out.

The aim of the present study is to develop an inspection and test method that can be used to conclude the operational performance of overstored membranes with great certainty, thereby extending the previously scheduled storage time. This task is not known in the literature until now. The novelty of the method is that the membrane cassettes already shipped do not need to be returned automatically to the manufacturer's factory after the due of the storage period. According to the new procedure samples are taken at the place of storage, are tested in the manufacturer's laboratory and can be decided cheaply and quickly for the need for re-impregnation (Fig. 2).

Fig. 1. Flow diagram of the present storage extension process.

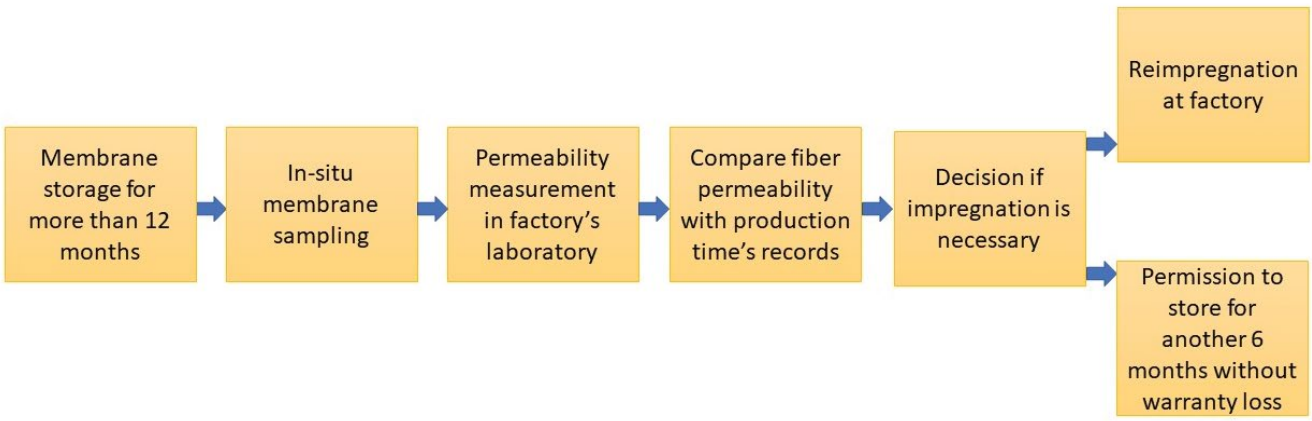

Fig. 2. Flow diagram of storage extension process based on in-situ sampling.

2. Materials and methods

2.1. Membrane type

Polyvinylidene-difluoride based wastewater treatment membranes were used in the study, with pore size between 0.02–0.04 μm. This membrane is a tubular, supported type, which means that it has an inner polyethylene terephthalate yarn frame. To this shoelace-like skeleton comes the membrane layer during the coating process. The final membrane fiber has approximately 2 mm in diameter (Fig. 3).

2.2. In-situ membrane sampling

This study was conducted by sampling 54 membrane cassettes. The sampling method aimed to be random, but also had to be taken not to destruct more membrane fibers than logically needed for laboratory analysis. In-situ sampling started with on-site measurements and examination. The producer's original packaging was dismounted, a protective crate was displaced, moisture-retaining foil was cut up on a small area. It was followed by sampling, getting two approximately 1,000 mm long fiber samples from each cassette. Samples were placed into gastight sampling bags for transportation to producer's premises because it was not possible to measure moisture content and fiber permeability on site. After sampling, the protecting aluminum foil was welded together airtight, crate reassembled, restoring the state of packaging identical to the original.

2.3. Single fiber permeability measurement

According to the manufacturer's standard operation process, every fiber batches are measured for permeability right after the production and before they release them to the next process step. We traced back the modules that were used in the 54 cassettes. With the traceability data we were able to recall the stored fiber performance values at the time of the production. These data were the source of the 2013 permeability at the later comparison. During the in-situ sampling we took every time at least 2 fibers from each cassette. Samples were taken randomly, but due to the structure of the cassettes and the populated modules it was not possible to reach the permeate joint side of the modules without a high risk of fiber damages. According to our previous measurements the temperature and the relative air humidity are homogenous inside of the crate, therefore the sampling place is not very important. Due to the hermetic sealing from the external environment, a small sample test can also provide information to the entire population. The more fibers we cut, the less filtration surface we have, so the sample size was kept on a minimum level. At the end of the storage time we had 5 times 2 fibers from 54 cassettes.

At the laboratory we measured the single fiber permeability by a custom-made, calibrated equipment in distilled water at 5 psi pressure with the following Eq. (1) [17,18]:

$$P = \frac{J}{\delta p} \Big/ \frac{\mu_1}{\mu_0} \tag{1}$$

where P is the permeability, J is the flux at δp pressure, μ_1 is the viscosity of water at the temperature of the measurement, and μ_0 is water viscosity at 20°C. Flux was calculated by the next Eq. (2) [17,18]:

$$J = \frac{\delta V}{A \times \delta t} \tag{2}$$

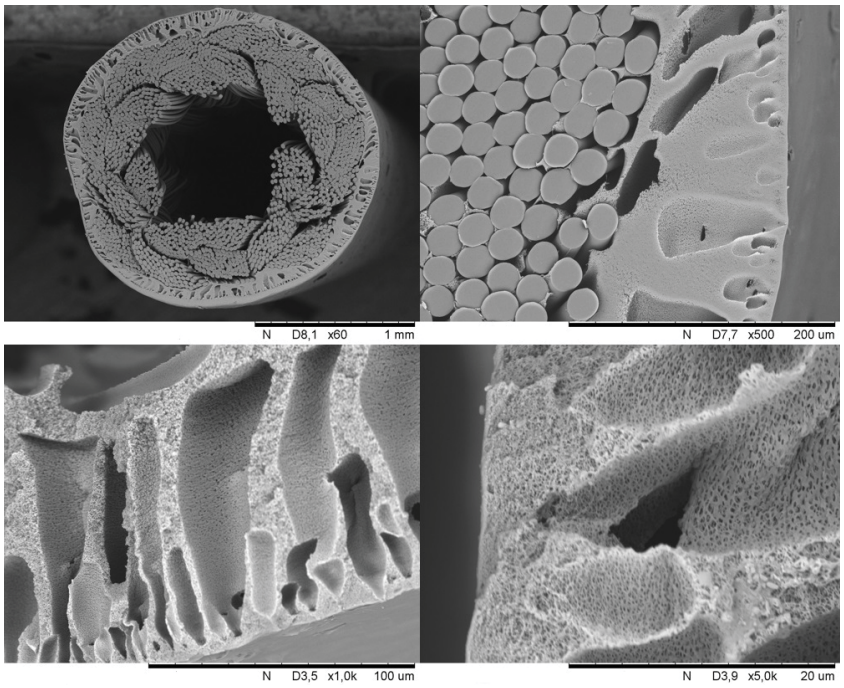

Fig. 3. SEM pictures of PVDF based supported membranes made with a Hitachi S-3000N microscope.

where J is the flux measured through the membrane surface A, δV is the amount of permeate and δt is the flow time of the liquid.

2.4. Statistical tools

The permeability data obtained from laboratory measurements were arranged to table and then compared them with statistical methods to the results of samples taken at the time of membrane production. As mentioned earlier every membrane fiber batches were measured for permeability right after the manufacturing and we don't store fibers for later inspections. That means that we have historical data about the fiber properties of every single membrane module. In this study we tracked back what was the first and the last production date regarding this project and we limited the permeability data to this period. The samples were compared with a histogram, the equality of variance was tested by F-test, and the equivalence of the permeability values by the group was checked by variance analysis. All statistical calculations were done by Minitab18 [19].

3. Results and discussion

3.1. Financial advantage of in-situ sampling

Presently, research was carried out together with developing a method that makes us able to decide after in-situ sampling whether it is required to impregnate the modules or not. The arising question is, why is it worth the producers to invest money and energy into this research, since this method will impact revenue. Only taking financials into consideration, it is not worth changing the present situation, since hundreds of thousands of US dollars can be lost during one single project; re-impregnation of an average water filtering cassette means a nearly 6,000 dollar bill to the customer.

Let us discuss the problem through a concrete project. In one of our in-progress projects, 54 cassettes containing modules have been waiting for immersion for about 5 y. The reason for the delay was that the civil works of the water treatment plant weren't finished in time and the customer had to postpone the immersion of the membranes repeatedly. According to the proper handling guidelines, after every 12 months, cassettes should be transported back to the manufacturing plant for re-impregnation. The cost of this would be 54 × 6,000 × 5 = 1,620,000 USD billed to the customer. Against that we have to set a 10,000 USD annual expert fee, paid by the customer, which sums up to 50,000 dollars. The difference between the two sums is obvious; by simply deducting the two numbers we can see that, without the re-impregnation process, the producer relinquishes 1,570,000 dollars revenue during the 5 y period in question.

The goal of a company living on the market is being profitable, so the question is, why would it let 1.57 million USD revenue slip away? There are many possible answers. Direct gain is the avoidance of production capacity loss. With this, more profitable products can be produced since re-impregnation can only be done by using the existing production infrastructure at the loss of actual production. Customer satisfaction is another advantage. A satisfied customer has a higher chance to repeat business than another one who is obliged to spend extra money on a service that cannot be calculated in advance and who is already in a stressful situation due to the construction delay of its project.

In addition to the above, transportation of the cassettes is an extra financial burden for the customer. Transportation cost in the case of our Middle East sample project considering a 9,000 km distance is 9,200 USD/cassette. This altogether means 54 × 9,200 × 5 = 2,484,000 USD extra expense. Summarizing 1.62 million and 2.484 million USD and compares it to the 50,000 USD expert fee, we can observe a 98.78% cost difference (Table 1). The expert fee contains the fiber samples' shipping cost since the fibers – due to their small size – were transported in the experts' personal luggage. The laboratory permeability measurements were included in the expert fee also since 54 fibers' inspection is a negligible workload compare to the laboratory technicians' daily routine.

In the study at this specific project there was no need to ship back any of the cassettes, therefore the saving was the highest theoretically possible. In other cases, some cassettes may need to be returned to the factory for re-impregnation while others may not. These issues are not addressed in the study as no such data are available, but it is obvious that differentiating return transport would always result in savings.

3.2. Possible financial scenarios

In general, we consider three scenarios possible. The first is that the result of the examination shows that no cassette has to be returned, so the customer is only charged for the costs of the expert inspection. The second scenario is to classify some cassettes as suitable for further storage, while for others, laboratory tests indicate the need for re-impregnation. In this case, the customer also has to pay the expert costs and the shipping and preservation costs of some membranes. The third case is the most unfavorable, as in this case, after in-situ sampling, it becomes clear that all cartridges have to be returned to the manufacturer, meaning that the cost of a full re-impregnation will be added to the expert fee.

In view of the costs mentioned above, it can be seen that declaring at least one cassette as qualified for further storage will save the customer more than expert costs. The risk is low, so customers can easily decide whether to request a complete re-impregnation or to choose the in-situ investigation.

3.3. Ecological footprint differences

The above, however, only the cost expressed in money. From society's point of view, environmental costs in the form of CO_2 emission are also important.

The extreme difference can be observed in the case of pollutant emission if we compare in-situ examination of the modules and re-impregnation in the site of production. The total CO_2 emission is in kilograms and was calculated with the next Eq. (3):

$$\text{Total emission}(\text{cargo}) = m \times M \times l \times n \times t \tag{3}$$

Table 1
Cost of on-site investigation vs. factory impregnation for 54 cassettes [USD]

	Factory impregnation	In-situ investigation	Difference	Possible saving
Annual re-impregnation cost/expert fee	324,000	10,000	314,000	810,800
Annual shipping cost	496,800	0	496,800	
5 years' re-impregnation cost/expert fee	1,620,000	50,000	1,570,000	4,054,000
5 years' shipping cost	2,484,000	0	2,484,000	

where m is the amount of CO_2 emitted per metric ton of airfreight and per km of transportation in kilograms, M is the weight of one cassette in tons, l is the transportation distance in kilometers, n is the number of cassettes and t is the number of years [20].

Transporting 54 cassettes yearly to and from equals to the emission 0.5 × 2 × 9,000 × 54 × 5 = 2,430,000 kg CO_2 to the atmosphere, while five visits to the site of two experts mean only 0.5 × 0.3 × 9,000 × 5 = 6,750 kg (Fig. 4), calculated with the next Eq. (4):

$$\text{Total emission}\left(\text{sampling}\right) = m \times M \times l \times t \tag{4}$$

where m is the amount of CO_2 emitted per metric ton of airfreight and per km of transportation in kilograms, M is the weight of 2 experts and their sampling equipment, l is the transportation distance in kilometers and t is the number of visits.

If we want to visualize this 2,423,250 kg difference, we can convert the CO_2 emission values to forest areas. According to technical literature [21], 1 ha of forest in Hungary can absorb 420 metric tons of CO_2, so for only this project 5.7857 ha forest should be planted to balance the cassette transport. On the other hand, for the experts' investigation, 0.016 ha is enough.

3.4. Statistical verification of the advantage of the in-situ fiber sampling method

At the beginning of 2019, after more than 5 y of storage, the membranes were installed to the wastewater treatment tanks. At that point we had hundreds of permeability measures so before the immersion of the membranes we could compare the fibers' performance at the production time and during the storage.

Fiber permeability values were figured with histograms. The sample data for each group can be approximated by a normal distribution, where the standard deviations are slightly changing. The first group – which is production permeability data from 2013 – contains 83 individual permeability measurements and the others 54 each, resulting from the number of the cassettes. The changing of the standard deviation is due to the sampling technique and not refers necessarily to the difference in product properties (Fig. 5). The permeability deviation between 48 and 72 gfd/Psi is a wide range, which shows the differences between the packaging units. Our assumption is that this is driven by a condensation–evaporation mechanism which we would like to explain in a later study. However, both values are within the factory acceptance range.

Levene's-test was used to check the equality of variances which proved to be equal according to the results. This is a requirement for ANOVA (Fig. 6). The next step was performing ANOVA testing (Fig. 7) which gave a $p = 0.065$ value at $\alpha = 0.05$, thus permeability values can be regarded as equal.

After 5 y production, at the beginning of 2019, the overstored membranes cassettes were immersed to wastewater. During the plant trial runs were not observed nor permeability decrements or membrane leaking. The membranes were in almost new condition and not only reached but exceeded the planned permeability and retention values.

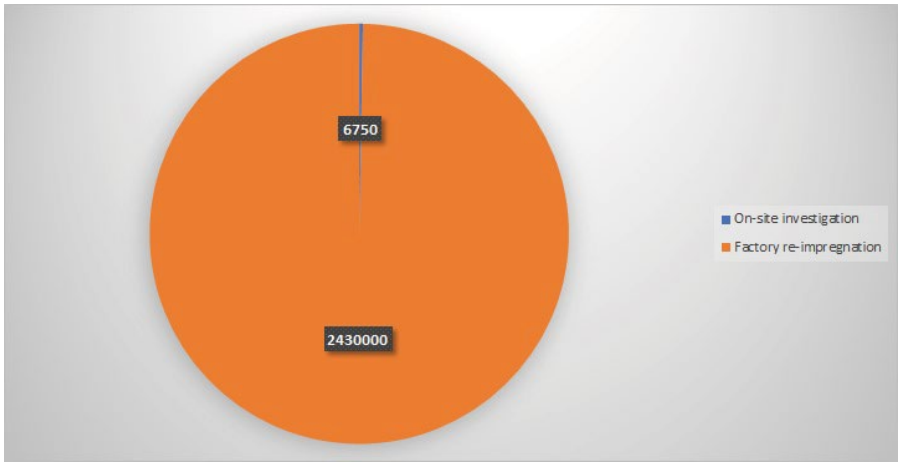

Fig. 4. Transport and travel-related CO_2 emission [kg].

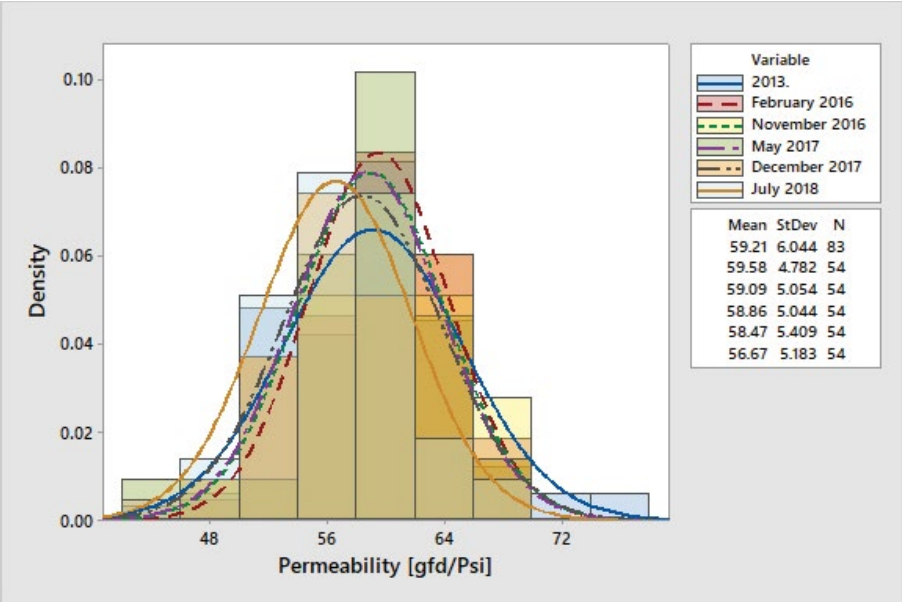

Fig. 5. Histogram of permeability.

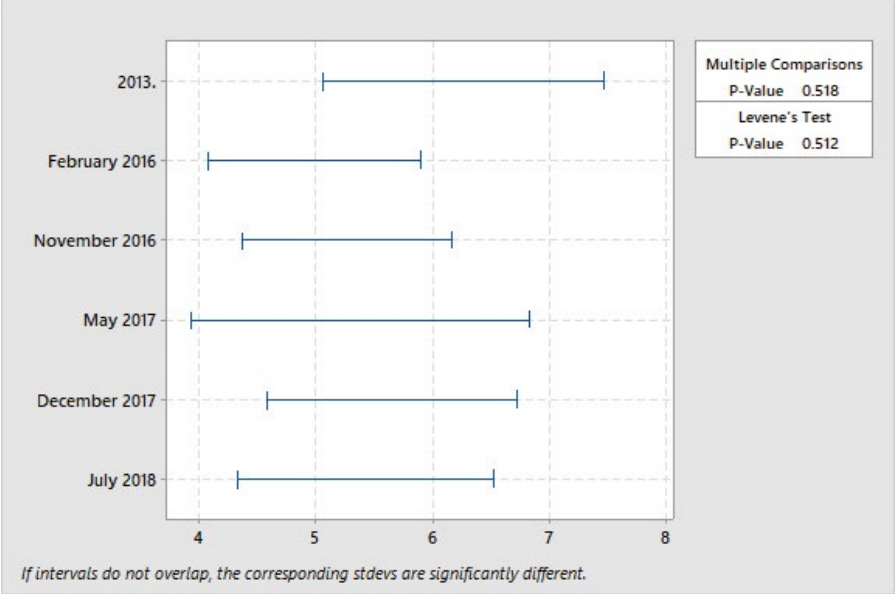

Fig. 6. Test of equal variances of permeability, multiple comparison intervals for standard deviation, $\alpha = 0.05$.

4. Conclusions

The factory impregnated membranes stored in proper conditions are suitable for up to 5 y of storage without compromising operating performance. During the study, we found that the current method of extending storage – in the case of the test project – was more than 82 times more expensive than the new sample laboratory test method. The ecological footprint can also be significantly reduced by 99.72% compared to conventional impregnation.

The next step could be to develop a real in-situ investigation method. The basics of this have already been laid, since fiber moisture was also measured during sample analysis and now we are looking for the correlation between fiber water content and permeability. If we find the descriptive function, we could determine the permeability by a quick on-site measurement of the fiber moisture and immediately decide whether to impregnate the modules or not.

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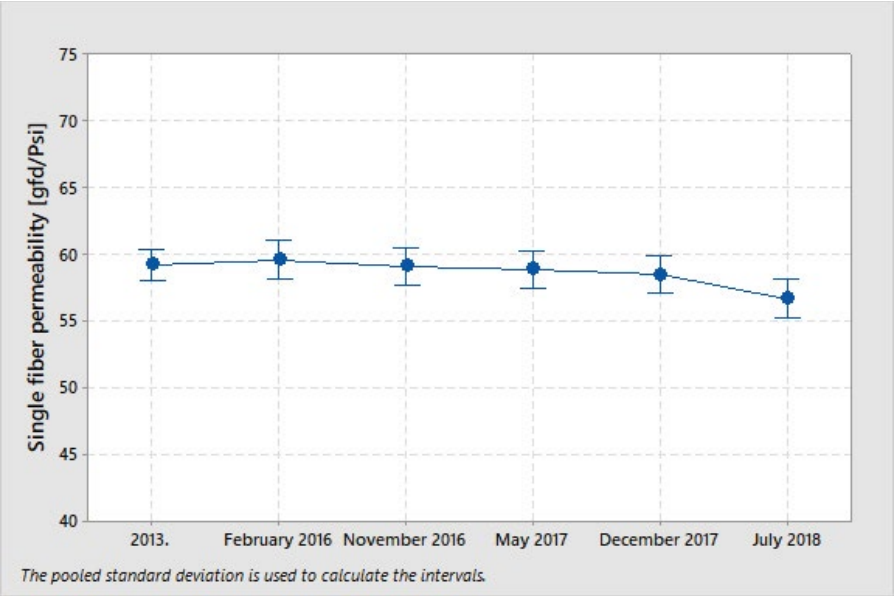

Fig. 7. ANOVA – Interval plot of permeability, 95% CI for the mean.

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