Investigating Bromide Leakage During Anion Exchange Regeneration

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The City of Sarasota (city) produces up to 12 mil gal per day (mgd) of potable water using cation exchange (CIX), reverse osmosis (RO), and tray aeration processes to serve its nearly 57,000 residents. Saving on salt import costs, the city currently regenerates its CIX system using filtered Sarasota Bay seawater in lieu of a high-strength brine (salt) solution. In efforts to reduce sulfate, the city has investigated the use of anion exchange (AIX) as an additional technology to its treatment portfolio. Moreover, the city would like to evaluate the viability of using filtered Sarasota Bay seawater to regenerate the proposed AIX process.

An AIX pilot unit was constructed onsite at the city's water treatment facility (WTF) and operated to evaluate the performance of two strong base chloride-form anion resins. Purolite A600E-9149 and Thermax A-32 resins were fed the city's sulfate-laden ion exchange (IX) feed water and run to exhaustion. Regeneration of the resin media included a manufacturer-recommended solution of 10 percent salt and the city's filtered Sarasota Bay seawater (seawater). Distilled water was used for rinse cycles postregeneration and samples were collected at periodic time intervals to determine resin performance and investigate the leakage of competing anions.

Results indicate that AIX performance in both resins decreases when seawater is used to regenerate compared to a traditional 10 percent salt solution. Bromide leakage was also observed in the treated AIX effluent of both resins under seawater regeneration conditions. Total trihalomethane (TTHM) formation potential of the bromide-containing effluent was analyzed and found to range from 134µg/L to 197µg/L after 168 hours (seven days) of formation. The main component of the TTHM concentrations at the 168-hour time period consisted primarily of bromoform, indicating that increased bromide concentrations in the treated pilot effluent contribute to the increase in formed disinfection byproducts (DBPs)

Introduction and Background

Ion Exchange Process

The IX is a process used in water treatment applications to remove aqueous ionic constituents by exchanging them with solid-phase ions of a similar charge. This is accomplished by synthesizing media with organic functional groups to obtain a charge at the media's surface. The IX process used for the removal of negatively charged ions is known as AIX, whereas the removal of positively charged ions is accomplished with CIX. In addition to water treatment, IX is used in the production of deionized water, industrial purposes, purification of organic and inorganic chemicals, analytical chemistry uses, and ion mixture separation processes (Schubert & Nachod, 1956).

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Generally in the form of spherical resin beads, IX media are configured in a fixed or fluidized bed fashion and housed in a vessel during operation. Water is passed through the media bed and aqueous ionic constituents are removed as they exchange with the resin media's solid-phase presaturant ion. As operation continues, the resin bed begins to saturate with the targeted constituent(s) and the treated effluent water begins to increase in the targeted constituent(s) concentration, known as breakthrough. Once the resin bed is fully saturated with the targeted constituent(s), the bed is considered exhausted and must be regenerated prior to subsequent operational use.

Figure 1 displays a graph illustrating breakthrough and exhaustion of an IX process, where operational run time is on the x-axis and effluent concentration of the targeted constituent(s) is on the y-axis.

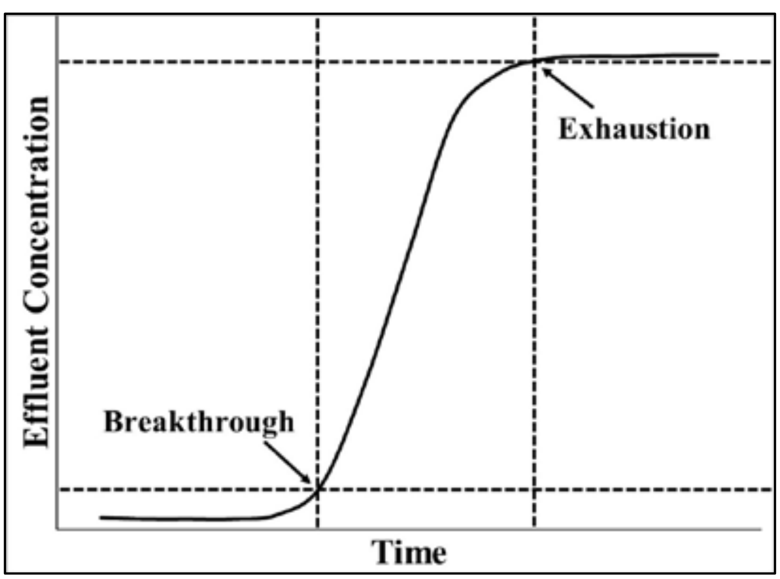

Figure 1. Ion Exchange Breakthrough/ Exhaustion Curve

Regeneration Methods

Regeneration of an IX process involves the replacement of the original presaturant ion back onto the resin media, eluting the saturated targeted constituent(s) that have accumulated during operational use. This is achieved by running a solution comprised of a high concentration of the presaturant ion through the resin bed. In water treatment, the presaturant ion is typically chloride or sodium, allowing a high-strength sodium chloride (i.e., salt) solution to be used for regeneration purposes. Common regeneration methods involve the use of a 10 percent strength salt solution that is run counter-current through the resin bed for a period of time, followed by a short rinse cycle of feed or treated water prior to completion. The spent salt solution and rinse water are typically considered waste streams, requiring disposal.

Because the regeneration process comprises a large portion of the overall cost and maintenance of IX, alternative regeneration methods have been researched and investigated. Medina et al. (2018) recently compared efficiencies of a fresh salt solution, a reused salt solution, and a treated reused salt solution for additional brine management options. Studies have also been performed on regenerating IX resin through multiple stages using different-strength brine solutions (Korak et al., 2017). The comparison of different salts, such as potassium chloride, sodium bicarbonate, and potassium bicarbonate, were evaluated by Maul et al. (2014) to measure regeneration efficiencies and their overall life cycle environmental impacts; however, less research is available on the use of alternative brine streams, such as seawater. Wilf et al. (1980) tested the use of seawater from the red sea as a regenerate solution for a CIX process, resulting in a viable implementation of the process. Coastal water utilities could benefit from seawater regeneration of IX systems, but more research is needed to evaluate the impacts associated with competing ions in seawater, such as bromide. Additionally, the lower ionic strength of seawater, when compared to a solution of 10 percent salt, leads to a lower regeneration efficiency and subsequent leakage of previously removed ions during succeeding operational runs.

Table 1. City of Sarasota Average Ion Exchange and Reverse Osmosis Feed Water Quality

Parameter	Units	IX Feed	RO Feed
pH	s.u.	7.64	7.13
Temperature	ºC	29.1	26.9
Conductivity	µS/cm	1,090	3,330
Turbidity	NTU	0.18	0.12
Alkalinity	mg/L as $CaCO_3$	171	136
TDS	mg/L	830	2,400
Sulfate	mg/L	396	858
Chloride	mg/L	25.2	588
Bromide	mg/L	<0.20	2.48
Fluoride	mg/L	0.49	1.17
Calcium	mg/L	126	279
Magnesium	mg/L	60.2	135
Sodium	mg/L	13.5	294
Potassium	mg/L	2.46	6.60
Strontium	mg/L	21.8	26.5
Silica	mg/L	25.7	21.9

Brominated Disinfection Byproducts

It is known that chemical disinfectants and oxidants added to water form byproducts when in contact with natural organic matter and other inorganic material, like bromide. Among the many DBPs that can be formed, only a small amount is currently regulated under the U.S. Environmental Protection Agency (EPA) Safe Drinking Water Act (SDWA). Five of the current regulated DBPs contain bromide, making it an important parameter in DBP formation (Heeb et al., 2014). Ding et al. (2012) demonstrated that the specific removal of bromide from water prior to disinfection is a desired treatment objective in reducing DBPs. Recently, Szczuka et al. (2017) and Liu et al. (2018) identified increased DBP formation from a saline water source due to elevated levels of bromide. Considering that certain seawater matrices contain high concentrations of bromide, AIX processes using seawater regeneration may experience bromide leakage due to ion's propensity to act as a competing anion to chloride.

Existing Treatment Conditions

The city's utilities department operates a potable water facility in the state of Florida, spanning a service area of 25 sq mi. Utilizing two main water sources, the city pumps water out of the Upper Floridan aquifer through 51 groundwater wells to produce 12 mgd of finished water. The city's treated water consists of a blend of RO permeate, CIX product water, and raw aerated bypass water prior to chlorination and distribution. The existing CIX process is currently regenerated using filtered Sarasota Bay seawater, saving on salt import and operations costs.

Table 1 displays the average water quality parameters of the IX and RO feed water.

Cation Exchange Treatment

At a capacity of 7.9 mgd, groundwater from the Upper Floridan aquifer is pretreated through tray aeration and chlorination at the Verna well field, approximately 22 mi from the city's WTF. Approximately 2.3 mgd of the pretreated raw water is bypassed and blended with the WTF's finished water, while the remaining 5.6 mgd is fed to the city's CIX process for hardness removal. The existing CIX process consists of four softening vessels, three of which are in operation at full production, with the fourth in regeneration. A strong acid cation (SAC) resin in the sodium-form operating in a fixed bed configuration is utilized for the selective removal of calcium and magnesium. Regeneration of the resin beds are accomplished using chlorinated Sarasota Bay seawater that is pumped directly from the Sarasota Bay and filtered at the WTF prior to use as a regenerate solution for the SAC resin. Sulfur dioxide is added to the used IX regeneration waste stream to remove residual chlorine prior to deep well injection disposal.

Reverse Osmosis Treatment

Brackish groundwater from the city's downtown well field is pretreated at the WTF with the addition of an antiscalant (Aquafeed 1025®) to suppress the formation of sparingly soluble salts and fed through one-micron cartridge filters prior to membrane treatment. It is then delivered as feed water to the city's RO process consisting of three two-stage process trains in a 28x14 pressure vessel configuration, housing six low-pressure RO membrane elements per vessel. Hydranautics CPA3 membrane elements are used in stage 1 and Hydranautics ESPA 2 elements are utilized in stage 2.

Operating at 75 percent recovery, the RO process produces 4.5 mgd of permeate water, which is then post-treated through degasification and sodium hydroxide addition. The treated RO permeate water is blended with the CIX product water and raw bypass water prior to chlorination and onsite storage before distribution. The rejected concentrate water, approximately 1.5 mgd, is degasified and disposed of via deep well injection.

Materials and Methods

Anion Exchange Pilot Unit

A four-column, AIX pilot system was installed at the city's WTF on behalf of Tonka Water™, a U.S. Water Brand. The pilot system is operated in a four-column design, where two columns combined is analogous to a full-length column. In this configuration, the effluent of the first column represents half-bed values and the effluent of the second column represents full-bed values. With the four-column arrangement, two full-bed anion resins can be operated in parallel for performance comparison and can be seen in Figure 2. Purolite A600E-9149 and Thermax A-32 strong base chloride-form anion resins were provided to the University of Central Florida (UCF) by the manufacturers and were tested for the targeted removal of sulfate under the operating parameters, displayed in Table 2.

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Each column maintained a filter screen, housed at the effluent orifice, and an 8-in. gravel bed below the resin media for support. Anion resin was added, in the form of resin slurries to reduce air pocket formation, until a resin bed depth of 3.1 ft was met in each column. Given that each column measured 3 in. in diameter, the achieved media bed depths allowed for a similar surface and volumetric loading rate to that of the city's full-scale CIX system. Each column was also equipped with a pressure gauge at the influent and effluent orifices to monitor pressure drop changes throughout operations. Influent water to the pilot unit was supplied from the city's onsite IX feed water storage tank and effluent-treated water was discharged to a 30-gal storage tank prior to disposal. Regeneration procedures were accomplished through the use of a 60-Hz centrifugal pump and an additional 30-gal storage tank to contain regenerate solutions.

Figure 2. Anion Exchange Pilot Unit

To determine the efficiency and impacts of using seawater to regenerate an AIX process, the columns were operated over 78 hours and 279 bed volumes until sulfate exhaustion was reached using the city's IX feed water. The columns were then regenerated using filtered Sarasota Bay seawater in a counter-current flow configuration until effluent conductivity values matched that of the seawater, approximately 53,300µS/cm, and rinsed using distilled water in a co-current flow configuration until effluent conductivity values matched that of the city's IX feed water, around 1,000µS/cm. Table 3 outlines the water quality characteristics of the filtered Sarasota Bay seawater.

Once regenerated, the columns were operated again over 78 hours, until sulfate exhaustion was reached. Samples from each column were collected in 125-mL plastic bottles at the start of operation, 18 hours into operation, and every four hours up to 78 hours of use. The same operation-regeneration-rinse process was repeated using a 10 percent salt solution during regeneration procedures for comparison to seawater. Saturation loading curves were determined and competing anions were analyzed to identify the elution of any additional anions, which may have exchanged onto the anion resin during operational runs. It was found that during seawater regeneration conditions, bromide concentrations in the treated water samples exceeded that of the city's IX feed water entering the pilot unit, indicating the occurrence of bromide leakage.

Table 2. Anion Exchange Pilot-Scale Operating

Parameter	Units	Pilot-Scale
Surface Loading Rate	gpm/SF	2.80
Volume Loading Rate	gpm/CF	0.446
Empty Bed Contact Time	min	16.8
Media Volume	CF	0.308
Media Height	ft	6.20
Bed Diameter	in	3.00
Flow Rate	gph	8.24

Table 3. Filtered Sarasota Bay Seawater Quality Characteristics

Parameter	Units	Filtered Sarasota Bay Seawater
pH	s.u.	8.02
Temperature	ºC	24.5
Conductivity	µS/cm	53,300
Turbidity	NTU	3.37
Alkalinity	mg/L as $CaCO_3$	111
TDS	mg/L	33,100
Sulfate	mg/L	2,640
Chloride	mg/L	18,200
Bromide	mg/L	80.5
Fluoride	mg/L	<0.10
Calcium	mg/L	399
Magnesium	mg/L	1,270
Sodium	mg/L	10,900

Disinfection Byproduct Formation Potential Evaluation

Upon determination of bromide as a competing anion, the operation-regeneration-rinse process was repeated using only the Thermax A-32 resin, collecting bulk water samples in five-gal tote containers at periodic time intervals. Bromide concentrations were measured for each time interval to identify the time period at which the highest level of bromide was found. The bulk water sample containing the highest amount of bromide was retained for use in determining DBP formation potential of the treated water.

To accurately evaluate brominated DBP formation potential of the treated AIX water, chlorine demand was first determined. This was accomplished by dosing several concentrations of chlorine and measuring the residual concentration over time, up to seven days. Chlorine dosage was identified as the dosage that obtained a chlorine residual between 0.2 and 1 mg/L after seven days of incubation at 30ºC, resulting in a determined dosage of 2 mg/L.

Using the determined chlorine dose, DBP formation potentials of the bulk water sample containing the highest amount of bromide were performed. The bulk water sample was split into two different sets: one sample with no alterations (no bypass) and one sample comprised of 33 percent IX feed water (33 percent bypass) to simulate the city's current bypass configuration.

The 33 percent bypass sample did not include blend additions of the city's RO permeate and was not representative of the city's final product water. The TTHM formation potentials were evaluated over a seven-day time period, while incubated at 30ºC.

Results and Discussion

Subsequent operation-regeneration-rinse cycles of the AIX pilot unit were performed using seawater and 10 percent salt regenerate solutions. Columns were fed the city's IX feed water during operational runs. Saturation loading curves were prepared and reviewed for performance and efficiency of sulfate removal. Figure 3 presents the results of both runs, identifying breakthrough and exhaustion values. During seawater regeneration conditions, full-bed sulfate exhaustion was observed at 212 bed volumes for the Purolite A600E-9149 resin and 210 bed volumes for the Thermax A-32 resin. During 10 percent salt regeneration conditions, full-bed sulfate exhaustion was observed at 225 and 220 bed volumes for the Purolite and Thermax resins, respectively

Treated effluent water samples were analyzed for the presence of additional anionic constituents. Concentrations of additional anions found in the treated effluent samples were compared to the city's IX feed water characteristics in efforts to identify the occurrence of anion leakage from seawater. Bromide values in the treated effluent samples under seawater regeneration conditions were observed above the city's IX feed water bromide concentration of <0.2 mg/L, seen in Figure 4a. In comparison, bromide values in the treated effluent samples under 10 percent salt solution regeneration conditions stayed below the city's IX feed water bromide concentration for the majority of operation, as shown in Figure 4b.

To further investigate the extent of bromide leakage under normal operating conditions, columns containing Thermax A-32 resin were regenerated with seawater and run until sulfate exhaustion was reached, collecting bulk water samples of the treated effluent at periodic time intervals. At 60 hours of operation, 215 bed volumes, a bromide concentration of 4.50 mg/L was observed in the treated effluent. Bulk water taken at this time was retained for use in determining DBP formation potentials. Figure 5 illustrates TTHM concentrations of the bromide-containing effluent water reaching 134µg/L at 168 hours (seven days). When blended with a 33 percent bypass of the city's IX feed water, TTHM concentration increased to 197µg/L at 168 hours.

The TTHM formation is comprised of four regulated DBPs that include chloroform, bromodichloromethane, dibromochloromethane, and bromoform. The compositions of TTHM were evaluated to determine the impacts of increased bromide concentration on brominated DBP formation. As observed in Figure 6, the major component of TTHM concentrations came from bromoform, a brominated DBP. At 168 hours, 85.7 percent of the bromide-containing effluent sample and 87.1 percent of the blended 33 percent bypass sample were comprised of bromoform.

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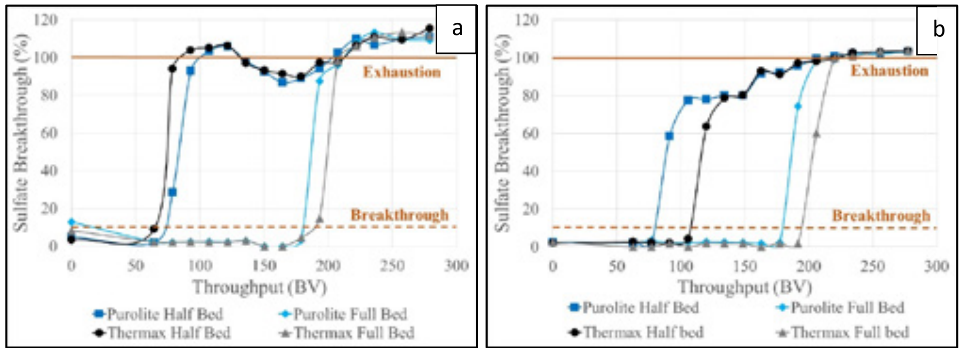

Figure 3. Sulfate Saturation Loading Curves Under (a) Filtered Sarasota Bay Seawater Regeneration Conditions and (b) 10 Percent Salt Solution Regeneration Conditions

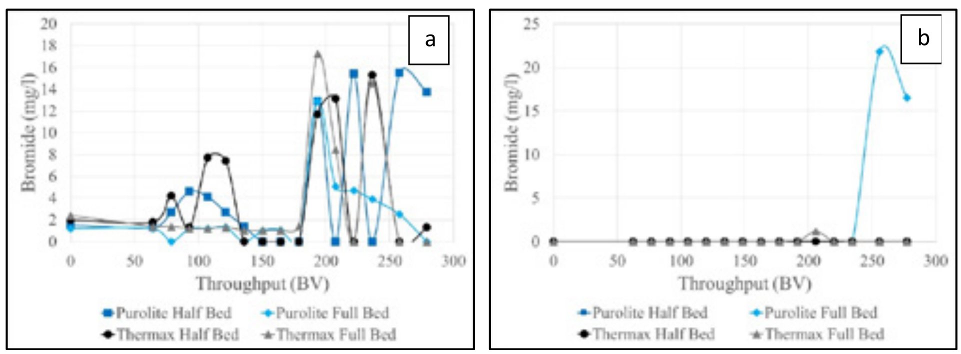

Figure 4. Bromide Elution Concentrations Under (a) Filtered Sarasota Bay Seawater Regeneration Conditions and (b) 10 Percent Salt Solution Regeneration Conditions

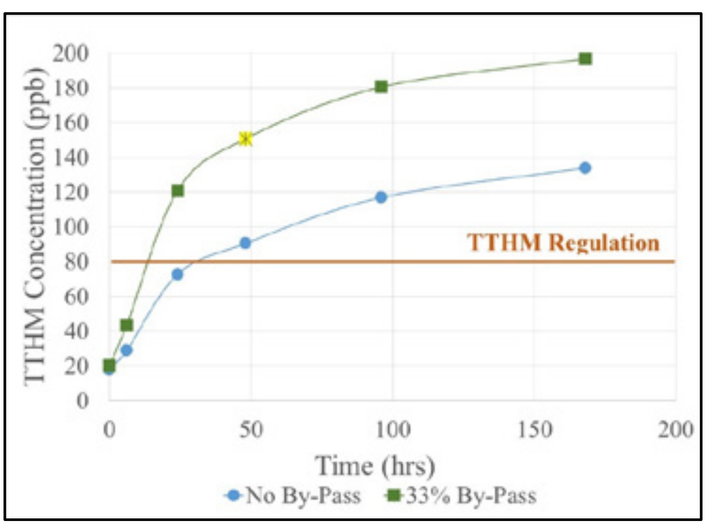

Figure 5. Total Trihalomethane Formation Curves
(x: value exponentially interpolated)

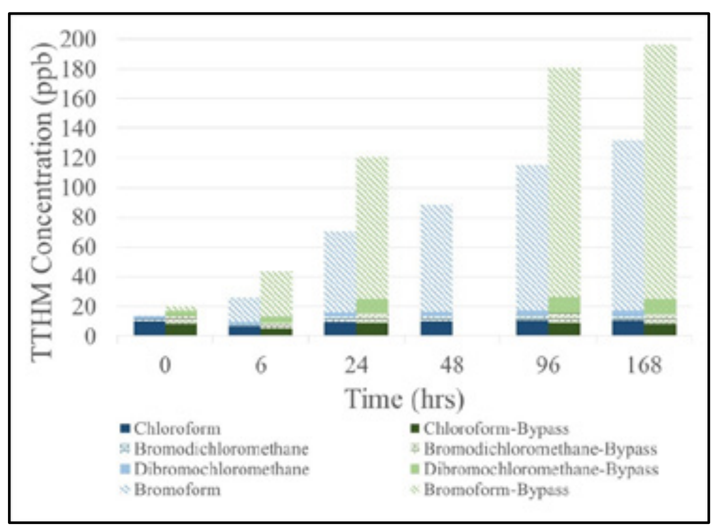

Figure 6. Total Trihalomethane Formation Composition

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Conclusion

During this study, two strong base chloride-form anion resins were tested at the pilot scale for their performance in removing sulfate, and were evaluated for the leakage of competing anions when alternative regenerate solutions were used. A manufacturer-recommended solution of 10 percent salt and filtered Sarasota Bay seawater was utilized to regenerate Purolite A600E-9149 and Thermax A-32 anion resins. Pilot column procedures involved operational runs of the anion resins until sulfate exhaustion was reached, regeneration of the resin media with different solutions, and a rinse cycle of distilled water. Samples were collected at periodic time intervals and analyzed to determine resin performance and anion leakage.

Sulfate exhaustion decreased from 221 to 212 bed volumes in the Purolite resin under seawater regeneration conditions when compared with 10 percent salt. Similarly, sulfate exhaustion in the Thermax resin decreased from 220 to 210 bed volumes. Bromide leakage was identified in both anion resins when seawater was used for regeneration. The resulting bromide concentration at 60 hours of operation, 215 bed volumes, in the treated effluent of the Thermax resin was 4.50 mg/L.

The TTHM formation of the bromide-containing effluent sample reached 134 µg/L after 168 hours of incubation. When blended with 33 percent of the city's IX feed water, the TTHM formation increased to 197 µg/L after 168 hours. The TTHM concentrations were comprised primarily of bromoform, 85.7 and 87.1 percent, respectively, after 168 hours.

Acknowledgments

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NEWS BEAT

The **Florida Coastal Management Program** (FCMP) has announced the availability of federal funds for projects related to coastal resource protection. Priorities include water quality improvements encompassing research, monitoring, or restoration, and protection of vulnerable coastlines. The proposed projects should be able to be completed within 12 months. They should be designed to generate and provide information, plans, or meet needs for protection, coordination. and response to hazards along Florida's coast.

Financial assistance is available in the form of reimbursement grants ranging from $15,000 to $74,000, depending upon availability of federal coastal management funds received from the National Oceanic and Atmospheric Administration (NOAA). The FCMP anticipates that grant recipients will not be required to provide nonfederal matching funds or services. Rule subsections 62S-5.002(4) and .003, F.A.C, describe the procedures for submitting applications and the procedures and criteria by which applications will be evaluated, respectively.

A copy of the rule may be obtained at: https://www.flrules.org/gateway/ChapterHome.asp?Chapter=6 2S-5. There is no specific application form; however, proposals must not exceed 10 pages in length (excluding the title page, project location map, and budget page). For projects involving construction, exotic species removal, and/or habitat restoration, applicants must submit a completed 306A Questionnaire with the application. The Questionnaire is not counted as part of the application page limit. The Questionnaire may be obtained at: https://floridadep.gov/sites/default/files/questionnaire306a.pdf.

Applications must be received no later than 4:00 pm (ET), Nov. 30, 2021. Applications shall be submitted in accordance with subsection 62S-5.002(4), F.A.C., or may be emailed to FCMPMail@FloridaDEP.gov. Mailed applications may be sent to: Florida Coastal Management Program, ATTN: Partner Agency Grants, Department of Environmental Protection, 2600 Blair Stone Road, MS 235, Tallahassee, Fla. 32399-2400.

For questions or to request a copy of Chapter 62S-5, F.A.C., and/or the 306A Questionnaire, contact Mrs. Holly Edmond at the previous address, call (850)245-2181, or send an email to Holly.Edmond@FloridaDEP.gov. in accordance with Section 120.74, F.S.