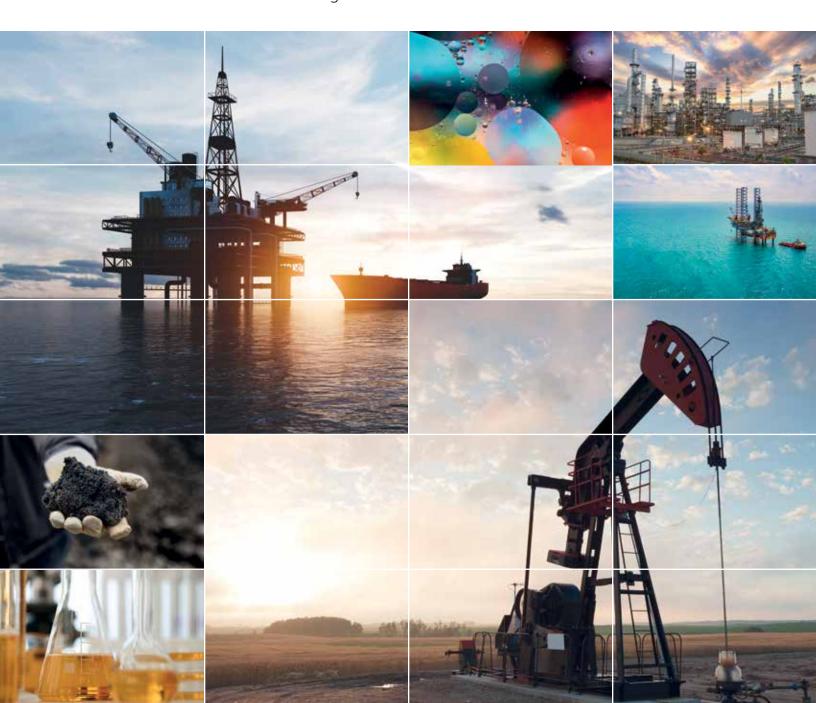


## DuPont Water Solutions for Oil & Gas - Produced Water

Addressing pressing needs for produced water treatment with DuPont's innovative technologies



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### **About DuPont Water Solutions**

Companies, communities and homes around the world choose DuPont Water Solutions to help make water safer and more accessible. Industries and markets count on us to become more efficient. Our innovation and collaboration with the world's best water experts enables ecosystems of innovation to deploy vital technologies in new, market-shaping ways.

With a global network of accessible knowledge and a marketleading portfolio of purification and separation technologies, we help enable improved water productivity from which improved health, profitability, and new possibilities emerge. In a world of increasing water scarcity, we provide a proven path that balances resource productivity and responsibility.





Our products are based on decades of industry experience, and include ion exchange resins, reverse osmosis and nanofiltration technology, ultrafiltration modules, degasification modules and wastewater treatment products, with globally recognized brands like FilmTec™ Fortilife™, Memcor® and the

DuPont™ Amber™ series to meet your water,

wastewater and other separation needs.

We provide support to markets and industries across the globe, including residential, municipal, power generation, oil & gas, healthcare, commercial industries, chemical & petrochemical, food & beverage and microelectronics, to meet the needs of a wide range of applications. We also provide consultancy services for minimal liquid discharge (MLD) applications.



Unmatched in our global reach, industry experience and expertise, our focus and dedication places us in a unique position to help industries, organizations, and communities prosper. We offer the broadest portfolio in the water treatment technology industry and provide leading innovations.

## The broadest portfolio in the industry

Water is the largest by-product by volume in Oil & Gas production and requires treatment for use, reuse and discharge. To improve productivity, water with specific quality requirements is injected into the well for secondary and tertiary recovery. For discharge, the organic load (expressed as BOD, COD, TOC or oil & grease) is usually a limit for wastewater disposal permits.

From injection to produced water, we provide a complete set of treatment technologies to handle oil and gas production needs.

Like no other supplier, we can provide ultrafiltration (UF), reverse osmosis (RO) elements, sulfate-removal nanofiltration (NF) membranes, degassing membranes and wastewater solutions like membrane bioreactors (MBR), polymeric adsorbents and selective ion exchange (IX) resins. The use and details of these products are further described in this brochure, providing a sample of our expertise and growing portfolio of technologies that targets the unique needs of hydrocarbon exploration and production.



# Produced Water and Petrochemical Wastewater

Preserving and restoring the world's water supply remains as one of the world's top environmental challenges. Minimizing waste is one of the principles behind any circular economy initiative. Failing to purify water before discharging it back into the environment has dire consequences. More stringent legislation across the globe as well as an increased awareness of corporate social responsibility towards sustainability are leading corporations to enforce and implement new solutions to tackle some of the issues that result from uncontrolled disposal of pollutants.

Effective removal of critical contaminants can help avoid:

- 1) The hindering of downstream unit operations
- 2) Fines/penalties for exceeding discharge permits
- 3) Polluting the environmen

In the end, it can be costly to ignore the importance of effectively removing certain contaminants. Finding costeffective solutions is as important as ever.

DuPont helps solve some of the Oil & Gas industry's most challenging environmental problems. We provide the right industrial water treatment options to handle oil and gas production needs.

#### **Product Portfolio**

DuPont Water Solutions offers a broad spectrum of proven technologies for a wide variety of treatment schemes – allowing customers to mix and match technologies to achieve their waste and process stream treatment objectives.



Biological treatment options such as MBR and MABR to treat challenging wastewaters



Ultrafiltration (UF) modules for suspended solids removal



Fouling resistant
reverse osmosis (RO)
and nanofiltration (NF)
membrane elements
for dissolved



Polymeric adsorbents and ion exchange (IX) resins for selective and non-selective removal





## Organics removal

Wastewater treatment capabilities in Oil & Gas require a focus on organic compound removal. The organic composition of a wastewater stream is often the key parameter for meeting discharge limitations or for recycling the water:

- The organic load expressed as BOD, COD, TOC or oil concentration is usually a limit for wastewater discharge permits. Municipal or public wastewater treatment plants (WWTP), may add surcharges to the cost of treating effluents based on the organic load.
- Downstream water recycle and recovery processes (such as reverse osmosis) are often sensitive to the organic load so pretreatment is required. In the case of environmental remediation of contaminated soils, the removal of the organic/ solvent/fuel is a must to meet overall standards.



#### Oil contamination in Oil & Gas effluents

The most common type of organic contamination in water in the O&G industry is oil. Oil is mostly found in the water from distillates in refineries, chemical processes or the water associated with hydraulic fracturing and drilling, also commonly known as produced water, which presents an opportunity to recover valuable hydrocarbons as well as to treat the water to make it suitable for recycling or disposal. Oil-in-water may appear in several different forms:

#### Free Oil

Free oil rises rapidly to the surface of the water tank under calm conditions when the oil drops are large enough, usually over 150  $\mu$ m. In this case, the oil can be removed by an overflow weir in the tank and a skimmer.

#### **Emulsified Oil**

Emulsified oil appears as small oil droplets in the water (from 1 to 150  $\mu$ m). They are stabilized by electrical charges due to the shear from travelling through pumps, splashing into a tank, or anything that will break up and disperse larger oil droplets. These droplets can be very difficult to remove with conventional mechanical techniques. Unless adsorbed onto solid particulates, paraffins can be considered part of emulsified oil.

#### **Dissolved Oil**

Dissolved oil is comprised of water-soluble oil compounds. These are uncharged non-polar carbon-containing compounds such as:

- Benzene, ethylbenzene, toluene, and xylenes collectively known as "BTEX".
- Gasoline range organics (GROs) typically C6 C12 compounds
- Total petroleum hydrocarbons (TPH)
- · Phenols and naphthenic acids.

#### Organics Removal Portfolio for Onshore and Offshore Applications

Product	Polymer	Best For
DuPont™ AmberLite™ ROC110 Oil-Coalescing Media	Styrene-DVB	Removal of emulsified oil with excellent physical stability
DuPont™ AmberSorb™ L493 Polymeric Adsorbent	Styrene-DVB	Removal of dissolved organic non-polar components
XAD™ 4 Polymeric Adsorbent	Styrene-DVB	Removal of dissolved organic polar components
XAD™ 16 Polymeric Adsorbent	Styrene-DVB	
DuPont™ AmberLite™ SCAV1 Ion Exchange Resin	Acrylic	Removal of hydrophobic and hydrophilic NOM species
DuPont™ AmberLite™ SCAV2 Ion Exchange Resin	Acrylic	

## **Emulsified Oil**

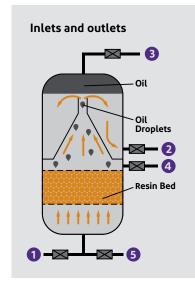
Emulsified oil can be removed by coalescing and decanting, using an ion exchange resin bed containing **DuPont™** 

AmberLite™ ROC110 Oil-Coalescing Media. This product has oleophilic properties that attract oil molecules very efficiently, usually more effectively than other coalescing technologies. The media resizes the small oil droplets from microns to millimeters in size, allowing them to be easily separated. Key features of a coalescer packed bed system includes:

- · Continuous operation
- · No regeneration is required
- · No chemicals or coagulants are needed
- · Can hold high concentrations of oil
- Resistant to elevated temperatures (up to 150°C) beneficial for heavy oils processing
- · Very long resin lifetime
- Systems can be designed for up-flow or down-flow operations

#### **Emulsified Oil Removal System:**

Oily water passes through the fixed ion exchange resin bed from the bottom to the top. The resin beads are coated with a layer of oil, leading to saturation and then supersaturation such that the oil can now slough off the beads as large droplets that can easily rise to the top to be skimmed off. There is no regeneration procedure. The oil is removed periodically from the top of the column. If proper filtration has been performed, backwashing is an infrequent event. The diagram illustrates an up-flow operation, but the system can also be designed for down-flow:



- 1. Oilv feedwater
- 2. Treated clean water
- 3. Recovered oil or hydrocarbons
- 4. Washing water inlet
- 5. Washing outlet

Treated water is extracted continuously from Valve 2. Withdrawal of the coalesced oil is not continuous, but only as required (for example, once a week) through Valve 3 at the top of the column.

## **Dissolved Oil**

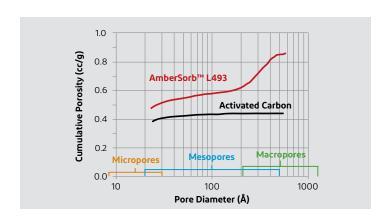
Polymeric adsorbents offer an alternative to activated carbon for the removal of a wide variety of organic compounds from industrial wastewater and produced water such as light hydrocarbons, volatile organics, aromatic and phenolic compounds.

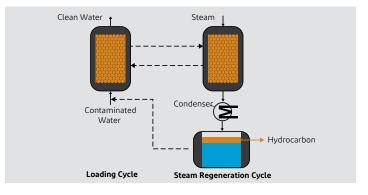
Most of the compounds found in dissolved oil can be removed by adsorption. Products such as **DuPont™ AmberSorb™ L493** and **AmberLite™ XAD™** can effectively remove a wide variety of these organic compounds.

Macroporosity comprises a sizable portion of the **DuPont™ AmberSorb™ L493** Polymeric Adsorbent compared to activated carbon, and these larger pores help to facilitate more effective adsorption and desorption kinetics.

Schematic of a Typical Steam-Regenerated System with DuPont™ AmberSorb™ L493 Polymeric Adsorbent: A two-

bed system in which one bed is in service at a time, removing hydrocarbons and producing clean, treated water. When the bed in service is completely loaded, it is swapped out for steam regeneration.







## Measurements for Organic Load

#### BOD (biological oxygen demand)

is the most widely used parameter to measure organic load. BOD or BOD5 indicates the amount of dissolved oxygen required by microorganisms to oxidize or decompose the organic matter in a water sample during a 5-day incubation period at 20°C.

#### COD (chemical oxygen demand)

is the most popular alternative to BOD because it can be performed in a few hours. The test uses a chemical (potassium dichromate in 50% sulfuric acid) to chemically oxidize the organics and inorganics in the water sample. Because inorganics are measured, a COD result is often higher than a BOD measurement

#### TOC (total organic carbon)

is gaining popularity because the test can be performed

in 5–10 minutes. A TOC measurement similar to a COD measurement in that it uses oxidation methods to break down the organics to CO<sub>2</sub>, followed by quantification.

#### O&G (oil & grease)

measures the hydrophobic components of wastewater (fat, oil, grease, and petroleum hydrocarbons) and can exist as emulsions which are tiny particles of the oil and gas suspended in water.

#### BTEX (benzene, toluene, ethylbenzene and xylene)

is a specific group of aromatic hydrocarbons that naturally occur in crude oil. In many cases, BTEX levels must be reduced to meet discharge limitations. Levels are typically measured by gas chromatography (GC) or gas chromatography mass spectrometry (GC, MS). Discharge limits for benzene can be in the parts-per-billion (ppb) range.

## Biodegradable organics and nutrients

Membrane-based biological treatment technologies such as membrane bioreactors (MBRs) or membrane aerated biofilm reactors (MABRs) harness the action of bacteria and other microorganisms to clean water, coupled with the filtration power of ultrafiltration (UF) membranes. This type of process is ideal for the removal of biodegradable organics (BOD, COD) and nutrients (nitrogen and ammonia) from wastewater.

#### Membrane Bioreactor (MBR)

A membrane bioreactor uses the combination of suspended growth biological treatment usually in the form of activated sludge, with membrane filtration equipment. Proven to deliver greater effluent productivity while reducing the lifecycle cost, Memcor® MBR technology uses a fully automated process that provides liquid/solid separation by combining biological waste oxidation and membrane separation. In turn, this eliminates the need for secondary clarification. It helps provide:

- A biological process apt for heavy COD loads
- A reduced footprint, usually 30–50% smaller than the equivalent conventional secondary clarifiers and media tertiary filtration
- Flexible, modular rack design

- Improved effluent quality, with low amounts of suspended solids, allowing the water to be reused.
- Plant expansions within the same footprint
- A solution that can be implemented with low CAPEX
- Pulsed, plug flow aeration, with reduced energy consumption compared to bubble aeration
- Flexibility to use with existing infrastructure
- A fully automated system



#### MBR and MABR Portfolio for Onshore and Offshore Applications

Product	Best For		
Memcor® B40	Municipal and industrial wastewater	<ul> <li>Reduce footprint</li> <li>Lower sludge production</li> <li>High loading rate capability</li> <li>High effluent quality</li> </ul>	

## Salinity management

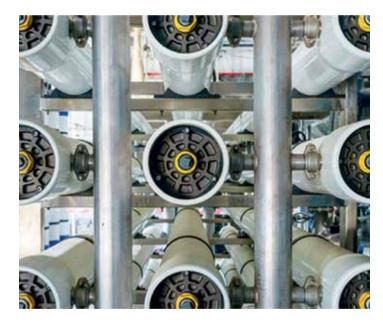
Oilfield produced water can often contain high levels of total dissolved solids (TDS) in addition to hydrocarbons, precipitates, and suspended particles. Dissolved solids mainly consist of sodium, calcium, and magnesium salts. The combination of the high salinity and hardness in produced water can be very detrimental.

Minimal liquid discharge (MLD) solutions can help address produced water regulatory challenges, particularly around salinity. High-recovery reverse osmosis systems have the potential to maximize water recovery while reducing the amount of energy required to operate, minimizing operating costs.

Low-energy reverse osmosis (RO) elements are suitable for produced water treatment. **FilmTec™ SW30HRLE Elements** are used in produced water treatment facilities. These durable, high-rejection and high-productivity reverse osmosis elements are designed for use in high-fouling or challenging feedwater conditions. **FilmTec™ SW30XHR Series** are the highest rejection membranes in the produced water portfolio, and are intended for high quality permeate water needs.

The FilmTec™ Fortilife™ XC product family is designed for facilities that need industry-leading nanofiltration (NF) and reverse osmosis solutions that are reliable, durable, and easy to clean.

The high temperatures often associated with produced water is the greater challenge when treating water with high salinity. New solutions that allow membrane systems to operate at high pressures and temperatures offer a promising alternative to conventional thermal-based alternatives for O&G wastewaters. FilmTec™ XUS180808 Ultra-High Pressure RO elements can operate continuously at pressures up to 120 bar.





#### Reverse Osmosis Membranes Portfolio for Onshore and Offshore Applications

Product	Best For
FilmTec™ SW30 Series	Treatment of high-salinity feedwater with challenging conditions
FilmTec™ Fortilife™ Series	Treatment of high-salinity feedwater with challenging conditions in high-recovery systems
FilmTec™ XUS180808	Treatment of extremely high-salinity water, typically concentrate, requiring pressure up to 120 bar
FilmTec™ Low Energy Products	Treatment of moderate salinity wastewater with challenging conditions





## Hardness Removal

In many cases, the removal of scale-forming divalent ions such as hardness and silica is more important than NaCl removal. Ion exchange softening resins can remove scale- forming cations, such as Ca2+, Ba2+ and Sr2+, with a removal efficiency greater than 99.5%. This usually eliminates any risk of carbonate or sulfate scaling. Additionally, the resin is easily regenerated with NaCl at hardness breakthrough.

DuPont<sup>™</sup> AmberLite<sup>™</sup> ion exchange (IX) resins are designed for use in industrial demineralization and softening applications offering high operating performance, long resin life, and a simplified and cost-effective operation. **DuPont<sup>™</sup> AmberLite<sup>™</sup> IRC83 H** is widely used in the treatment of unconventional O&G wastewater streams because of its high capacity and stability.

Additionally, – depending on feedwater characteristics, and existing pretreatment – nanofiltration (NF) membranes are another good candidate for water softening: they provide a high water flux and a lower rejection of monovalent ions (<90%) compared to reverse osmosis (RO) membranes. NF elements like

FilmTec™ NF90-400/34i, FilmTec™ NF270-400/34i or FilmTec™ Fortilife™ XC-N can be used for industrial water softening.



## Ion Exchange Resins and Reverse Osmosis Element Portfolio for Onshore and Offshore Applications

Product	Туре	Best For
DuPont™ AmberLite™ IRC83 H	IX	Very high-capacity dealkalization and softening WAC resin for oil sand applications and high salinity waters
DuPont™ AmberLite™ HPR8300 H	IX	High-capacity dealkalization and softening resin (WAC) for high salinity waters
DuPont™ AmberLite™ HPR1100 Na	IX	Uniform particle size (UPS) gel, SAC resin for dealkalization of low-salinity waters
DuPont™ AmberSep™ Chelating Resins	IX	Softening of waters with a salinity > 30,000 ppm of dissolved salts
FilmTec™ Fortilife™ XC-N	NF	NF element for sulfate removal in industrial wastewater streams
FilmTec™ NF270	NF	NF element for energy-efficient hardness removal
FilmTec™ NF90	NF	NF element for hardness removal requiring high rejection rates

## **Heavy Metals**

Among the wastes identified in the Oil & Gas industry, produced water containing heavy metals is amongst the most dangerous given its toxicity; it is also strictly regulated. Produced waters are often enriched with:

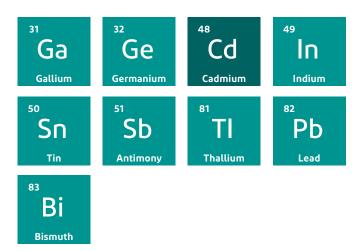
Iron (Fe)
Copper (Cu)
Manganese (Mn)
Cadmium (Cd)
Lead (Pb)
Nickel (Ni)
Chromium (Cr)
Mercury (Hg)

They are usually found in concentrations that exceed safe discharge limits and regulations.

Heavy metals can be removed from water at neutral pH as cations. For this, DuPont recommends the use of a weak acid cation (WAC) exchanger. Several products exist that can be recommended, such as **DuPont™ AmberLite™ IRC83 H** and **AmberLite™ HPR1100 Na**. Both resins can be regenerated with NaCl brine or disposed of in accordance with local requirements once they are loaded with metals.

In acidic conditions, heavy metals can form anionic complexes that can be removed with anion exchange resins. To remove these complexes, the recommended solution is the use of a strong base anion resin (SBA) such as **DuPont™ AmberSep™ 21K XLT** or **AmberLite™ HPR9200 Cl**.

Most of these metals can also be selectively removed from solution with chelating resins such as **DuPont™ AmberSep™ IRC748 Resin, AmberSep™ GT74, or AmberSep™ 43600**.



Mercury can also form colloidal complexes that can be reliably removed with **DuPont™ IntegraTec™ PVDF-UF SFP Modules**.

Since multiple types of metals can be in the same stream, multiple removal techniques may need to be employed in series. Contact your DuPont Water Solutions expert for more information.

#### **Metals Removal Portfolio for Onshore and Offshore Applications**

Product	Best For
DuPont™ AmberSep™ IRC748 UPS Chelating Resin	Selective removal of heavy metals
DuPont™ AmberSep™ 43600 Chelating Resin	Selective removal of heavy metals
DuPont™ AmberSep™ GT74 Ion Exchange Resin	Selective removal of heavy metals
DuPont™ AmberSep™ 21K XLT Ion Exchange Resin	Selective removal of Cr(VI) and metals forming an anionic complex
DuPont™ AmberSep™ G26 H Ion Exchange Resin	Selective removal of Cr(III)
DuPont™ AmberLite™ IRC83 H Resin	Non-selective weak acid cation exchanger
DuPont™ AmberLite™ HPR1100 Na Resin	Non-selective strong acid cation exchanger
DuPont™ AmberLite™ HPR9200 Cl	Non-selective weak base anion exchanger resistant to organic fouling
DuPont™ AmberLyst™ A21	Non-selective weak base anion exchanger
DuPont™ IntegraTec™ PVDF-UF SFP Modules	Removal of colloidal complexes containing mercury





## Powering performance worldwide

With a large global manufacturing footprint, strong R&D expertise and technical support services and systems, we supply high market volumes with high quality. DuPont partners with you, our customer, to understand unmet needs and develop tailored solutions

## TECHNICAL SERVICE, RESEARCH & DEVELOPMENT

Alphaville, Brazil Athlone, Ireland Chauny, France Edina, MN, USA Greifenberg, Germany Huzhou, China Hyderabad, India KAUST Jeddah, KSA Mexico City, Mexico Midland, MI, USA Shanghai, China Singapore Soma, Japan Tarragona, Spain\* Wilmington, DE, USA Windsor, Australia

#### **COMMERCIAL OPERATIONS**

Bangkok, Thailand Beijing, China Budapest, Hungary Dubai, UAE Chengdu, China Delhi, India Edina, MN, USA Freienbach, Switzerland Greifenberg, Germany Guangzhou, China HCM City, Vietnam Hong Kong, China Jakarta, Indonesia Johannesburg, South Africa Kuala Lampur, Malaysia Manila, Phillippine Marlborough, MA, USA Melbourne, Australia

Mexico City, Mexico Midland, MI, USA Milan, italy Moscow, Russia Mumbai, India Nairobi, Kenya Neu Isenburg, Germany Newton, MA, USA Paris, France Sao Paulo, Brazil Seoul, Republic of Korea Shanghai, China Singapore Surubyia, Indonesia Taipei, China Taiwan Tokyo, Japan Warsaw, Poland

Wilmington, DE, USA

#### **MANUFACTURING**

Athlone, Ireland Chauny, France Edina, MN, USA Fombio, Italy Greifenberg, Germany Huzhou, China Jubail Industry City, Saudi Arabia Midland, MI, USA Qingpu, China Soma, Japan Windsor, Australia

\*Global Water Technology Center

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