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StandardGuide for Use of Membrane Technology in Mitigating Hazardous Chemical Spills[1]

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1. Scope

1.1 This guide covers considerations for the use of membrane technology in the mitigation of dilute concentrations of spilled chemicals into ground and surface waters.

1.2 This guide addresses the application of membrane technology alone or in conjunction with other technologies.

1.3 The values stated in either SI units or inch-pound units are to be regarded separately as standard. The values stated in each system may not be exact equivalents; therefore, each system shall be used independently of the other. Combining values from the two systems may result in non-conformance with the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* In addition, it is the responsibility of the user to ensure that such activity takes place under the control and direction of a qualified person with full knowledge of any potential or appropriate safety and health protocols.

2. Terminology

2.1 *Definitions of Terms Specific to This Standard:*

2.1.1 *concentrate, retentate*—in reverse osmosis and nanofiltration, respectively, the portion of the feed solution that does not pass through the membrane is called concentrate, while the term retentate is more commonly used for ultrafiltration and microfiltration.

2.1.2 *crossflow filtration*—a filtration process in which the feed flows almost parallel to the filter or membrane surface. It is also called tangential flow.

2.1.3 *flux*—a measure of the rate at which the permeate (or filtrate) passes through the membrane per unit area of membrane. It is reported in units of $L/m^2/day$, $m^3/m^2/day$, or $gal/ft^2/day$.

2.1.4 *fouling*—the accumulation of unwanted deposits or scales on a membrane that results in a flux reduction.

2.1.5 *Langelier Saturation Index (LSI)*—a method used to determine the calcium scaling potential, that is, calcium carbonate of a membrane at concentrations below 5000 ppm TDS.

2.1.6 *membrane technology*—separation of the components of a fluid by means of a pressure gradient and a semipermeable membrane. The various classes of membrane technology are differentiated primarily by the size or molecular weight, or both, of rejected material. The main divisions are (*1*) microfiltration (MF), (*2*) ultrafiltration (UF), (*3*) nanofiltration (NF), and (*4*) reverse osmosis (RO).

2.1.7 *microfiltration (MF)*—a pressure-driven process whereby a contaminated liquid stream is separated using a filtration process involving a compatible membrane. Dead-ended and crossflow techniques are used. Suspended solids and macromolecules are removed on the basis of size. Pore size is normally 0.1 to 5.0 µm, and operating pressures usually range from 20 to 350 kPa [3 to 50 psig]. Membrane materials, such as polypropylene, polytetrafluoroethylene (PTFE), and metal oxides, are frequently less susceptible to chemical degradation than those used for other branches of this technology.

2.1.8 *nanofiltration (NF)*—a pressure-driven process whereby a contaminated liquid stream is separated and purified by a process involving filtration, diffusion, and chemical potential across a compatible membrane. Divalent and multivalent species with a molecular weight above 80 are removed as are uncharged and univalent molecules with a molecular weight above 200. Operating pressures normally run between 1380 and 2760 kPa [200 and 400 psig].

2.1.9 *osmotic pressure*—as related to membrane technology, the pressure that must be applied to the more concentrated solution to halt flow of the solvent from the less concentrated solution through a semipermeable membrane into the more concentrated side.

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2.1.10 *permeate, filtrate*—the stream that has passed through the membrane and is therefore free of, or has a much reduced concentration of, contaminants. Permeate is commonly used for the treated water obtained from nanofiltration and reverse osmosis processes, while filtrate is more commonly used for the treated fluid obtained by ultrafiltration and microfiltration operation.

2.1.11 *pervaporation (PV)*—a vacuum-driven membrane process applicable to the separation of liquid mixtures. During the separation, the dissolved, more volatile constituents are removed from a less volatile carrier stream, as a vapor, through a semipermeable membrane and then condensed on the downstream side.

2.1.12 *reverse osmosis (RO)*—a pressure-driven process in which a liquid stream is separated and hence purified by passing it over the surface of a semipermeable membrane. Both dissolved and suspended materials in a molecular weight range from 40 to 200 are removed, with charged species being removed more easily. In the case of nonpolar molecules, molecular structure "bulkiness" becomes important. Some are rejected well with a molecular weight of 60, while others with a molecular weight of 100 are not. Differences among membrane material can be very important in this aspect. This process discriminates between solutes on the basis of their ability to either (*1*) preferentially adsorb onto the membrane pore surfaces and move through the membrane pores by capillary action, or (*2*) dissolve in and diffuse through the membrane. Reverse osmosis uses applied pressures between 1380 and 10 350 kPa [200 and 1500 psig]. As the concentration difference between the solutions on the two sides of the membrane increases, the osmotic pressure of the solution increases and, in turn, the applied pressure requirement. In general, solutions containing organic and inorganic compounds ranging from low ppm up to 55 000 ppm are commonly treated with this technique.

2.1.13 *semipermeable membrane*—membranes that are selective in the components that they allow to pass through them.

2.1.14 *ultrafiltration (UF)*—a pressure-driven process whereby a contaminated liquid stream is separated and purified by a crossflow filtration process involving a compatible membrane. Suspended solids and dissolved molecules in the 500 to 300 000 molecular weight range are removed mainly on the basis of size. This represents a membrane that has a pore size ranging between 0.0015 and 0.2 µm. Ultrafiltration uses pressures of 105 to 1380 kPa [15 to 200 psig].

3. Significance and Use

3.1 *General*—This guide contains information regarding the use of membrane technology to recover and concentrate hazardous materials that have entered surface and ground water as the result of a spill. Membrane technology may be applied alone or in conjunction with other treatment techniques, as follows:

3.1.1 Different types of membrane are used in series with filters to treat highly contaminated solutions reaching concentration levels of several parts per million of organic and inorganic materials.

3.1.2 Different types of membranes are applied in series to treat very dilute concentrations (parts per billion level) of organic and inorganic compounds. Each membrane type has the ability to remove specific compounds, thus producing a concentrated fraction. This fraction may require final off-site treatment but provides a significant reduction in transportation costs due to the large volume reduction achieved.

3.1.3 Membranes may be used in conjunction with destruction technologies such as advanced oxidation processes (AOPs). This method is recommended for dilute solutions. The membrane technology portion concentrates the compounds to an optimum level for AOP destruction.

4. Constraints on Usage

4.1 *General*—Application of membrane technology to the cleanup of spills results in the generation of two streams. The first stream is treated and has a reduced concentration of contaminants, while the second is concentrated and has an increased concentration of contaminants. This concentrated stream must be destroyed, reprocessed, or disposed of in an appropriate manner. There may also be constraints that are created by the physical and chemical sensitivity of membranes and, as a result, characteristics of a membrane system must be taken into consideration whenever membrane units are used. These considerations are described as follows.

4.1.1 *Membrane Material:*

4.1.1.1 The material used to construct the membrane is crucial to its success. In general, for spill remediation, the UF, NF, and RO membranes require materials that have a good temperature and pH resistance, as well as chemical stability, to ensure that the membrane is unaffected by the solution being treated. The increasing demands on the performance of membrane materials are exceeding the capability of organic polymers currently available. Consequently, inorganic membranes have been developed in order to satisfy the need for better performance. Today, high-quality organic and inorganic membranes are commercially available.

4.1.1.2 Inorganic membranes are classified in four groups: ceramic, carbon, metal, and polymer analog. Many developments in inorganic membranes have been achieved, but many inconveniences have yet to be overcome, such as their high cost and low surface area/volume, which retards the expansion of their application. In the case of organic materials, several kinds of polymers are used that allow for the development of membranes with various properties. The following improvements might be noticed: lower cost, longer life time, lower replacement rates, reduced chemical consumption, reduced operating pressure for given flux level, use in a broader range of pH, higher ion rejection, easier cleaning due to effective foulant removal and reduced biological attack, lower energy consumption, as well as reduction of capital cost. Polymeric membranes with very high performance have been designed, but their great complexity makes commercialization difficult. Polymeric membranes currently on the market are available in symmetric and asymmetric configurations.

4.1.1.3 Asymmetric membranes are more commonly available than the symmetric type, especially for UF, NF, and RO. These asymmetric membranes are made of two layers of the

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same polymer. They have a thin and dense surface skin and a porous substructure that adds strength and support to the thin skin without reducing the permeate flow. The symmetric configuration has a homogenous structure that provides a very high hydraulic resistance. Another type of membrane, very similar to the asymmetric, is the thin film composite. The most obvious difference is that the two layers are made individually, from two different kinds of polymers for better performance. The characteristics of several polymeric materials currently available are listed in Table 1.

4.1.2 *Pretreatment:*

4.1.2.1 Pretreatment of the feed is of primary concern when membranes are used in spill cleanup. Although each membrane configuration is affected differently by inorganic foulants, most membranes are affected adversely by oil, grease, and parts per million concentrations of inorganic compounds, including iron, manganese, magnesium, calcium, carbonate ion, and sulphate species. Some organic species, especially at high ppm levels, may also have detrimental effects and cause irreversible damage to the membranes.

4.1.2.2 The pH of the feed solution is often adjusted to dissolve or precipitate inorganics, to prevent membrane fouling on the membrane surface that leads to a performance decline (that is, lower permeate flow rate and increased pressure drop between the feed and concentrate sides). The degree of pretreatment required will depend on the concentration of foulants in the feed stream, membranes used, and membrane cleaning schedule.

4.1.3 *Membrane Cleaning Agents:*

4.1.3.1 A membrane cleaning schedule will depend on the severity of membrane fouling. As mentioned above, a decrease in permeate flow of more than 10 % of the normal flow rate will generally be an indication that cleaning or flushing, or both, is required. It is also good practice to conduct membrane cleaning during periodic maintenance or before long shutdown periods. It is useful to determine the type of foulants on the membrane surface before cleaning. Chemical analysis is the best method; however, in situations in which this may not be possible, foulants may be determined by other means such as visual inspection. Chemical cleaning clears the membrane surface by dissolving the fouling substances with reagents. Table 2 provides a description of common inorganic foulants.

4.1.3.2 Each major foulant type will require a specific cleaning procedure. If the performance does not improve sufficiently after the first cleaning procedure, the application of another procedure may lead to a better result. Fouling on the membrane surface is usually complex and often requires several cleaning procedures successively. For example, successive cleaning with detergent and citric acid results in generally more effective cleaning than either alone. Table 3 lists several of the common cleaning agents used for membranes.

4.1.4 *Flushing and Cleaning Procedures:*

4.1.4.1 *Flushing*—One of the most convenient foulant removal procedures is flushing. Flushing cleans the membrane surface using a large quantity of feedwater at low pressure. It is effective for cleaning membranes that have been slightly fouled. The general operating conditions are as follows:

(1) Flushing Water—Permeate (treated water),

(2) Pressure—190 to 590 kPa [28 to 86 psi],

(3) Water Flow Rate—High flow rate but pressure drop limited to less than 10 psi/element,

(4) Temperature—Ambient but less than 30°C [86°F], and

(5) Period—0.5 h.

4.1.4.2 *Cleaning (Polymer Membranes Only)*—Chemical cleaning is ordinarily used after the flushing procedure. A flush is also recommended after chemical cleaning to wash off dissolved solids and suspended solids in the modules. The general operating conditions for UF membranes are as follows: It is important to realize that the operating conditions differ according to the type of membrane used. Therefore, it is strongly recommended to refer to the manufacturer's directions before proceeding. If no instructions are available, the following operating conditions for UF membranes may be used:

(1) Chemical Cleaning Agents—As listed in Table 3.

(2) Cleaning Water—Permeate 40 to 80 L [11 to 22 gal]/200-mm [8-in.] module and 10 to 20 L [3 to 5 gal]/100-mm [4-in.] module.

(3) Pressure—Less than 345 kPa [50 psi].

TABLE 1 Features of Several Polymeric Materials

Polymers	Hydrophilic	Maximum Operating Temperature, °C	Chemical Resistance	Cost	UV Resistance	pH Range Resistance
Cellulosic CA, CN, CN/CA	yes	126	fair	low	good	fair
Nylon 6, 66 polyamide	yes	135	good	low	good	good
PVDF	no	135	good	medium	poor	good
PVDF modified	yes	135	good	high	poor	good
PTFE, film	no	135	excellent	high	poor	excellent
Polysulfone	no	135	good	medium	good	excellent
Polysulfone modified	yes	135	good	medium	good	excellent
Polyacrilonitrile		...	fair	low		
	yes	...	fair	low	good	fair
PAN/PVC	no				good	fair
Polyvinyl-chloride	no	...	fair	low	good	good
Polycarbonate	no	...	fair	medium	good	good
Polycarbonate modified	yes	140	fair	medium	good	good
Polyester	no	135	excellent	medium	good	excellent
Polypropylene	yes	...	excellent	low	fair	excellent
Polyethylene	yes	...	excellent	low	fair	excellent

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