Water Technologies & Solutions
technical paper

PFAS removal in the United States

two case studies compare three removal technologies

background

Companies in sectors as diverse as power generation, semiconductors, refining, chemical manufacture, consumer packaging, outdoor equipment, clothing, and flooring materials are grappling with the rapidly growing concern over the use, discharge, and remediation of Poly- and Perfluoroalkyl substances, known as PFAS. With the list of PFAS compounds growing continually, and with the list now numbering more than 4700 different species, the characterization, testing, removal, concentration and destruction challenges are multiplying in complexity. Fortunately, there is an answer to address and manage the complexity. Industry is increasingly turning to SUEZ – Water Technologies & Solutions, for assistance in mitigating the challenges of PFAS in their processes, wastewater, groundwater, and the local environment. SUEZ deploys its expertise in recognition, testing, characterization, pretreatment, concentration, removal, remediation, destruction and regulatory compliance. We are the one stop shop for any industrial, municipal or military organization, that is today grappling with the complex questions surrounding this increasingly recognized threat.

Many companies are getting themselves "ahead of the curve." While the use and discharge into either a receiving body of water, or into the atmosphere, may not currently be regulated by the EPA, or subject to local or state Environmental limits, companies are nevertheless taking stock of their use and potential release mechanisms for various PFAS materials, including air emissions. Whether the original source is from an Industrial Process, Fire Fighting Foam, whether manufactured via Electrofluorination, or Telomerization, whether the material is an original PFAS or a so called NEW PFAS material (or a mixture), SUEZ has the answers for our customers today.

In this paper, we share[1] two recently introduced solutions for customers located in the United States.

Figure 1 **SUEZ responds immediately when you have a need, where you have a need, with the combination of technologies that you need, and at the flow rate required, anywhere in the world.**

Find a contact near you by visiting www.suezwatertechnologies.com and clicking on "Contact Us."

CASE STUDY #1 – PFAS removal at a US customer site

challenge

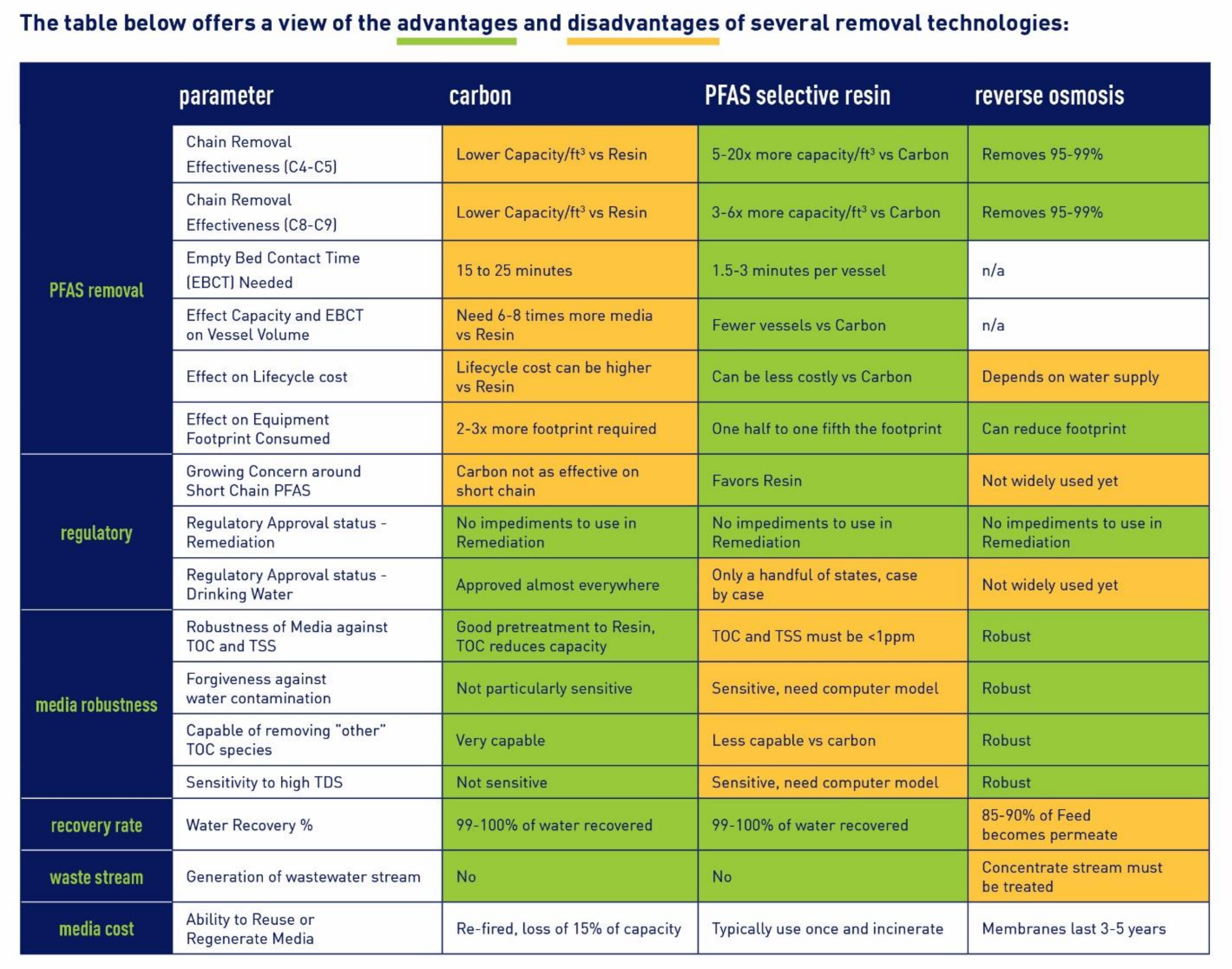
This customer faced a challenging mix of PFAS materials in their process water, resulting from both incoming source water and material aids needed in the process. The incoming challenge was thought to be a mix of PFCAs (perfluoro carboxylic acids) and PFSAs (perfluoro sulfonic acids). Upon testing, SUEZ identified PFOA (perfluorooctanoic acid), PFOS (perfluorooctane sulfonic acid), PFHpA (Perfluoroheptanoic acid), PFNA (Pefluorononanoic acid), and new PFAS compounds including PFPA (Perfluoro-2-propoxypropanoic acid), together with other interfering components including alcohols and hydrocarbons. Table 1 shows a partial list of the process parameters and water chemistry are shown below:

Figure 2: SUEZ has extensive analytical laboratory capabilities globally

Table 1: process parameters and water chemistry at customer site

Desired flow rate	350 gpm
Pressure	80 psi
Temperature	70°F
P-Alkalinity	210 ppm as $CaCO_3$
M-Alkalinity	330 ppm as $CaCO_3$
Chlorides	120 ppm
Sulfate	8 ppm
Nitrate as NO_3	11 ppm
pH	9
Suspended solids	<1 ppm
Turbidity	<1 NTUs
TOC (ppm)	<20
Aromatics	Non-detect
PFOA (perfluorooctanoic acid)	0.2 ug/L
PFOS (perfluorooctane sulfonic acid, sulfonate)	1.2 ug/L
PFHpA (Perfluoroheptanoic acid)	0.7 ug/L
PFNA (Pefluorononanoic acid)	0.1 ug/L
NEW PFAS compounds (total)	0.5 ug/L
PFPA (Perfluoro-2-propoxypropanoic acid)	0.3 ug/L
Other PFAS	0.2 ug/L
Grand Total PFAS in water	2.9 ug/L
Desired PFAS – treated product water	0.01ug/L

SUEZ engineers modeled various removal and concentration mechanisms to arrive at the optimal solution. Three well known technologies available for PFAS removal include, but are not limited to, Reverse Osmosis, Carbon Adsorption, and Specialty Anion Exchange Resin. Some of the advantages and disadvantages of these technologies are shown in the summary table below:



The table below offers a view of the advantages and disadvantages of several removal technologies:

	parameter	carbon	PFAS selective resin	reverse osmosis
PFAS removal	Chain Removal Effectiveness (C4-C5)	Lower Capacity/ft^3 vs Resin	5-20x more capacity/ft^3 vs Carbon	Removes 95-99%
	Chain Removal Effectiveness (C8-C9)	Lower Capacity/ft^3 vs Resin	3-6x more capacity/ft^3 vs Carbon	Removes 95-99%
	Empty Bed Contact Time (EBCT) Needed	15 to 25 minutes	1.5-3 minutes per vessel	n/a
	Effect Capacity and EBCT on Vessel Volume	Need 6-8 times more media vs Resin	Fewer vessels vs Carbon	n/a
	Effect on Lifecycle cost	Lifecycle cost can be higher vs Resin	Can be less costly vs Carbon	Depends on water supply
	Effect on Equipment Footprint Consumed	2-3x more footprint required	One half to one fifth the footprint	Can reduce footprint
regulatory	Growing Concern around Short Chain PFAS	Carbon not as effective on short chain	Favors Resin	Not widely used yet
	Regulatory Approval status - Remediation	No impediments to use in Remediation	No impediments to use in Remediation	No impediments to use in Remediation
	Regulatory Approval status - Drinking Water	Approved almost everywhere	Only a handful of states, case by case	Not widely used yet
media robustness	Robustness of Media against TOC and TSS	Good pretreatment to Resin, TOC reduces capacity	TOC and TSS must be <1ppm	Robust
	Forgiveness against water contamination	Not particularly sensitive	Sensitive, need computer model	Robust
	Capable of removing "other" TOC species	Very capable	Less capable vs carbon	Robust
	Sensitivity to high TDS	Not sensitive	Sensitive, need computer model	Robust
recovery rate	Water Recovery %	99-100% of water recovered	99-100% of water recovered	85-90% of Feed becomes permeate
waste stream	Generation of wastewater stream	No	No	Concentrate stream must be treated
media cost	Ability to Reuse or Regenerate Media	Re-fired, loss of 15% of capacity	Typically use once and incinerate	Membranes last 3-5 years

solution

SUEZ evaluated alternative technologies to meet this customer's challenges

Reverse osmosis (RO) – As one may surmise from the table, RO (figure 3) often has exceptional ability to remove PFAS materials. The molecular weights are typically above 200 Daltons, and furthermore, most PFAS materials are charged in normal aqueous solutions, having ionized one hydrogen (proton) from the carboxylic or sulfonic functional group. This ionization can be expected to be complete across the full range of normal pH encountered in ground, process, and waste water. In any case, since the pH in this situation is high (pH = 9) there is no concern that the PFAS materials were not fully ionized. Because of the molecular weight, the hydrophobicity of the molecule, and the charge, SUEZ determined RO would be able to remove the PFAS materials to greater than 99.9% – at least 3 logs of removal with a single pass membrane system.

In addition to this removal, the RO also removes a range of other contaminants, such as TOC, suspended solids, and ionic contamination, which would be helpful to the customer's process. While this would have been sufficient for the process involved at this customer, a second challenge presented itself. The RO—any RO—produces a waste stream that contains all the contaminants that do not pass through the membrane. Thus, all the PFAS materials would be concentrated into a stream of approximately 35 gpm, and this stream would have to be further treated to permanently remove the PFAS before discharge. While SUEZ makes RO systems that can achieve 90%+ recovery, the existence of this waste stream was deemed to be too complicated for the application. The customer wanted something simpler.

Figure 3: SUEZ proprietary membrane purification element and Membrane System. Capable of 3+ log removal of PFAS.

Carbon Adsorption – The second solution considered was carbon adsorption (Figure 4). Carbon has been used from time immemorial, for purifying drinking water, process water, air, and a host of other process streams. Due to its vast surface area, and because of the uniquely strong influence of van der Waals forces at the atomic level within granular carbon, the material is capable of removing a vast variety of contaminants from water, air and other streams. The advantage of carbon in this case, is that it can remove a lot of different contaminants, and is somewhat forgiving of particles and turbidity in the water. Carbon also attracts traditional organic molecules (molecules that contain lots of C-C bonds saturated with Hydrogen) very strongly, and with high capacity. In many cases, there are few alternatives for the use of carbon adsorption, as it may be difficult or impossible to find a suitable substitute. Unfortunately, PFAS is not a traditional organic molecule. It is purely man-made, never occurring in nature. The very name PFAS signifies the near or complete saturation of the Carbon bonds with Fluorine atoms, rather than with Hydrogen atoms, and this aspect renders the PFAS molecule much less readily attracted to carbon. Therefore, while carbon can adsorb some PFAS, both the kinetics and capacity of carbon suffer when compared to other removal materials. Nevertheless, since the customer's water contained other organics, and since organics normally would need to be removed in conjunction with PFAS removal, carbon was carefully considered, either for use by itself, or in conjunction with (upstream of) Specialty Ion Exchange resin. Two factors tilted the decision away from carbon in this case. First, a high removal efficiency for the benign 'other' organics was found to be not necessary. Second, and more importantly, the use of carbon would have necessitated over 5 times the number of vessels, quantity of media, plus associated piping, space, pumping and monitoring, to achieve the same result.

Figure 4: Tanks at the Manufacturing Plant.

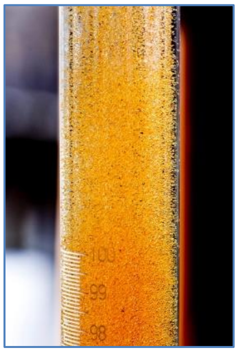


Figure 5: Specialty Ion Exchange Resin

Specialty Anion Exchange Resin – The third technology evaluated for the application was Specialty Anion Exchange Resin (Figure 5). Anion Exchange Resin has advantages and disadvantages, depending on the water matrix, the type of PFAS encountered, and the floor space available for equipment. Two exceptional advantages of resin are:

- The kinetics of resin removal are 5-8 times higher than those of Carbon. So the speed of removal is in the same order of magnitude as Reverse Osmosis. Not instantaneous, but fast. In general, an EBCT^2 or Empty Bed Contact Time of approximately 1.5 to 3.0 minutes total, is needed for the removal of various PFAS materials to a level of non-detect (Non-detect is variously reported as around 1 – 5 ppt, or 0.001 – 0.005 ug/L). For comparison, Carbon might need an EBCT of

15-25 minutes, also depending on the water matrix, and the type of PFAS encountered. For both carbon and resin, Carboxylic acids are not removed as well as sulfonic acids, and short chain PFAS such as butanoic (C4) are not removed as effectively as long chains such as nonanoic (C9). However, these observations around carboxylic and chain length are acute for carbon. Since carbon does not rely upon ionic charge as a removal mechanism, it's kinetics and capacity are not as fast as those for resin.

- The dual removal mechanism of resin (both ionic charge, and affinity/van der Waals) tends to give resin approximately 5-20 times as much mass loading capacity per cubic foot of media. The capacity allows resin to last much longer before breakthrough of the offending PFAS compound. Typically, PFOA or another carboxylic will break through first, and especially so for shorter chain lengths.

After evaluating all the choices at this customer, SUEZ engineers determined that the most cost-effective solution would be a two-pass container system with resin loaded into a lead lag configuration. Lead lag typically adds 30% to 50% to the capacity of a resin system compared to single pass, and thus is generally preferred for long term commitments (Figure 6).

Figure 6: SUEZ proprietary multi vessel water purification system with interstage testing and automation control

results

1. Specialty Anion Exchange Resin, for broad range PFAS removal, was selected as the final choice.
2. The selected treatment train was a simple pump➔vessel➔ arrangement, with the two vessels able to exchange place readily in the lead – lag operation paradigm.
3. The resin was briefly backwashed to stratify the resin. This is not required but is recommended to maximize capacity.
4. The resin was then forward rinsed with approximately 100 to 500 bed volumes to equilibrate to the alkalinity, and anionic content of the feed.
5. PFAS-out Specification was met immediately.
6. PFAS testing was completed at least weekly for the first few months, then switched to monthly thereafter.
7. An uptick in testing frequency is planned toward the end of the expected run length minus 3 months.
8. When the lead vessel "breaks through", typically to a level of 30-40 ppt of PFAS, the lead vessel is emptied, refilled with new resin, and converted into the new lag vessel (with valves, not by vessel relocation).
9. The extracted used resin is put into super sacks, allowed to drain for 7 days to 'drip dry' over an approved drain, then picked up by the vendor and incinerated at high temperature (accompanied by certificate).
10. The used resin is typically not considered hazardous unless chemically altered. The PFAS is bound strongly to the resin.
11. Meantime the former lag vessel, at that time typically has plenty of capacity left.
12. Thus, the former lag vessel is switched to the new lead position.
13. Each vessel holds 95 cubic feet of Specialty Anion Exchange Resin supplied by the industry leader in specialty resins.
14. The expected throughput for the water encountered, was estimated to be 150,000 Bed Volumes, which would equate to approximately 200-300 days of run time before vessel exchange, based on the customer's 70% - 80% expected up (running) time.
15. After several months of successful running time, the system continues to perform to expectation and is consistently reducing the PFAS-out to a level of <0.01 ug/L.
16. The customer is extremely happy with the result.

CASE TWO—PFAS removal at a different customer in the United States

challenge

As before, this customer faced a mix of PFAS materials, together with many other components in the process water. In this case there were more than four significant PFAS compounds, some found to be already in the incoming feed water for the process (intake contamination), and some being added by the customer as a process aid. Part of the incoming challenge was thought to be a mix of PFCAs (perfluoro carboxylic acids) and PFSAs (perfluoro sulfonic acids). However, customer and SUEZ testing identified PFOS (perfluorooctane sulfonic acid), PFBA (Perfluorobutane sulfonic acid), PFHxA (Perfluorohexanoic acid), and PMPA (known variously as Perfluoro methoxy propanoic acid or Perfluoro-2-methoxypropanoic acid) together with several potentially interfering fluorinated compounds, some of which are not PFAS.

The main challenge for the customer was to reduce the volume of water that needs to be treated for safe disposal. This customer had been removing the waste from site, for treatment by incineration or other techniques. By substantially reducing the volume of treated water the customer was enabled to save over $1,000,000 per year in operating costs. Furthermore, the in-process water was able to be converted to PFAS free boiler feed water, thus reducing the water footprint of the facility by over 80%. This became a double win for the customer. Table 2 shows a partial list of the process parameters and water chemistry.

Table 2: process parameters and water chemistry at customer site

Desired flow rate	110 gpm
Pressure	30 psi feed
Temperature	65°F
Desired Recovery of Overall System	80%
P-Alkalinity	4500 ppm as $CaCO_3$
M-Alkalinity	6300 ppm as $CaCO_3$
Sulfate	6630 ppm
Sodium	6520 ppm
TDS	17,335 ppm
pH	9.6
Suspended solids	10 ppm
Turbidity	5 NTUs
TOC	550 ppm
Various Alcohols (<C7)	150 ppm
Aromatics	Non-detect
PFOS (Perfluorooctane sulfonic acid)	1.15 ug/L
PFBA (Perfluorobutane sulfonic acid)	0.12 ug/L
PFHxA (Perfluorohexanoic acid)	0.50 ug/L
PMPA (Perfluoro methoxy propanoic acid)	0.94 ug/L
Grand Total PFAS in water	2.80 ug/L
Desired PFAS – treated product water	Non-detect

solution

As in Case One, SUEZ engineers evaluated the potential contribution of all three key technologies in the effort to treat the in-process water. It quickly became apparent that multiple technologies would likely be needed to meet the objective of non-detect for boiler water, together with 80% recovery of the process water. The solution was pilot tested for a period of months and proved to be feasible and cost effective.

The best solution was a combination of all three SUEZ technologies: Membrane + Carbon + Ion Exchange, as shown in the “results” item 2, below.

The challenge could be summarized by:

1. Suspended Solids removal
2. Concentration of PFAS into 20% of original water volume
3. Removal of residual organics from Membrane permeate
4. Polishing of the 80% purified water to prepare it for boiler feed.

After the successful pilot test the customer asked SUEZ to install a full-scale Mobile system to begin treatment immediately. The results have been excellent, and the customer is pleased.

results

1. A combined technology approach, for broad range PFAS removal, was selected as the final choice.
2. The selected treatment train is SUEZ Filtration➔SUEZ Membrane pass 1➔SUEZ Membrane pass 2➔Carbon Adsorption➔Ion Exchange Polish
3. The first SUEZ Membrane is for high TDS applications. The second is for polishing the permeate further. Each of the 2 membrane passes, reduces PFAS concentration in the permeate by at least 3 logs of reduction, so that the product is below the detection limit.
4. The standard ion exchange resin was then able to produce 0.06 micro-Siemen water for boiler feed.
5. PFAS-out and boiler feed Specifications were met within the first week as the system stabilized.
6. Periodic PFAS testing and other parameter testing was planned and implemented.
7. Membranes will be tested at the end of the engagement to ensure there is no "cycling up" or concentration of PFAS in the membrane. None is expected.
8. The ion exchange resin is not being relied upon to remove any PFAS since the two Membrane passes have already achieved that objective. Thus, the resin is standard, rather than specialty resin.
9. The 80% recovery objective was met, saving water, and the concentration of waste to a 20% volume was also met.
10. The customer is very happy with the result.

overall summary

SUEZ leads in the technology of PFAS contamination removal and remediation, drinking water treatment, waste water treatment, plant operation and maintenance, sludge waste management, and many other aspects of water resource management. In these two case studies we reviewed the solutions for two challenging in-process PFAS control, concentration, and removal issues. In the first case, after a thorough technical comparison, it turned out that a simple 2 vessel, specialty resin-based solution in the lead lag configuration proved to be the most effective and economic solution. It was implemented within a matter of weeks, and the client is delighted with the result.

In the second Case Study, a more complex challenge presented itself. SUEZ designed and installed a system to a) treat 110 gpm of waste water, b) remove PFAS from the waste water, c) concentrate the PFAS waste water to 20% of the original volume, d) achieve non-detect PFAS in the Membrane permeate, e) polish the permeate with Ion exchange, and f) recycle the 80% to the boiler. This solution saved the customer more than $1,000,000/year after treatment costs were factored in.

Figure 7: **SUEZ offers systems from 5 gpm up to 5000 gpm and beyond. Fully Mobile, ready for immediate emergency deployment.**

SUEZ difference

- When you engage with SUEZ, we will start with testing your water streams, perform a mass balance, evaluate your discharge conditions, understand and master your regulatory framework, measure your economics, consider local and national "headline risks", and provide you the best, tailored, overall solution.
- We may use technologies including Ion Exchange, Carbon Adsorption, Reverse Osmosis, along with pretreatment including Clarification, Ultrafiltration, Media Filtration; as well as concentration technologies such as thermal/crystallization/zero liquid discharge, along with Laboratory and on-site Water Analysis, among many other services.
- Understanding of the special needs of Industrial, Municipal, Military and Firefighting use cases, for remediation, process treatment, drinking water, discharge, regulatory knowledge, solids management, and PFAS destruction.
- As an owner or operator of dozens of municipal and private drinking water systems, municipal drinking and wastewater systems, and solid waste handling or treatment facilities, SUEZ knows your challenge from the perspective of the owner/operator—in other words, from your perspective. Our own operations specialists are available to help with your needs.
- SUEZ serves over 450,000 industrial and business customers globally, generates over $17Bn in annual sales, invests over $120M per year in research and development in 17 R&D centers, located throughout the world, and has been granted over 3,200 patents. We serve the entire range of Industrial, Municipal and firefighting site applications, with over 90,000 employees worldwide.
- SUEZ is the world leader in Total Organic Carbon Analysis with our TOC Analytical instruments, in Remote Monitoring and Diagnostics with our InSight Cloud Based Reporting, and in Analytical Testing with our many laboratories located around the world.
- With over 80 years in the water business, SUEZ is your best available partner to address your PFAS treatment needs.

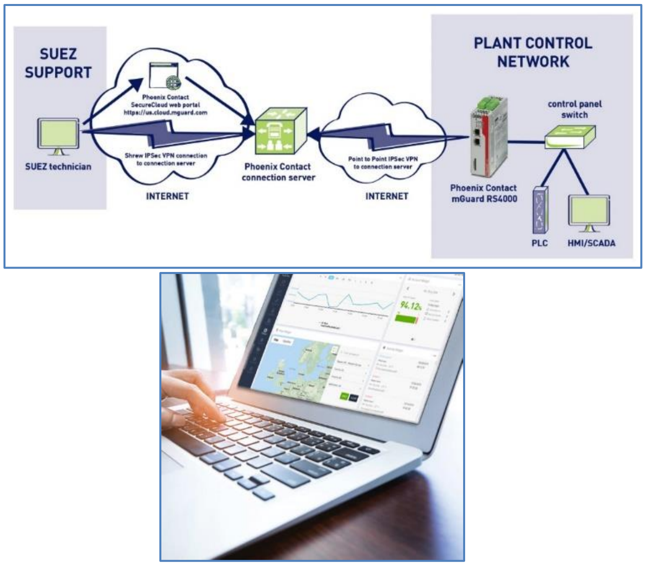


Figure 8: **InSight* Remote Monitoring and Diagnostics with Cloud Based Analytics Package. Results available 24/7/365.**

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[1] *NOTE: Details and figures in the case studies included have been altered or blended between various SUEZ locations, to maintain confidentiality, while preserving valid conclusions regarding technical solutions.*

[2] *EBCT means the amount of time the flowing water remains in contact with the bed of resin or carbon through which it is flowing. It does not refer to the interstitial space, which is why it is called EMPTY bed contact time. For example, a flow of 100 gallons per minute through a bed of 300 gallons (40 cubic feet) of media (carbon or resin) would take 3 minutes. This would equate to an EBCT of 3 minutes.*