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**Opportunities for reuse**

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**DOI**

[10.2166/9781789060676\\_0417](https://doi.org/10.2166/9781789060676_0417)

**Publication date**

2021

**Document Version**

Final published version

**Published in**

Sustainable Industrial Water Use

**Citation (APA)**

Spanjers, H. (2021). Extreme industrial effluents: Opportunities for reuse. In C. Davis, & E. Rosenblum (Eds.), *Sustainable Industrial Water Use: Perspectives, Incentives, and Tools* (pp. 417-425). International Water Association (IWA). [https://doi.org/10.2166/9781789060676\\_0417](https://doi.org/10.2166/9781789060676_0417)

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# Chapter 39



## Extreme industrial effluents: Opportunities for reuse

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**Keywords:** biological treatment, high temperature, industrial water reuse, physiochemical treatment, saline effluents, toxic effluents, used process water, water reuse

### 39.1 PURPOSE AND STRUCTURE OF THIS SECTION

Many industries produce effluents that exhibit extreme properties: high salinity, toxicity, and concentrated inhibitive or refractory contaminants. These effluents may come from a specific process in the company, or in mixed effluent (residual water or wastewater) that needs treatment before disposal in the environment. The trend to separate process effluents and recycle them within individual process operations only increases the extreme characteristics of the residual water. These extreme characteristics can limit the performance of water treatment technologies, jeopardizing further purification and reuse of water, and also opportunities for resource recovery. This chapter focuses on treatment options and reuse opportunities for extreme effluents generated in the manufacturing (secondary) industry.

### 39.2 INTRODUCTION

Industrial process operations include a wide range of water qualities, from ultrapure feed water to very concentrated process effluents. Moreover, the amount of water used and effluent produced vary considerably. Process water is used for many purposes, including transport, heating, steam production, cooling, cleaning, as a medium for reactions, and as a component in products. Major water consuming industries include:

- food and beverage
- pulp and paper

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DOI: 10.2166/9781789060676\_0417

- textile, chemical
- pharmaceutical
- oil/gas, and
- energy.

These industries not only consume large quantities of water, they also generate residual waters with a wide range of qualities. In general, industry is a large water consumer and in the chemical industry, for example, direct and indirect water costs have been estimated to reach up to 2% of total production costs. In this context, 'direct' water costs include the cost of water supplied to the facility whereas 'indirect' costs include the costs related to water treatment and transport throughout the industrial process and ultimate disposal of wastewater. Indirect costs may also include maintenance and repair cost due to corrosion, scaling, and biofouling, resulting from insufficient water treatment.

In industries with large water consumption, there is a strong incentive to increase water efficiency and reuse. Reuse of water within industrial operations entails treatment of process effluents to achieve required water quality for process feed water to the various unit operations. This, in turn, results in more concentrated residual waters and brine streams. For example, the use of membrane technology to recover clean water from a process stream by retaining all salts generates a residual saline concentrate. Treatment of residual streams to very high quality, especially streams with high concentrations of contaminants, requires knowledge and expertise of advanced treatment techniques as well as accurate, reliable process monitoring and control.

### 39.3 EXTREME EFFLUENTS

Extreme effluents are water streams from industrial process operations, which exhibit properties that pose challenges to (further) treatment or discharge into the environment. Extreme effluents can cause corrosion and deterioration of concrete and steel structures and equipment, and can affect the performance of chemical and biological treatment systems, which makes the recovery of resources (water, heat, salt, specific compounds) difficult. Extreme effluents are characterized by one or a combination of the following properties:

#### 39.3.1 High variability

Industrial production processes often follow a daily, weekly, or even seasonal pattern, resulting in strong variations in amount and quality of process effluents. Biological and physicochemical treatment systems are usually designed to process relatively constant hydraulic and contaminant loads, and strong input variations adversely affect system performance. Large fluctuations in amount and quality of industrial effluents may be overcome by using equalization tanks before treatment.

#### 39.3.2 High temperature

Many industrial processes are operated at high temperatures, for example, during distillation and cracking, to dissolve fat, to increase reaction rates or by using steam for sterilization or transport. Although technology exists to recover heat from low grade residual heat, industries often choose to waste the heat along with the process effluent, resulting in hot streams. High temperature can adversely affect the biological material in bio-treatment systems, and fouling, scaling, and corrosion are enhanced.

### 39.3.3 High salinity

Saline process effluents can be a result of water treatment using ion exchange technology or membrane filtration because these technologies produce saline regenerates and concentrates, respectively. Hydraulic fracturing, or fracking, where water is used to remove oil and gas from shale formation, generates saline effluents containing salts that are released from the deep rocks. Another source of saline effluents are processes where salt is used, like in dyeing textiles which results in production of saline dye bath effluents. Other industries producing saline effluents include tanneries, seafood processing, and chemical industries. Saline waters present a challenge to treatment and recovery technologies. For example, biological and chemical oxidation of organic contaminants from saline water is impeded by high salinity, it is difficult to extract pure salts from mixed brines, and the recovery of water is energy-intensive. Moreover, high salinity may lead to increased corrosion rates of equipment and structures.

### 39.3.4 Low or high pH

Acids and bases have many applications across industries. For example, acids are used for cleaning steel (pickling) and as a raw material for many chemical products. Bases are used in the paper pulp industry to remove lignin from wood, in the food industry to peel fruit, and for scouring of natural fibers in the textile industry. Both acids and bases are used for cleaning in place (CIP) of the interior surface of pipelines, vessels, filters, and other process equipment without dismantling, especially in the food and beverage industry and the pharmaceutical industry. In a typical CIP operation the equipment is consecutively rinsed with (amongst other solutions) caustic and acid, generating effluents with subsequently very high pH and very low pH. Generally, pH has a substantial impact on physiochemical treatment processes and on the rate of corrosion and scaling. Microorganisms cannot tolerate values below pH 4 or above 9.5, and most biological treatment processes can only operate optimally in a narrow range between pH 6.5 and pH 7.5.

### 39.3.5 Inhibitive or toxic compounds

Many industries use biocides to control microbial growth in equipment and products. Microbial growth affects the quality of products in the food and beverage, cosmetic, and pharmaceutical industries and must be avoided. Microbial growth (i.e., biofouling) can also affect the performance of process equipment such as membranes, cooling and heating systems, pumps, and valves. In cooling systems biocides are often used to suppress biofouling in order to reduce corrosion and the risk of development of legionella. After their use, biocides end up in the process effluents, and can even pose challenges to biological treatment systems, as these compounds suppress biological growth. Besides biocides, numerous substances used and produced in the chemical industry (including pharma, chemical, textile, etc.) exhibit toxic or inhibitive behavior in biological treatment systems affecting nitrification and the degradation of otherwise degradable organic compounds. If the substances are both toxic (or inhibitive) and biodegradable, then careful design and operation of biological treatment systems may enable successful removal of these compounds. High concentrations of salt in saline effluents or brines also suppress microbial activity in biological treatment systems.

### 39.3.6 Refractory compounds

Recalcitrant or refractory organic compounds are resistant to biological or physiochemical degradation, and include natural and synthetic (xenobiotic) substances. For example, in the meat processing industry effluents may be generated containing high concentrations of natural humic compounds (also termed natural organic

matter, NOM), which are non-degradable. Another example is the production of industrial demineralized water from surface water, which results in a concentrate that has a high humic compound concentration. Although relatively harmless, humic substances render a brownish color to recovered water and salts, which makes them less suitable for reuse. Other naturally occurring refractory substances are found in effluents of the petroleum industry. Many industrial effluents, including pharma and chemical, contain recalcitrant synthetic organic compounds, often termed xenobiotics, that are nondegradable and sometimes toxic in biological treatment systems.

### 39.3.7 Corrosive compounds

Water can be more or less corrosive depending on its mineral composition. Corrosion is the disintegration of metal through chemical or electrochemical reactions between the metal and its environment. Corrosion is a serious problem in industrial water installations such as boilers and recirculating cooling systems. Corrosion rate increases with dissolved solids concentration (i.e., salinity), although some ions like carbonate and bicarbonate decrease corrosivity. Some ions are extremely aggressive to metals, particularly chloride and sulfate. Chloride can be found in many industrial process effluents, and is, in fact, the major constituent of saline waters and brines, such as those generated during regeneration of ion exchange resins and reverse osmosis filtration. Sulfate in process effluents is a result of the use of sulfuric acid that is commonly used in many industries, especially the manufacture of a wide range of chemicals and in the fermentation industry. Besides dissolved solids, gases such as carbon dioxide, hydrogen sulfide, and oxygen also contribute to the corrosivity of water. A special case is ammonia, present in for example some condensates, which is extremely corrosive to copper alloys. Besides the presence of corrosive constituents, a low pH (acidic) water also accelerates corrosion.

On the other extreme, very pure water (e.g., some condensates) can be very corrosive to most metals when small quantities of carbon dioxide or organic acids are dissolved in it. For example, in water-steam systems, if carbon dioxide in the feed water is carried over via the steam this may result in low pH in the condensate and consequently corrosive conditions. As condensates are generally very pure, they are obviously often considered for reuse. However, small amounts of contaminants can make the condensate unsuitable for direct reuse as feed water or other purpose.

The treatment and reuse of corrosive water poses a challenge to both treatment processes and process equipment. When corrosive effluents are treated for reuse or resource recovery, approaches to reduce corrosivity, include pH correction, de-aeration, addition of scavengers, and corrosion inhibitors.

## 39.4 MANAGING EXTREME EFFLUENTS

### 39.4.1 General

Extreme process effluents must be treated for reuse or (less preferably) disposal. Treatment may involve the recovery of water, constituents, heat, or a combination of these. The choice of the technology or combination of technologies depends on the quality of the effluent, the goal of resource recovery and the location of the industry. Table 39.1, below, lists a number of treatment technologies that have been successfully used to treat extreme effluents. Despite the additional capital cost, equalization tanks may be used to balance or moderate fluctuating hydraulic load, temperature, and pH in order to alleviate the impact on the treatment technologies. However, it should be noted that certain treatment and recovery technologies require concentrated effluent streams, and their performance may be negatively affected by lower concentrations.

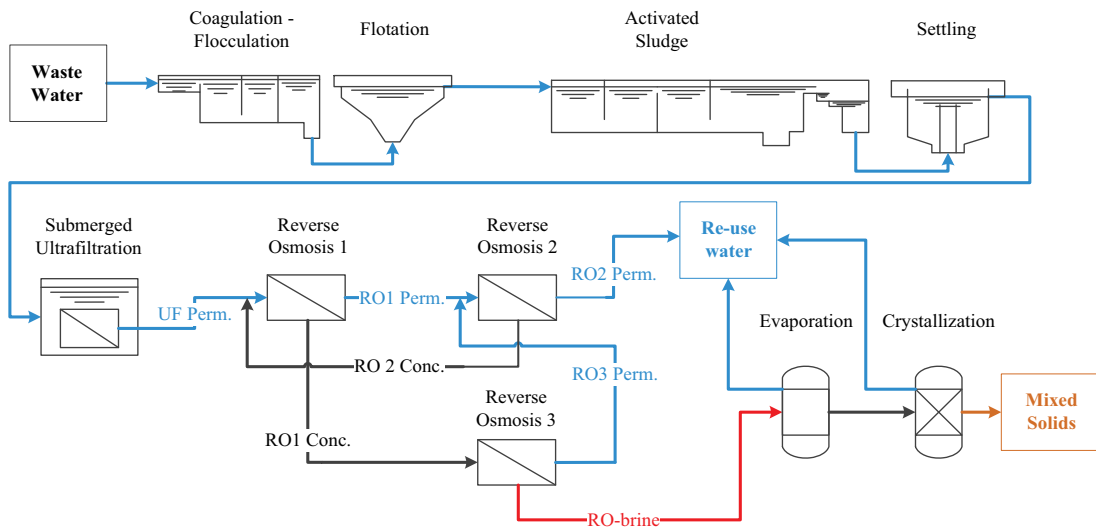
The following examples, based on real cases, describe the treatment of three different categories of extreme process effluents, technologies, and resources.

**Table 39.1** Treatment technologies for extreme process effluents.

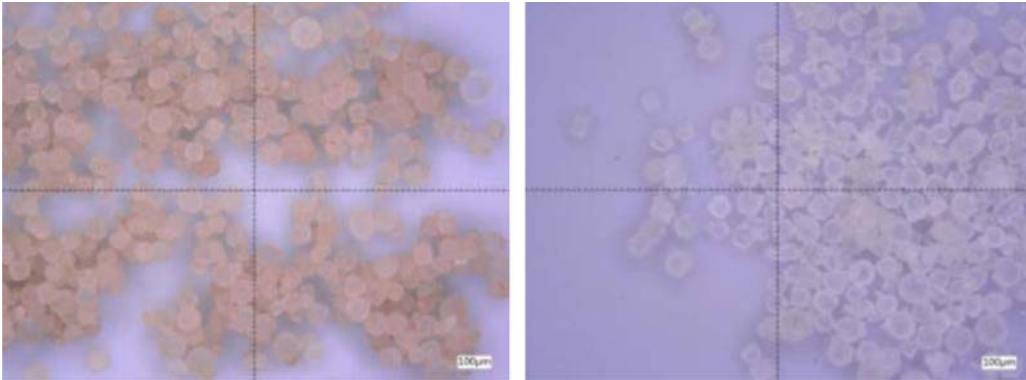
Aerobic or anaerobic biodegradation Chemical and electrochemical oxidation Ion exchange Coagulation, flocculation, flotation, sedimentation Membrane filtration Electrodialysis Evaporation Crystallization Disinfection Other
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### 39.4.2 High salt – low organics

The application of zero liquid discharge (ZLD) aims at full water recovery from residual waters. Since many ZLD technologies, such as advanced membrane treatment and thermal evaporation, are energy intensive or costly, application of ZLD can be facilitated where excess waste heat is available and where shortages of (fresh) water sources or limits on discharge of effluents justify the cost of reuse. In this example ZLD strategy is applied in a full-scale petrochemical wastewater treatment plant (WWTP) to maximize the recovery of water for reuse purposes. Figure 39.1 depicts the layout of the treatment plant. After removal



**Figure 39.1** Scheme of the ZLD WWTP. The water streams are indicated in blue and black and the RO-brine stream is indicated in red. The produced mixed solids stream is indicated in brown. (van Linden *et al.*, 2019)



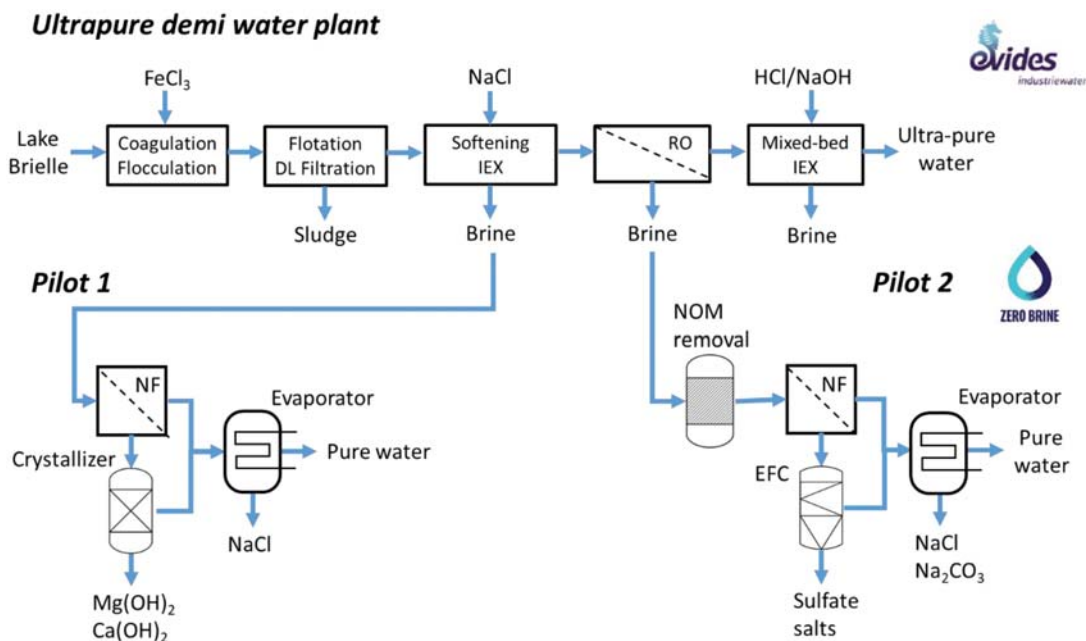
**Figure 39.2** Photomicrographs (40× magnification) of the mixed solids (left) and the washed solids (right). (van Linden *et al.*, 2019)

of suspended solids and organic substances by a combination of coagulation/flocculation/flotation and biodegradation, and removal of dissolved solids by reverse osmosis (RO), clean water is obtained that is suitable for direct reuse. The concentrated brine from the RO is further treated by evaporation and crystallization to recover the remaining water, resulting in mixed solids consisting of salts and various organic substances (NOM). The salts can potentially be reused provided the level of NOM is reduced. Investigations are being carried out to test two approaches to separate the salt and NOM. One approach is the separation of NOM from the RO brine by various technologies. Examples are nanofiltration, electrodialysis, and ion exchange, which all effectively separate the salt and NOM. Note, however, that these technologies lead to new waste streams that contain the NOM. The other approach is the removal of NOM from the salts (mixed solids) using the SALEX technology, which involves washing of the salts with a saturated salt solution. This approach also generates a new waste stream, that is, the spent washing solution containing the NOM.

Figure 39.2 compares microscopic pictures of the raw mixed solids and the washed solids. It can be seen that the NOM, responsible for the brown color of the salt crystals, was effectively removed, making the salt suitable for reuse.

### 39.4.3 Medium salt – medium organics

Many industries generate saline effluents, or brines, as a result of various production processes. The composition of these brines, including impurities such as organic matter, may vary widely depending on the type of industrial process. Although sodium chloride is often the main component, other salts and minerals can be present and may be recovered. In this example, brine from an industrial ultrapure demineralized water production plant is treated to recover water, salt, and magnesium in two large-scale pilots in an industrial area in the Port of Rotterdam. This European Horizon H2020 project ([ZERO BRINE](#), 2019) aims to facilitate the implementation of the circular economy in various process industries. The demin water plant takes water from a lake to produce ultrapure demineralized water for a number of companies in the industrial area. The plant generates two types of residual brine: ion exchange regenerate from the softening units and RO concentrate, which are separately treated in the two different pilots (Figure 39.3). The regenerate contains regeneration salt, that is, sodium chloride, and the hardness ions magnesium and calcium.



**Figure 39.3** Scheme of ultrapure demineralized water plant generating residual brines, and pilots to recover water, salts, and minerals from the brines. NF: nano filtration, EFC: eutectic freeze crystallization, NOM: natural organic matter.

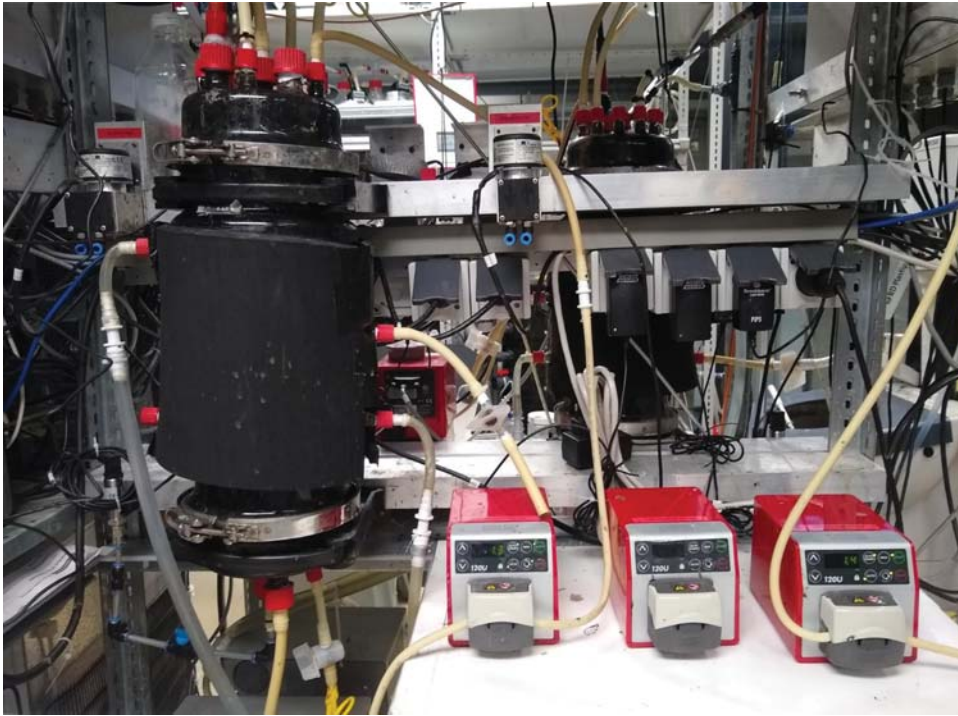
Pilot 1 consists of an ultrafiltration unit, a crystallizer, and an evaporator, and is designed to recover from the regenerate the minerals magnesium hydroxide and calcium hydroxide, the salt sodium chloride, and pure water. Recovered magnesium and calcium minerals have market value, sodium chloride can be reused to regenerate the ion exchange unit, and pure water can be reused in the demineralized water plant. Pilot 2 treats the RO concentrate to also recover sodium chloride and pure water, and in addition sulfate salts. For the latter, eutectic freeze crystallization (EFC) is used, and the brine is pretreated by electrochemical oxidation to remove natural organic matter to avoid organic impurities in the salts. In both pilots the evaporator is supplied with waste heat from neighboring industrial processes.

#### 39.4.4 High organics – low/medium salt

The food and beverage, petrochemical, and textile industries, and many others generate effluents that are high in biodegradable organic matter. These effluents are typically treated using anaerobic technologies, which enable the recovery of biochemical energy in the form of biogas. However, the effluents are becoming increasingly associated with extreme conditions, such as the presence of refractory or toxic compounds and high salinity that adversely affect biomass retention or reduce biological activity in bioreactors.

Conventional industrial anaerobic reactors are based on the retention of active biomass by using granulation. Extreme conditions lead to the disintegration of granules and hamper the formation of new granules, resulting in a loss of active biomass. In membrane bioreactors, however, all the biomass is retained by using microfiltration or ultrafiltration membranes, resulting in sustained capacity to degrade





**Figure 39.4** Lab-scale anaerobic membrane bioreactor treating saline phenolic wastewater under thermophilic conditions (Muñoz Sierra *et al.*, 2020).

the organic matter, even under extreme conditions. Moreover, since all solids including bacteria are retained, specialized microorganisms are allowed to develop, which are able to degrade refractory substances that might be present in the water. Last but not least, the use of membranes results in a treated effluent that is completely free of solids, which can be relatively easily further polished and reused in the company.

An ongoing research project at Delft University of Technology is developing anaerobic membrane technology for the treatment of saline phenolic industrial effluent at elevated temperatures (i.e., thermophilic conditions). Phenolic effluents, such as those generated in the coal coke industry, have been treated at lab scale (Figure 39.4). Removal efficiencies up to 96% have been achieved for various compounds including phenol, cresol, and resorcinol, at a salinity of 16 g sodium per liter and a temperature of up to 55°C. The technology is now ready for demonstration in an industrial pilot reactor; at the time of writing, a site in The Netherlands has been identified and the pilot is currently under design.

## 39.5 CONCLUSIONS

Many industries generate extreme effluents, and the increase in the separation of process streams and water reuse creates even more such challenging streams. Technologies are nowadays available to recover water and constituents from extreme effluents and eliminate any remaining impurities. More sustainable use of water by industry can be achieved when companies take the following actions:

- Identify new opportunities to separate process effluents and remove contaminants to recover water and useful materials.
- Avoid diluting concentrated process effluents with dilute effluents, to allow effective recovery of constituents and clean water, respectively.
- Employ proven technologies such as membrane filtration, vacuum stripping, and crystallization used in refinery processes to recover water and useful materials from process effluents.
- Redesign conventional biological water treatment technologies or combine them with new technologies to make them more resistant to extreme conditions. For example, biological treatment is often less chemical- and energy-intensive compared to physiochemical treatment, and contaminants in biological treatment effluent can often be further processed to recover water and materials.
- Use residual, low grade, heat that is often available in many companies to operate thermally driven recovery technologies.

Because of the large variety of extreme effluents across the water intensive industries, there is no one technology that fits all situations; hence any recovery and reuse project must be preceded by a pilot-scale study. However, given the range of technologies available, it is becoming increasingly feasible to make industrial water practices more sustainable by reusing water and recovering constituents from extreme effluents.

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