ELECTRIC POWER RESEARCH INSTITUTE

CONSIDERATIONS FOR TREATING FLUE GAS DESULFURIZATION WASTEWATER USING MEMBRANE AND PASTE ENCAPSULATION TECHNOLOGIES

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THE ELECTRIC POWER RESEARCH INSTITUTE (EPRI) PREPARED THIS REPORT.

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NOTES

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Abstract

This report establishes a framework for evaluating membrane and paste technologies to treat flue gas desulfurization (FGD) wastewater. Also provided is an overview of the engineering and economic gaps that should be further evaluated. There are limited data on the application of membranes and paste encapsulation for FGD wastewater treatment. This is an emerging area of study, and more research on full-scale/commercial applicability of combining these technologies should be conducted.

Introduction

Membrane-based water treatment technologies are used in many industrial applications to treat various water sources. Although the adoption and use of membrane technologies are based on application-specific objectives, membrane systems often provide benefits over other treatment technologies, such as reduced energy demand, high treatment throughput, and sufficient reliability. Like any other water treatment technology, deploying membrane systems requires consideration of pre-treatment and waste management. Depending on the application, the type and extent of pre-treatment could have significant impacts on the robustness of the membrane system and the overall cost of the treatment process. Likewise, when considering holistic water treatment, waste and residual management must be incorporated into system design and operation.

One challenge in deploying membrane technologies is the management of concentrated brine and solid waste generated by the membrane and pre-treatment systems. Few technologies are available to effectively manage water treatment waste products, and the most common approach involves evaporating the remaining water (to crystallize the soluble constituents) and sending the solid waste to landfills. The evaporation process requires some form of thermal energy, which can lead to high overall treatment costs, depending on the demand. Resulting crystalline solids are often managed in a lined landfill, where they can redissolve into the landfill leachate and could ultimately be discharged back into the environment. If the concentrated water stream is relatively pure in salts (that is, generally devoid of trace metals), there are some applications that could use these crystallized salts as a beneficial product (for example, road salts for de-icing). The concentrated water stream itself could also be used in industrial applications (such as oilfield drilling[1]), assuming that it meets standards established by the end-user.

Coal-fired power plants currently use membrane technologies in multiple areas to treat individual or combined water sources. Applications of membrane technologies in power plants include production of demineralized water for the boiler/steam cycle and

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[1] *N. Siefert et al. (2018), "Produced Water Treatment for Beneficial Reuse." Retrieved from https://www.netl.doe.gov/sites/default/files/netl-file/N-Siefert-Water-Treatment.pdf*

treatment of cooling tower blowdown for reuse and/or discharge. In many countries, including the United States, new regulations for wet FGD wastewater are under development or have recently been released. Coal-fired power plant operators are considering technologies that could be used to treat FGD wastewater and are evaluating membrane-based treatment systems. There are two reported commercial applications of membrane-based systems treating FGD wastewater—both are installed at power plants in China, but publicly available information is very limited.[2,3]

Currently in the United States, there are no commercial membrane-based systems treating FGD wastewater. At least three facilities have thermal evaporation systems treating FGD wastewater. Similar to membrane processes, evaporation processes produce concentrated brines and/or solid waste that must be managed according to environmental requirements. The Electric Power Research Institute's (EPRI's) research is focused on determining the feasibility of managing these brines and solids using encapsulation technologies through solidification and stabilization mechanisms. The encapsulation process combines brine, solids, fly ash, and additives to form a cementlike product that achieves physical and chemical immobilization of constituents while meeting necessary requirements for landfill application. One form of encapsulation technology being evaluated is a flowable "paste" that can be transported by pumping instead of trucking and has properties that enable flexible curing conditions based on changes in mixing recipes.

Treatment Objectives

In general, treatment objectives for FGD wastewater management will be site-dependent and therefore might not be the same for the industry as a whole. General considerations for treatment objectives could include the following:

- Treatment systems should be reliable and operate under flexible conditions, possibly including changing unit/plant capacity factors and variable feed water composition and/or flow rates.
- Water reuse and discharge strategies can change; not every site will be able to reuse water at all times. Therefore, discharge of treated water should be considered along with reuse applications.
- There should be a balance between clean water recovery (which impacts wastewater/brine/concentrate and solid waste production) and treatment costs. Operational and source water variability could lead to challenging treatment scenarios that might not be included in design specifications (in part because these conditions are not known or predictable when the project begins). Careful consideration is needed in the early stages of project development to determine the best approach to defining the typical treatment capacity and subsequent costs to various operational scenarios.
- The combination of concentrated wastewater with solid waste generated by the membrane pre-treatment process, fly ash, and other amendments should be engineered to produce a stable solid byproduct suitable for landfill applications. Each site/landfill will need to determine the desired physical and chemical properties of the resulting solid and leachate.

The following is a summary of key concepts and considerations that should be included when conducting techno-economic analyses for treatment of FGD wastewater using membrane and encapsulation technologies. This is not a comprehensive list because it does not provide in-depth information (compositions, flow rates, and so on) for specific FGD wastewater applications and does not present membrane treatment process flow sheets and design criteria. Rather, this report is meant to serve as a starting point for discussions on developing membrane and paste technologies for FGD wastewater treatment given the lack of commercial examples available. The processes depicted in Figure 1 represent the main components of membrane and paste treatment systems that are covered herein.

Membrane Treatment

Membrane treatment technologies use microporous or nonporous materials to selectively separate various constituents from water. The most common membrane materials are composed of synthetic polymers, but there are applications using ceramics and other materials. The membrane itself can be fabricated into various forms based on the technology and application. Examples of the different forms are flat sheets, spiral-wound, and hollow fiber.

[2] *J. Tracy, M. Pendergast, M. Nowosielski, D. Wang, and X. Chang, "Forward Osmosis Based Membrane Brine Concentration of Wastewater Streams in Coal-Fired Power Generation."* International Water Conference Proceedings*, 15(43). 2015.*

[3] *W. Heins, "No Liquid, No Problem: Chinese coal plant implements zero liquid discharge." Water & Wastes Digest. Retrieved from https://www.wwdmag.com/wastewater-treatment/no-liquid-no-problem.*

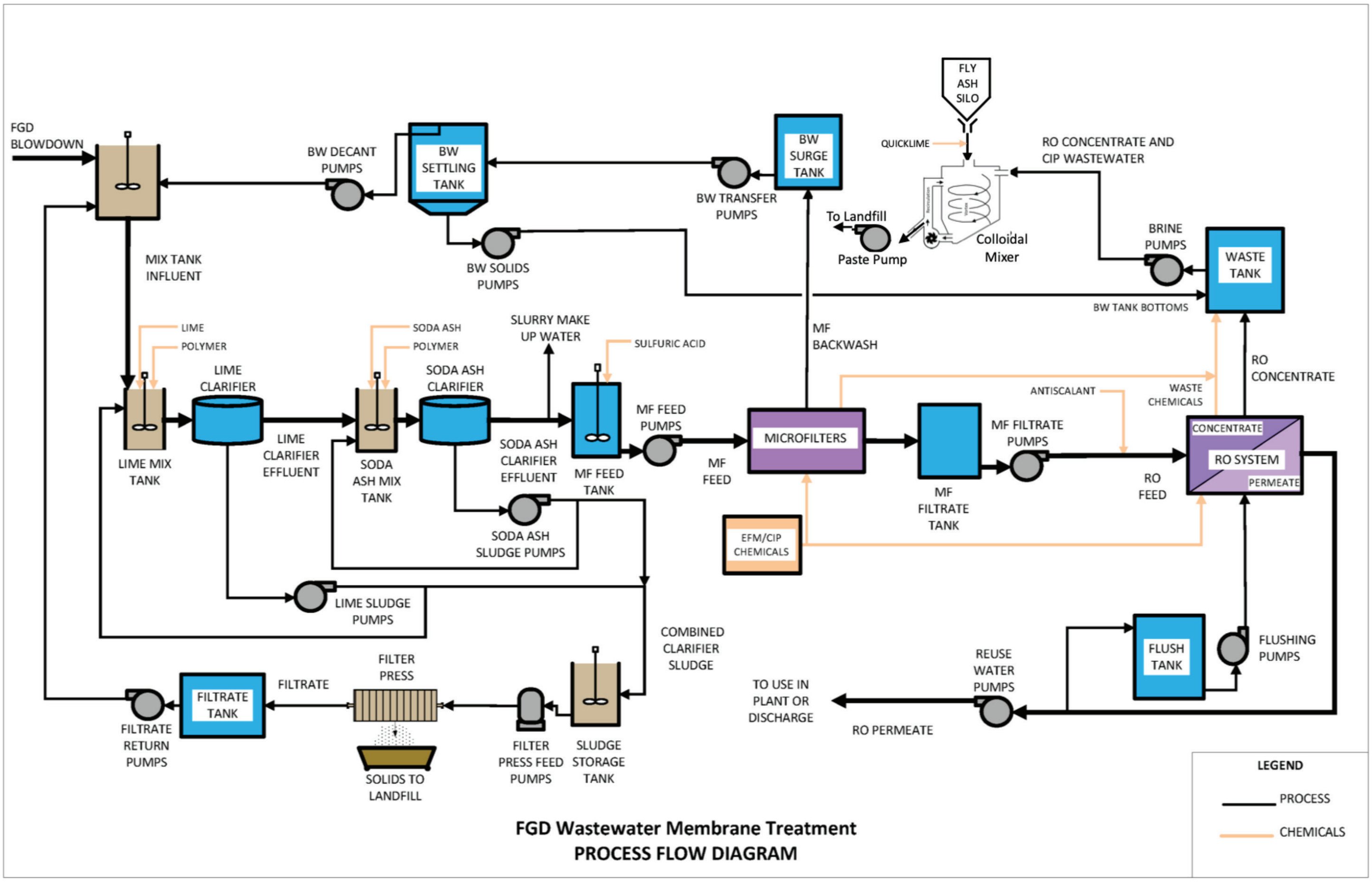


Figure 1 – Main processes for treating FGD wastewater using membrane and paste encapsulation technologies

For microporous membranes, separation is dependent on the membrane pore size, which acts as a barrier to the constituents in the feed water. Examples of microporous membrane applications are microfiltration (MF) and ultrafiltration (UF). For nonporous materials, separation occurs at a molecular level and is based on the solubility[4] and diffusivity[5] of each constituent in the feed water. Examples of nonporous membrane applications include reverse osmosis (RO) and forward osmosis (FO). Additional details on membrane technologies can be found in EPRI reports *State of Knowledge: Power Plant Wastewater Treatment – Membrane Technologies* (3002002143) and *Membrane Treatment Guidelines* (3002011342).

Key Terms

membrane fouling. A form of membrane contamination where a substance in the feed water deposits on the surface or in the pores of the membrane.

membrane recovery. The amount of permeate produced per feed water flow rate. For example, a reverse osmosis system designed to treat 100 gpm and operating at 50% recovery produces 50 gpm of permeate and 50 gpm of concentrate.

membrane scaling. Precipitation of soluble species on the membrane surface or in the pores of the membrane.

[4] Solubility *is the extent to which a constituent (solute) can dissolve in water (solvent).*

[5] Diffusivity *describes the rate at which a specific molecule moves from an area of higher concentration to an area of lower concentration.*

salt rejection. The percentage of soluble species that do not pass through the membrane. It is calculated using the measured concentration of a specific constituent (such as sodium) in the feed water and permeate.

$$\% \, Salt\ Rejection = \frac{C_f - C_p}{C_f} \, x \, 100 \qquad \text{Eq. 1}$$

where C_f is the concentration of the constituent in the feed water and C_p is the concentration of the same constituent in the permeate.

water flux. The volume of clean water (permeate) produced per membrane surface area over a given period. It is expressed as gallons of permeate per square foot of membrane per day (gfd) or liters of permeate per square meter of membrane per hour (lmh).

Technical Considerations

Membrane treatment technology selection and operations are highly dependent on source water characteristics, and membrane systems have limitations. Various conditions and characteristics—such as the concentrations of suspended solids/particles and dissolved solids, scaling potential of the constituents, presence of foulants and oxidizers, chemical properties (pH and oxidation-reduction potential), and temperature—affect membrane reliability. Pre-treatment is often critical for maintaining the reliable operation of membrane-based systems, and the type and extent of pre-treatment will depend on the membrane process chosen, source water characteristics, and the treatment objectives (including the waste management plan). Pre-treatment can also represent a significant and majority portion of the total cost of a system (as covered in this report under "Economic Considerations and Cost Factors").

Due to the lack of commercial FGD wastewater treatment applications, the following information is extrapolated from other commercial applications. FGD wastewater is a complex water matrix due to the presence of many challenging ions. Different types and configurations of membrane systems could conceptually be considered for the treatment of FGD wastewater. Commercially available systems include UF, nanofiltration (NF), RO, and FO, all of which have been considered in various EPRI research studies. The type(s) and configuration of membrane systems will depend on feed water quality, treatment objectives, and waste management practice; membrane manufacturers typically provide specific capabilities/requirements for new systems. It is possible that more than one of the membrane technologies previously listed would be needed to treat FGD wastewater.[6]

The main difference between membrane types is the quantity/percent of constituents rejected and the amount of clean water produced. UF can reject small particles like colloidal silica, but it is not capable of rejecting ions (including most metal ions, unless they are chemically complexed [that is, made larger]). NF typically rejects between 50% and 70% of monovalent ions (sodium, chloride, and so on) and >90% of multivalent ions (calcium, magnesium, sulfate). RO/FO is capable of rejecting 99% of all ions/ dissolved solids in seawater applications, with seawater having a similar concentration of total dissolved solids (TDS) as FGD wastewater. However, there are major differences in the ions that make up the TDS concentration (for example, calcium sulfate in FGD wastewater versus sodium chloride in seawater). See Table 1 for a comparison of example seawater and FGD wastewater compositions.

Table 1 – Comparison of seawater and FGD wastewater compositions reported by total recoverable analysis

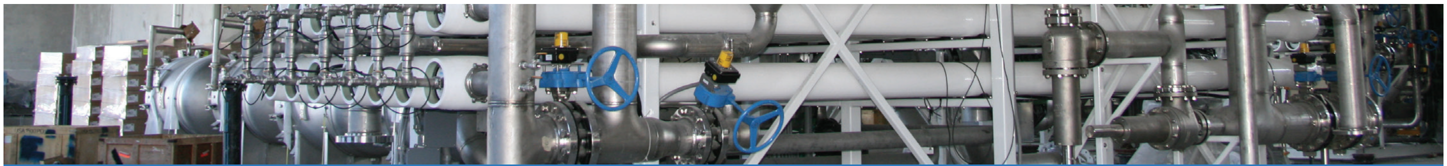
Parameter	Example Seawater Concentration (mg/l)[7]	Example FGD Wastewater Concentration (mg/l)[8]
Ca	410	3,290
Mg	1,310	3,250
Na	10,900	2,520
Mn	0.0004	86
Fe	not reported	566
Al	not reported	331
B	4	242
SO4	2,740	16,093*
Cl	19,700	7,180*
TDS	35,000	25,310*

Note: asterisk indicates that the value is modified from reference to account for charge balance.

[6] *See reference in footnote 3, which describes a membrane process treating FGD wastewater in China using UF, NF, and RO (along with pre-treatment technologies and brine crystallization).*

[7] Volume 1: Survey of Available Information in Support of the Energy-Water Bandwidth Study of Desalination Systems*, LBNL-1006424. Advanced Manufacturing Office, Office of Energy Efficiency & Renewable Energy, U.S. Department of Energy: October 2016.*

[8] *Modified from U.S. Environmental Protection Agency 2015 Technology Development Document, Table 6-3.*



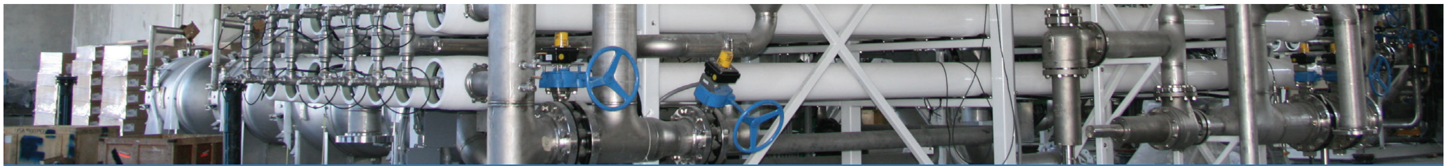
The rejection of dissolved solids by membrane technologies is impacted by the water composition in the feed stream. **Suboptimal pre-treatment can lead to fouling, scaling, and general loss of performance, requiring frequent chemical cleaning and/or membrane replacement.** For example, the designed water flux of an RO system is largely dependent on the fouling potential in the feed water. Removing the majority of foulants prior to RO and FO membranes will allow the RO/FO system to operate at a higher flux and produce a higher percentage of permeate compared to lower flux values. For seawater RO applications, the design flux is typically 5–8 gfd (8–14 lmh). Researchers conducting investigations with partial chemical softening of FGD wastewater from a power plant in Italy reported pseudo-steady state flux between 1.1 gfd and 1.4 gfd (1.9–2.3 lmh).[9] As the authors point out, additional softening would have improved RO membrane performance by minimizing fouling.

The extent to which foulants are removed can represent a significant portion of the overall pre-treatment cost because chemicals and specific treatment equipment are needed to remove various foulants. Insufficient removal of foulants can lead to plugged areas on the membrane that might not be removed by flushing or chemical cleaning. Common foulants include suspended solids, metal precipitates (those containing calcium, magnesium, aluminum, and so on), polymers used in upstream systems, and organic matter; see Figure 2.

In addition to flux, the composition (and quality) of the water supplied to the membrane will also affect the recovery, salt rejection, cleaning frequency, and membrane life. Scaling (the precipitation of dissolved solids on the membrane surface) occurs when the concentration of the constituent is above the saturation limit (see Figure 3 for an example of scaling). Many constituents could reach their saturation limit at the membrane surface, and pre-treatment to reduce the concentrations of ions is generally required. Common scaling substances in FGD wastewater are calcium sulfate, calcium carbonate, magnesium compounds, and silica. Removing these ions usually requires chemical softening with lime (targets carbonate hardness and magnesium) and/or soda ash (targets non-carbonate hardness, such as calcium sulfate). Chemical softening is commonly achieved using clarifier systems and solids management systems (filter presses, for example). **Chemical softening of FGD wastewater will require more chemical consumption by volume and produce larger amounts of solid waste than trace metal precipitation processes.** If dissolved solids that produce scaling, such as calcium sulfate, are not sufficiently removed in pre-treatment, solid precipitants will form on the membrane surface and block water from passing through to the permeate. Reduced permeate flow leads to lower recovery, and if the membrane surface is not cleaned in a timely manner, the membrane could experience long-term issues that lead to reduced salt rejection (even after eventual cleaning) and shortened membrane life. Reduced salt rejection leads to poor-quality permeate, and reduced membrane life will raise operating costs.

Figure 2 – Examples of fouling on a membrane surface

[9] *C. Conidi, F. Macedonio, P. Argurio, A. Cassano, and E. Drioli, "Performance of Reverse Osmosis Membranes in the Treatment of Flue-Gas Desulfurization (FGD) Wastewaters." Environments, 5(71), 2018. doi:10.3390/environments5060071.*



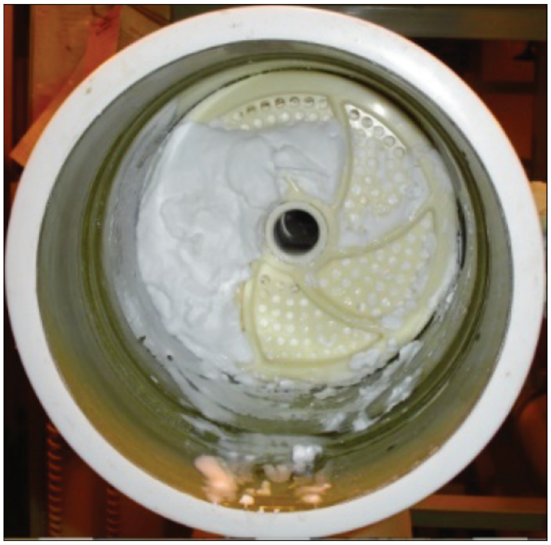


Figure 3 – Scaling on a membrane surface

Using the FGD wastewater composition in Table 1 as an example, achieving near-complete chemical softening (that is, chemical precipitation of calcium and magnesium to achieve <100 mg/l of each) for a 300-gpm system would require more than 1,900 lb/hr (861 kg/hr) of calcium hydroxide (as lime) and 900 lb/hr (408 kg/hr) of sodium bicarbonate (as soda ash).[10] This chemical softening process would address scaling from calcium, magnesium, and silica compounds and result in a sodium-based water for treatment by the membrane system following additional pre-treatment (such as pH reduction). Solid waste from the softening process could be incorporated into an encapsulation process with the membrane concentrate/ brine or handled separately. However, data on the performance of sodium-based brines in certain encapsulation processes are limited. This report further examines the state of knowledge on encapsulation for sodium-based brines in "Encapsulation Processes."

FGD wastewater could be impacted by biological growth (such as algae), and it is critical to mitigate biofouling prior to any membrane. Generally, this is accomplished with pre-filtration and disinfection, followed by a reducing agent if free chlorine remains in the water supplied to the membrane. However, each site will need to evaluate the need and use (frequency) of disinfection products. Free chlorine can cause the membrane to deteriorate rapidly (especially at alkaline pH). Nonchemical technologies for mitigating biological growth in membrane treatment systems have been demonstrated on surface water applications.[11] Their applicability in FGD wastewater applications has not been investigated by EPRI.

Even with proper pre-treatment, most NF and RO systems use antiscalant injection as a scaling mitigation measure. Antiscalant becomes critical in systems with higher percent recovery as concentrations approach the saturation limit during operations. Despite efforts to mitigate fouling and scaling, membrane systems still require maintenance cleanings. Depending on the extent of pre-treatment, cleaning cycles can range from once per week (with limited pre-treatment) to once per six months (with maximum pre-treatment). These cleaning cycles generate additional waste that must also be managed/treated.

Membrane life expectancy varies based on pre-treatment, operating conditions, and maintenance care. RO membranes used in power plant demineralized treatment systems typically last between three and five years when the system is operated correctly. There is a limited dataset on membrane life expectancy for FGD wastewater treatment, but EPRI is conducting long-term studies to document conditions impacting membrane integrity and membrane life.

Each application of membrane treatment will require designs developed by engineering personnel to determine the appropriate pre-treatment steps and membrane system based on the feed water composition and treatment goals. Table 2 presents common approaches to mitigating reduced membrane performance caused by scaling, fouling, and chemical attack. Each potential mitigation mechanism is subject to the type of condition and specific species that lead to the condition. For example, acid injection can be used to mitigate scaling caused by calcium carbonate, but it will not prevent silica scaling.

[10] *Calculated based on stoichiometry and assuming equilibrium; actual values might be different.*

[11] Boiler Makeup Water Dechlorination Using Advanced Ultraviolet Technology at Plant Bowen Water Research Center*. EPRI, Palo Alto, CA: 2014. 3002002146.*

Table 2 – Examples of mechanisms to mitigate damaging membrane conditions

Membrane Condition	Potential Mitigation Mechanisms
Scaling	Acid injection
	Scale inhibitor injection
	Chemical and/or ion exchange softening
Fouling	Chlorination
	Biocide injection
	Media and pre-filtration
Chemical attack	Oxidizing agent injection
	Reducing agent injection
	Sulfite ion injection
	Activated carbon adsorption and filtration
	Ultraviolet irradiation

Note: Mitigation mechanisms are subject to site-specific conditions. Consult with the technology provider or engineering personnel for each specific case.

The separation of constituents from the feed water will have different impacts on the membrane used. NF, RO, and FO are limited to pre-treatment characteristics, and the membranes can experience degradation over time due to fouling. The amount of clean water produced relative to the feed flow rate (the *percent recovery*) will be impacted by many factors. Based on other industry applications and assuming that high- quality pre-treatment is maintained, recovery could be >90% for UF systems, up to 95% for NF systems, and between 50% (single-pass) and 75% (multi-pass) for RO systems. Recall from the previous discussion that ion rejection is also an important factor when choosing membrane systems. Adding more RO units can increase the overall recovery but will result in higher capital and operating and maintenance (O&M) costs for a given treatment capacity.

Long-term (greater than one year in duration) research testing under relevant conditions is needed to monitor the performance of membranes in FGD wastewater applications.[12] For example, there is a concern that the highly oxidized nature of the water could significantly reduce membrane life compared to other industrial applications. Limited information is available on the exact forms/types of oxidants in FGD wastewater (the chemistry is complicated, and analytical measurements are not sufficiently detailed), but it is suspected that many types are present and contribute to membrane degradation.

Economic Considerations and Cost Factors

A membrane treatment process requires multiple systems to support operation. Pre-treatment and waste management are two of the largest systems that must be integrated with the membrane system to ensure that treatment objectives are consistently achieved. The following factors should be considered when planning the initial design parameters for new membrane systems for FGD wastewater treatment:

- Feed water equalization
- Chemical softening
  - Chemical injection equipment
  - Lime, soda ash, and polymer chemicals
  - Solids management equipment (such as filter presses) and associated chemicals (such as polymer)
- Particulate and suspended solids removal technologies with associated maintenance
  - Clarification
  - Coagulant, flocculant, and polymer chemical addition
  - Biocide chemical addition
  - Solids management equipment and chemicals
- Biofouling mitigation and free-chlorine removal
- Oxidant reduction with chemical injection or adsorption
- pH adjustment and antiscalant
- Membrane chemical cleaning (clean-in-place system)
  - Caustic and acid
  - Waste management
- Membrane treatment systems
  - Microfiltration or ultrafiltration
  - Reverse osmosis

[12] *"Results from Long-Term Research on Membrane Treatment for Flue Gas Desulfurization Wastewater."* Conference Proceedings: 2019 Power Plant Water Management Workshop and User Group Meeting. *EPRI, Palo Alto, CA: 2019. 3002016922.*

- Balance-of-plant systems and equipment
  - Instrument air
  - Instrumentation and controls
  - Chemicals management
  - Interconnecting piping, tanks, and so on
  - Site work (for example, concrete and building)

The potential impacts of key components, such as electrical energy and O&M requirements, on total system costs are not defined for FGD wastewater applications. For seawater desalination (which has a TDS concentration similar to some FGD wastewater applications), these costs are made up of the following components[13] (values in parentheses represent the contribution of that component to the overall cost):

- Electrical energy (44%)
- Fixed cost (37%)
- Maintenance and parts (7%)
- Membrane replacement (5%)
- Labor (4%)
- Consumables (3%)

In this example, electrical energy represents the greatest fraction of the treatment costs for membrane-based seawater desalination. Fixed costs include capital expenditures for permitting, construction activities, equipment, and capital amortization. The other components are related to operations and maintenance of the process.

Encapsulation Processes

Key Terms

chemical stabilization. Integration of constituents into a mineral matrix within an encapsulated material through chemical reactions.

paste. 1) A description of a material consistency. In the context of wastewater encapsulation using combustion byproducts and additives (typically, cement or quicklime), this describes a flowable solid material similar to a cement grout or mortar. 2) A term used to describe a mixing, transportation, and placement system used for a flowable solid material. These systems allow for material to be pumped within a small-diameter pipeline at high velocity to avoid material settling and then passively placed or deposited directly into a disposal site.

permeability versus hydraulic conductivity. Permeability (k) is a material property describing the ease with which a fluid can move through a solid material's pore structure. A related term, *hydraulic conductivity* (K), relates a material's permeability to the properties of the fluid (dynamic viscosity [μ] and density [ρ], typically of water) moving through the pore structure of a solid matrix (see Equation 2).

$$k = \mathrm{K}\frac{\mu}{\rho * g}\text{, where } g \text{ is the gravitational constant} \qquad \textit{Eq. 2}$$

physical solidification. Development of an impermeable matrix that physically inhibits the movement of water (and chemical species) through a solid matrix. Hydration reactions typically result in the combination of particles (while not necessarily stabilizing constituents) reducing system porosity and connectivity of pores to lower overall permeability.

pozzolan. A siliceous and aluminous material that alone possesses little ability to undergo cementitious reactions, but in the presence of calcium hydroxide and water will form cementitious compounds (ASTM C595M).

setting versus hardening. The term *setting* describes a short-term property whereby a material transitions from a flowable state, losing plasticity and converting into a solid material with barely measurable strength. Hardening follows setting as a material begins to develop strength.[14]

wastewater encapsulation. Wastewater encapsulation has been researched as a long-term solution for sequestering constituents derived from wastewater sources into a solid matrix where they will be bound both physically and chemically. The ultimate success of this application will be defined by the amount of constituent(s) retained in the materials over the long term to help mitigate future environmental challenges.

[13] Bandwidth Study on Energy Use and Potential Energy Savings Opportunities in U.S. Seawater Desalination Systems. *DOE/EE-1628, Advanced Manufacturing Office, Office of Energy Efficiency & Renewable Energy, U.S. Department of Energy: October 2017.*

[14] *F. Lea and P. Hewlett,* Lea's Chemistry of Cement and Concrete 4th Edition. *Butterworth-Heinemann Publisher, Oxford, UK, 2003. Pg. 241.*

Technical Considerations

Economical wastewater encapsulation might give some facilities a way to reduce environmental risk and is therefore considered a potential long-term environmental goal. Paste is a material-handling option, in the same category of mobility as trucking and conveying, that could be used as a tool to allow for transportation of material into a landfill. A paste system allows for transporting a flowable solid material that has a higher moisture content compared to other solid materials that are transported by trucking or conveying. In some cases, a higher moisture content could be desirable to achieve long-term encapsulation (covered in the following). Additionally, with a paste system, material placement into the disposal area is part of an integrated process. By using a system of deposition pipes, valves, and spigots at the end of the transportation pipeline, flowable solid material can be placed passively into distinct areas of a disposal area and allowed to react chemically in place. This disposal method avoids the use of earthwork equipment and avoids double-handling, which is commonplace for compacting a trucked or conveyed material. Also, using earthwork equipment breaks up a material, which could lead to increased permeability compared to a monolithic paste material that is allowed to cure and harden in place.

Short-Term Physical and Chemical Properties Versus Long-Term Encapsulation

When considering wastewater encapsulation approaches, there are often short-term physical and chemical properties of the material that are desired. These properties should not be confused with or necessarily considered a proxy for meeting a site's long-term wastewater encapsulation goals. For a paste material, short-term physical properties could include the development of strength in the deposition area such that the material can be walked or driven on (within hours to weeks). Development of strength does not necessarily mean that the material will develop into a low-permeability material over time. In fact, strength can be gained too quickly, which can lead to a more permeable system.

An example of a short-term chemical property is the result obtained by subjecting a material to a toxicity characteristic leaching procedure test (specifically, Method 1311). The intended use of the results of this test is to delineate how a waste material can be classified (Subtitle D or Subtitle C) and thus disposed. The leaching protocol used an acidic solution and a 20:1 liquid-to-solid ratio and was originally designed for municipal waste. Results should not be interpreted to directly represent leachate chemistry and provide little information on long-term wastewater encapsulation performance.

Moisture Content and Encapsulation Chemistry

When considering wastewater encapsulation, the majority of work to-date relies on cement hydration chemistry. Typical hydration reactions observed in concrete, such as the formation of calcium silica hydrate and calcium aluminum hydrate, also typically form in encapsulation systems due to the availability of alumina and silica from fly ash, calcium from additives (and the wastewater in some cases), and water molecules from the wastewater.

The water present in a pozzolan-based encapsulated material behaves similarly to a cement system. Water molecules become integrated into the crystal lattice of the hydrate minerals formed. This integrated water is deemed to be the material's nonevaporable water content. When investigating wastewater encapsulation, a paste system that allows for a higher moisture content might be favorable. As hydration reactions are allowed to proceed, materials become chemically bound, and uptake of water (and other constituents) into the crystal lattice fills in porous areas of the materials matrix, thereby reducing overall permeability. Therefore, if enough water is not present to allow these hydration reactions to proceed, permeability will not be optimized, and fewer water molecules and other constituents will be chemically bound. **In a paste system, the goal is to provide sufficient moisture for chemical reactions to fully proceed, but to not provide excess *free water*, which is water in the system above what can be chemically incorporated into hydration reactions.** In practice, the exact liquid-to-solid ratios as well as the type and amount of additive required are site-dependent and could change over time as ingredient material properties change.

In addition to water being integrated into the hydrate mineral structure, other constituents are also bound chemically. One example is ettringite, which typically forms when sulfates are present. However, ettringite can also uptake selenium into the crystalline matrix as a substitute for sulfate molecules.[15] Similarly, other

[15] *M. Zhang and E. Reardon, "Removal of B, Cr, Mo, and Se from Wastewater by Incorporation into Hydrocalumite and Ettringite."* Environmental Science & Technology*, 2003. 37: pp. 2947–2952.*

hydrate minerals can form to uptake halides. Hydrate minerals, such as Friedel's and Kuzel's salt, integrate chloride ions into the mineral structure along with calcium, sulfate, and aluminum.

The kinetics of hydration reactions are also temperature-dependent, slowing with decreasing temperature. Therefore, encapsulation mix designs and deposition plans might have to be adjusted to account for the slower reaction rate in colder climates and winter.

Effects of Wastewater Chemistry

To date, EPRI research on FGD wastewater encapsulation has focused on systems where the wastewater is principally composed of divalent cations (such as calcium and magnesium) and chloride and sulfate anions. Because of the known mineralogies highlighted in the preceding—chiefly pozzolanic hydration reactions that all require calcium hydroxide—these wastewater chemistries have demonstrated positive encapsulation results as long as the fly ash and additive chemistries are also optimized. However, **little research has been conducted on wastewaters that could result from a wastewater treatment system where chemical softening has taken place (that is, wastewater primarily in the form of sodium-based compounds).** Preliminary mineralogical testing of some encapsulation mixes with concentrated FGD wastewater containing monovalent ions, such as sodium and potassium chloride, has shown that these salts appear to not react chemically, but are isolated as salt precipitates within the crystalline matrix.[16] Additionally, academic research with cements and concrete shows that chloride binding into cement from a sodium chloride is significantly lower than for a calcium chloride brine.[17,18] In these cases, isolation of monovalent salts relies solely on the physical solidification of the overall matrix instead of chemical stabilization. Therefore, the downstream implications to concentrate management of membrane processes where chemical softening is employed should be considered.

Effects of Wastewater Concentration

There are no established maximum or minimum wastewater concentrations (such as TDS) for wastewater encapsulation. In theory, as long as enough additives are used such that the chemical system is optimized and stoichiometrically balanced but also allows enough water molecules to remain available for key reactions to proceed, chemical stabilization and physical solidification could be achieved. Therefore, the wastewater concentration being considered for encapsulation will likely depend on other factors, such as cost for volume reduction, fly ash availability, and encapsulation additive costs. Within the context of FGD systems, it is expected that volume reduction technologies (that is, membrane and/or thermal treatment systems) will be needed to reduce wastewater volume to an extent that encapsulation could be an option. The extent of volume reduction required will be based on the economics of the volume reduction process as well as the available solid materials (fly ash and additives) available for encapsulation.

Effects of Water Treatment Chemical Additives

To date, little research has been conducted on how chemical additives required for upstream membrane systems (for example, membrane chemical cleaning waste) will impact encapsulation chemistry. **Acids, surfactants, salts, sugars, and scale-inhibiting chemicals are all known to impact the setting and hardening behavior within concrete.** Limited EPRI testing has shown that paste mixes that included membrane cleaning chemicals (citric acid and sodium dodecylbenzene sulfonate) that had been further concentrated in a subsequent thermal evaporation process did not set up (become established solids), gain strength, or perform similarly to other samples using a waste brine alone.

Effects of Fly Ash Type and Quality

The type of fly ash available at a site can have a wide range of impacts on both technical and economic factors. For most Class F fly ashes (that is, Illinois Basin and other eastern bituminous coals) that are pozzolanic but not self-cementing, alkaline additives, such as quicklime or cement, will be required for encapsulation chemical reactions to proceed. Class C fly ash (that is, subbituminous,

[16] Program on Technology Innovation: Mineralogical Investigation of a Brine Encapsulated Monolith: Mineralogical Analysis Methods, Results, and Lessons Learned. *EPRI, Palo Alto, CA: 2017. 3002011759.*

[17] *J. Tritthart, "Chloride binding in cement II. The influence of the hydroxide concentration in the pore solution of hardened cement paste on chloride binding." Cement & Concrete Research 1989. Vol. 19 pp. 683–91.*

[18] *C. Arya, N. Buenfeld, and J. Newman, "Factors influencing chloride binding in concrete."* Cement & Concrete Research *1990. Vol. 20. pp. 291–300.*

low-sulfur western fuels) tends to have a high fraction of native calcium and is often self-cementing; therefore, fewer additives are needed. However, these materials can pose material-handling challenges, such as setting too quickly, when incorporated into a paste. Therefore, additives, such as set retarders and rheological modifiers, might be needed.

Within the context of both ash types, the quality of the fly ash can impact the effectiveness of encapsulation. Changes to the source coal being burned as well as changes in upstream process (coal milling, boiler performance, and so on) can lead to changes in ash quality. The presence of unburned carbon is known to impact air entrainment in concretes and cements containing fly ash, and excessively high levels of unburned carbon typically have lower strengths. However, for wastewater encapsulation, commercial properties and high strengths are not typically necessary. Encapsulation mix designs containing ash with a high fraction of unburned carbon have not been extensively investigated by EPRI, but reduced reactivity could mean that mix designs would need to be adjusted and additional additives required to achieve the desired performance. Fly ash impurities derived from environmental control systems (activated carbon, trona, or hydrated lime, for example) could also impact encapsulation mix designs, but this has not yet been evaluated in EPRI's encapsulation research portfolio.

Economic Considerations and Cost Factors for Paste Systems Process Integration

There remains more to study and explore on the integration of membrane wastewater treatment and encapsulation systems. For example, concentrate storage should be considered in the context of matching wastewater flow rates to the paste system throughput. As with most water treatment processes, a paste system generally performs better in steady-state operation as opposed to a batch mode. Operating a system in batch mode would increase maintenance activities for main components (mixer, pipeline, and so on) because the paste material would need to be cleaned out of equipment between runs.

Paste Equipment Costs: Mixing, Transport, Placement, and Landfill Management

Mixing and transport costs for paste systems are likely to be capital expenditures, whereas dry materials management is usually an O&M cost. Major capital equipment is expected to include the following:

- Material-handling and metering equipment
  - Silos and augers for dry solids
  - Tanks and pumps for liquids
- Mixing
  - Pug mill(s)
  - Grout mixer(s)
  - Pan mixer(s)
  - Paste short-term storage equipment (for example, agitated grout tank)
- Pumping
  - Positive displacement piston or progressive cavity pump(s)
  - Associated piping and distribution materials
- Transportation
  - Piping
  - Maintenance equipment

Capital equipment costs for paste systems will vary and are dependent on site-specific factors. The required long-term properties of the paste in the landfill, which dictate the initial paste viscosity as well as the distance between the mixing area and deposition area, will likely have the largest impact on cost. As viscosities and pumping distances increase, larger pumps with higher discharge pressures as well as the amount and strength of pipe required increase, too. The processing capacity of the system will also have a large impact on the overall cost.

When conducting design reviews for costing analysis, it is important to note that similar equipment has been used for installation of both paste and grouting systems in the mining and mineral processing industries. Additionally, a few paste systems have been installed for the singular purpose of transporting fly ash to a disposal area. One conference paper reports that the

total installed cost for paste systems ranges from $3M (100 tons/hour [90.7 metric tons/hour] system) to $11M (73 tons/hour [66.2 metric tons/hour] system), with the higher cost for the smaller system being due to more extensive upstream processing equipment, such as a thickener.[19] Additionally, feasibility-level (+/-50%) engineering estimates available to EPRI from a few sites, each with site-specific scenarios, show a major capital equipment cost of $3M–$15M, including upstream dry material storage silos.

When analyzing capital equipment, it is important to consider the amount of flexibility that should be incorporated into the design. For example, changes in a paste mix design can be driven by a change in weather, coal type, or upstream environmental controls and water treatment systems. Addressing these changes might involve variations to mix designs and mixing equipment operations. As previously explained, mix design optimization is site-specific, and mixes will likely need to be changed over time. By incorporating instrumentation and controls technologies used in the concrete industry, such as real-time density, moisture, and viscosity meters, mix designs can be adjusted and controlled. Additionally, changing from one type of additive to another (cement/quicklime) could be important when trying to accommodate only one set of material-handling and storage equipment.

Paste Operating Costs

Chemical additives are likely to be the largest operating expenditure for paste systems. In general, the concentration of the wastewater used in encapsulation is directly proportional to the amount of an additive needed to achieve acceptable long-term results (higher concentrations require more additive). Additional additives might be needed for sites using less reactive Class F ash. For a hypothetical mix design, a site's annual cost for additives is expected to be in the range of $100–$150/ton ($110–$165/metric ton). This is based on the following:

- Calcium chloride wastewater and Class F ash
- A constant annual wastewater flow rate of 25–75 gpm
- 30–40% by total mass wastewater
- 67.5–52.5% by total mass fly ash
- 2.5–7.5% by total mass additive

The relative importance and impacts from the factors listed on the annual cost of additives are shown in a tornado diagram in Figure 4. Assuming median values for all assumptions, an annual cost for additives is calculated to be approximately $2M. The volume of wastewater to be sequestered and the amount of additive required have the largest impact on cost, ranging between $1M and $3M per year for the high and low assumptions. Intuitively, the cost of the additive influences the costs as well.

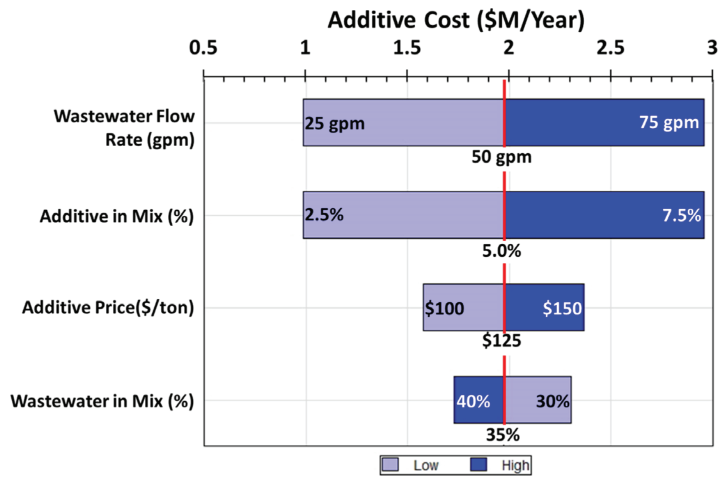


Figure 4 – Factors impacting additive cost for a hypothetical scenario

An inverse relationship can exist between the amount of wastewater in the paste mix and the cost of additives whereby a larger volume of liquid is sequestered per unit mass of fly ash and lime. For this scenario, at a flowrate of 25 gpm, ~95,000 tons/year (~86,183 metric tons/year) of lime and ~285,000 tons/year (~258,548 metric tons/year) of fly ash would be required, assuming average values for all other cost factors. This analysis does not incorporate a comparison to other ash-handling approaches/ technologies. For example, a paste system is expected to require less labor support than traditional methods (that is, trucking dry material).

Paste placement and landfill management costs are not fully understood and are typically further complicated by the presence of existing ash disposal and landfill management costs. Assuming the use of an existing landfill and that most of the ash used for paste is already being disposed of, most of the cost of paste disposal is already accounted for with existing landfill costs. **Additionally, existing landfill sites would need to evaluate if permit modifications would be needed to receive the paste material. Such**

[19] *S. Longo, "Paste and Ash Systems: Case Studies," in* World of Coal Ash, *2015.*

evaluations would include space availability and compatibility with the landfill liner. For sites that do not already have a landfill permitted or constructed, this cost would need to be considered as well. Permitting and constructing a landfill can take considerable time and could add to the overall technology installation timeline.

Although the cost to place material passively and directly out of a pipe should be less labor-intensive than using equipment to compact dry material in a conventional landfill, other costs would be incurred with a paste landfill. These costs could include creating berm structures to contain the material until it hardens in place; however, berms could likely be created by digging up a lower layer of material or by using other available materials from on site, such as bottom ash, helping to offset the cost. Although they are not a cost inherent only to paste, in order to sequester constituents, more extensive landfill management practices—such as more frequent intermediate cover systems and stormwater diversion—might be necessary.

Effects of Ash Sales

Based on EPRI site material balance studies, FGD wastewater sites burning high-chloride eastern coals would need to use a majority fraction of produced fly ash in the encapsulation mix as well as consider thermal evaporation beyond membrane treatment to have effective material liquid-to-solid ratios. This finding is also true for a high-liquid-content paste system. For other sites and wastewaters, the amount of fly ash required might be only a small fraction of the total ash produced. The availability of fly ash can therefore have a major impact on how much wastewater can be encapsulated.

Selling fly ash into beneficial-use markets creates a revenue stream and avoids landfill disposal costs. However, for sites where encapsulation is needed, the implications of having less ash available could outweigh the revenue from ash sales. With less ash available, additional wastewater treatment (volume reduction) could be required to enable successful encapsulation of all wastewater within the available ash. Increasing the capacity of the wastewater treatment process could result in higher overall costs, especially if the degree of volume reduction necessitates the use of a thermal evaporative system instead of or in addition to a membrane system. Alternatively, with less fly ash available, larger quantities of additives could be used. This would likely outweigh the revenue gains from ash sales because the cost of additives is typically much higher than the revenue gained from selling fly ash. EPRI research has found that other combustion byproducts that do not contain the silica or aluminum required for pozzolanic hydration reactions (such as gypsum) are not an effective solid additive.

Future Research and Next Steps Toward Commercial Applications

The goal of the research presented in this is report is to produce results that could be used throughout the lifecycle of commercial applications, from conceptual design to system decommissioning. Summarized next are the opportunities for additional research and investigation that are needed to better understand membrane and paste technologies to treat FGD wastewater.

Membrane Treatment Research Opportunities

- Study the impacts of membrane fouling, scaling, and loss of performance and methods to mitigate these impacts
- Perform long-term testing of NF and RO membrane materials, and document membrane longevity over defined chemical and operational conditions
- Develop enhanced sensors and controls that can perform real-time analysis of the membrane system and change operating parameters to mitigate potential upsets
- Study nonchemical biofouling mitigation technologies
- Identify the types of oxidants in FGD wastewater and test methods/technologies that prevent membrane degradation

Paste Technology Research Opportunities

- Expand the encapsulation datasets to include more chemistries and time-based results
- Evaluate the relationships between short-term and long-term encapsulation properties (requires time to collect long-term results)
- Investigate encapsulation of sodium-based wastewater using fly ash and additives
- Study the impacts of chemical softening solids and membrane chemical cleaning waste incorporated into an encapsulation process
- Perform testing that simulates batch operations of paste systems, and characterize the operations and maintenance impacts

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