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Managing Water in the West

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and Development Report No. 140

Use of Dendrimers to Enhance Selective Separation of Nanofiltration and Reverse Osmosis Membranes



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14. ABSTRACT (Maximum 200 words) A novel method to separate boron from seawater was developed. Following a systematic study of materials, new compounds were synthesized with a high density of functional moieties; these new compounds were also able to form a micelle structure that can be easily separated and recovered by ultrafiltration (UF) membranes. A cost-effective technology based on the reaction of a glycidyl ether and amine showed particular promise. Using this technology, a compound was synthesized with glycidyl hexadecyl ether and N-methyl-D-glucamine at mild conditions. The compound showed exceptionally high boron absorption. By adding 3,000 parts per million (ppm) of the synthesized compound to a solution containing 10 ppm boron, all of the boron was adsorbed into the micellar phase. The micellar phase could then be separated from water with the UF membrane, resulting in nearly 100-percent removal of the boron from solution. In the view of commercial application, this study also demonstrated that the boron adsorption compound could be regenerated and reused, reducing chemical costs and waste generation. Finally, various process configurations were proposed for the application of this technology to boron reduction for seawater reverse osmosis plants.					
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**Desalination and Water Purification Research and
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Use of Dendrimers to Enhance Selective Separation of Nanofiltration and Reverse Osmosis Membranes

**Prepared for Reclamation under
Agreement No. 05-FC-81-1176**

by

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**U.S. Department of the Interior
Bureau of Reclamation
Technical Service Center
Water and Environmental Services Division
Water Treatment Engineering Research Group
Denver, Colorado**

August 2009

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Acronyms and Abbreviations

\$/kgal	dollars per thousand gallons
DGEBA	diglycidyl ether of bisphenol A
DMF	dimethylformamide
DMG	N-decanoyl-N-methylglucamine
DMSO	dimethyl sulfoxide
gfd/psi	gallons per square foot of membrane per day/pounds per square inch
HGE	glycidyl hexadecyl ether
HGE-MGA	product from reaction of glycidyl ether with N-methyl-D-glucamine
uS/cm	microsiemens per centimeter
MGA	N-methyl-D-glucamine
MWCO	molecular weight cut-off
NF	nanofiltration
NMP	1-Methyl-2-pyrrolidinone
PAMAM	polyamidoamine
PEI	polyethyleneimine
RO	reverse osmosis
UF	ultrafiltration

1. Executive Summary

A novel method to separate boron from seawater has been developed. A literature review disclosed that compounds containing amine groups, carboxyl groups, and hydroxyl groups can strongly chelate boron from solution. A systematic study found that compounds containing amine and hydroxyl groups are particularly effective for boron absorption. New compounds were synthesized with a high density of these functional moieties, these new compounds were also able to form a micelle structure that can be easily separated and recovered by ultrafiltration (UF) membranes.

A variety of compounds were synthesized to determine their suitability for enhancing boron rejection by reverse osmosis and nanofiltration (NF) membranes. A cost-effective technology based on the reaction of glycidyl ether and amine showed particular promise. As a result, the low-cost, readily available chemicals, glycidyl hexadecyl ether and N-methyl-D-glucamine, were selected. These chemicals could be reacted at mild conditions, stirring at 80 degrees Celsius (°C) without any catalyst, and produced a boron adsorbing compound with a long hydrophobic tail (C16) and a functional hydrophilic head. The synthesized compound formed micelles in a water solution which could be easily separated by a UF membrane having molecular weight cut-off of 10,000 Daltons. The compound showed exceptionally high boron absorption. By adding 3,000 parts per million (ppm) of the synthesized compound to a solution containing 10 ppm boron, all of the dissolved boron was adsorbed into the micellar phase. The micellar phase could then be separated from water with the UF membrane, resulting in nearly 100-percent removal of the boron from solution. The boron absorption by this novel compound was effective at high salinity, such as seen with seawater. At high salinity, the complex resulted in the same boron rejection by a NF membrane.

In the view of commercial application, this study also demonstrated that the boron adsorption compound could be regenerated and reused, reducing chemical costs and waste generation. Further, the boron-chelating ability of the compound was restored after desorption of the boron by an acid solution. Studies showed that the regenerated compound had the same activity as the virgin material. Finally, various process configurations were proposed for the application of this technology to boron reduction for seawater reverse osmosis plants.

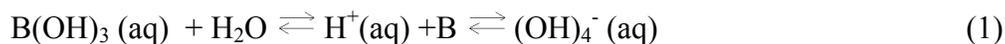
2. Background and Introduction

The production of potable waters can be conducted by removing dissolved materials and ions in water using membrane separation technology with nanofiltration (NF) membranes and reverse osmosis (RO) membranes.

The NF membranes, also called softening membranes, have been developed specifically for treatment of waters that have salinity in the potable range but contain concentrations of some constituent, such as hardness or organic matter, (Bertrand, 1997; Fu, 1995)) that is unacceptably high. Although some NF membranes show 80~90-percent rejection of monovalent ions, such as chloride, sodium, and potassium (Cl^- , Na^+ and K^+), the majority show low rejection of dissolved monovalent ions and are mainly used to remove divalent ions and dissolved organics (Ventresque, 1997). The rejection of divalent ions such as sulfate, calcium, and magnesium (SO_4^{2-} , Ca^{2+} and Mg^{2+}) are significantly higher than monovalent ions. For these loose NF membranes, however, boron rejection is similar to monovalent ions, in the range of 0~10 percent. Because these NF membranes pass monovalent salts and minimize osmotic pressure, they can be used to treat seawater to easily remove components without greatly increasing the pressure for processing. Thus, they may have potential for removing boron, if the boron can be in a form that is easily rejected by the NF membrane.

The RO membranes, especially seawater RO membranes, have very high overall rejection, in the range of 99.5~99.8 percent. These may also benefit from the RO membrane by selectively enhancing boron reduction. However, boron rejection, even of the best seawater commercial membranes, is only 92~93 percent. Engineers would prefer that boron rejection would be more on the order of the membrane salt rejection. The boron rejection of brackish RO membranes at neutral pH is even much lower, in the range of 50~70 percent. Therefore, in RO projects where boron concentration in permeate is specified at the level below 1 part per million (ppm), a partial or complete two-pass system is necessary.

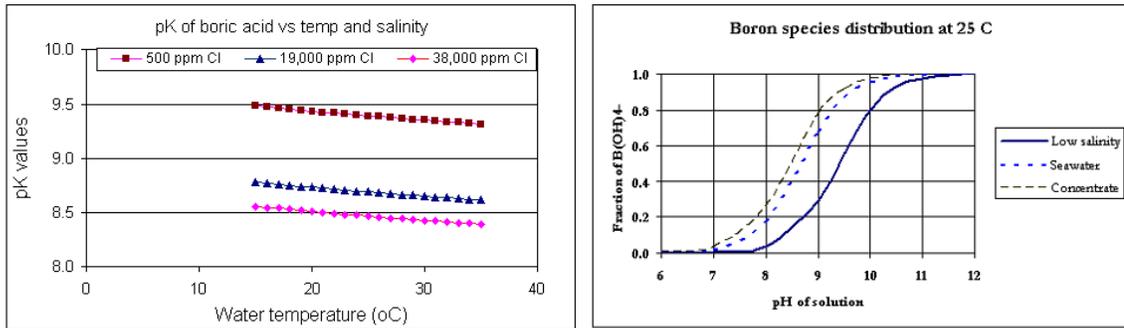
Boric acid is a very weak acid in water solution. Its ionization equilibrium may be represented as:



$$K = \frac{[\text{H}^+][\text{B(OH)}_4^-]}{[\text{B(OH)}_3]} \quad (2)$$

The value of equilibrium constant (K) depends on pH, temperature, and ionic strength, which are a function of water salinity. Figure 1 gives the values of pK

as a function of temperature and salinity of water (A). The value of $-\log(K)$ of boric acid equilibrium constant, designated as pK, is in the range of 8.4–9.5, depending on ionic strength of the solution and temperature (Stumm, 1981). The equilibrium between boric acid and borate ion shifts to higher borate values with increasing pH, decreasing temperature, and increasing ionic strength of solution. The practical importance of this relationship is that, at given temperature and ionic strength, a higher fraction of boric acid will be dissociated in solution of a feed pH. Due to small size and lack of electric charges at low and neutral pH, the boric species are poorly rejected by the RO membranes. At high pH, with an increased ionization rate of boric acid, the rejection rate increases.



(A) (B)
Figure 1. Ionization of boric acid at various conditions: (A) Effect of temperature and salinity and (B) effect of pH and salinity.

Therefore, in the two-pass system, the pH of the second-pass feed has to be increased to about 10 to ionize boric species for increasing boron removal (Gaigon, 2003; Bush, 2003; Wilf, 2005). Economics of this process could be improved by either developing a seawater membrane with higher boron rejection and/or developing a membrane for the second pass that would have high boron rejection but high passage of other ions so that pressure would be minimized.

Research work on the development of a “functionalized” membrane is being conducted at a number of academic laboratories. One of the concepts is to have functionalized molecules on the membrane surface that would serve as “molecular gates” and control passage of species through the membranes (Bhattacharyya, 2003). This idea has its own merits, and it is likely that, in the future, it will be developed to the level that will enable commercial implementation. The potential limitation of this approach is that for each application, a different niche membrane type would be required. Therefore, the specialized membrane would be significantly more expensive than the current membrane elements, which are manufactured and sold almost as commodity products.

A different approach to increase boron rejection is to enhance the selective separation by adding a chemical that would bind specifically to the constituents to be removed. The greater size of the combined molecules would increase their rejection and enable improved separation using the current commercially available membranes. The groups of chemical compounds that can be used for this purpose are nanoscale materials.

Dendrimers are one of the best candidate materials. Dendrimers are nanoscale compounds that can be formulated to have specific affinity for selected group of ions or molecules (Diallo, 2005). The dendrimers are highly branched molecules with functional groups that can be formulated to provide the required properties of water solubility, specific activity, solubility in defined pH range, and so on. Ideally, dendrimers are synthetic macromolecules possessing three-dimensional architecture that consists of a central core; highly branched, but regular iterative building units; and numerous peripheral ending groups (Newkome, 1996; Tomalia, 1990, 1990, 1993, Fréchet, 1994; Majoral, 1999; Fischer, 1999; Bosman 1999; Grayson, 2001). For example, polyamidoamine (PAMAM) dendrimers have been used as chelating agents to remove certain metal ions from waste water (Diallo, 2005) and from contaminated soil (Xu, 2005). Other chelating modified PAMAM and poly(propyleneimine) dendrimers also have been reported to be good ligands for a variety of hard metal cations (Cohen, 2001; Rether, 2003), or to be described as “nanosponges” for the removal of polycyclic aromatic hydrocarbons (Arkas, 2003) or other particles (Pistilis, 2002). However, commercial dendrimers such as PAMAM are too expensive to apply in water treatment. Furthermore, the complicated synthetic method for the preparation and modification of dendrimers leads to higher preparation cost.

Micelles are one of the alternative structures of dendrimers. Ideally, micelles also possess a three-dimensional architectural structure consisting of a hydrophobic core and numerous peripheral hydrophilic ending groups (Tanford, 1974). Amphiphilic compounds can form a micelle structure in aqueous solution. Water-repulsive, long hydrophobic tails aggregate inside of the micelle, which produces nanoscale particles. On the other hand, the surface of micelles is composed of high-density hydrophilic moieties, as shown in figure 2. Even though the size of micelles depends upon the aggregation number and length of hydrophobic chain, nanoscale micelles can be prepared by controlling the length of hydrophobic chains and the concentration of materials. To remove species of interest from water, the hydrophilic peripheral area of the micelles must be designed with special functional groups that recognize and bind the species of interest, such as boron.

Design of an RO membrane processing system is another challenge in the reduction of boron content from water. Poor rejection of boron species by RO membranes can be improved with the modification of the membrane processing system and operation conditions. At elevated pH, the ionization rate of boric species increases, improving the rejection rate. Especially in the semiconductor industry, RO operation at elevated pH has been applied in processing first-pass pass RO permeate (Faigon, 2003; Bush, 2003; Wilf, 2005). Seawater applications with low boron concentration limits usually require a two-pass system configuration. In such a design, permeate produced in a seawater system operating at low or neutral feed pH is reprocessed with brackish RO, operating at elevated feed pH. A simple two-pass configuration has a disadvantage of low overall recovery rate, increased processing cost, potential scaling of the second-pass unit, and inability to consistently produce a permeate with very low boron concentration.

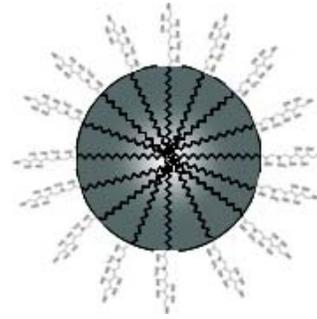


Figure 2. Schematic diagram of micelle structure.

Therefore, research for the purification of water with limited boron was conducted using two approaches, including the development of compounds showing binding affinities with the boron and the design of RO membrane processing system through application of specially developed compounds.

3. Conclusions and Recommendations

Literature reviews indicated that compounds composed of amine groups, carboxyl groups, and hydroxyl groups can strongly chelate boron molecules. A systematic study for the moieties showing good boron absorption resulted in the study of amine and hydroxyl groups, which show very high boron absorption from water. In addition, molecular complexes were designed with a high density of the functional moieties and which form micelle structures, which can be easily separated using UF membranes. For industrial application of the technology, a simple method was developed to synthesize the chemicals at low cost. The compound of interest was the reaction of glycidyl ether and amine. Commercially available cheap chemicals, including glycidyl hexadecyl ether and N-methyl-D-glucamine, were selected as glycidyl ether and amine. These chemicals reacted at mild conditions, stirring at 80°C without any catalyst, and produced the desired compound. The compound of interest comprises a long hydrophobic tail (C16) and a functional hydrophilic part. The developed compound formed micelles in a water solution and was separated easily by UF membrane (MWCO 10,000). The compound showed exceptional boron absorption ability from water. By adding 3,000 ppm of the developed compound in 10 ppm boron water, the entire amount of the boron was absorbed by the developed compound. The boron rejection was almost 100 percent when passed to a NF membrane. Almost all of the boron from a 10-ppm solution was absorbed by adding 3,000 ppm of the adsorbing compound. The boron absorption ability of the developed compound was not affected by high salinity. In the viewpoint of commercial application, regeneration and reuse of the boron-absorbed compound leads to lower cost for water purification. The developed compound was successfully regenerated in acid solution. The regenerated compound demonstrated the initial boron-absorption capacity of the virgin material. Consequently, this research successfully developed novel compounds for the absorption and separation of boron, as well as the recovery and regeneration of the adsorbing compound. A cheap method of preparation also was developed and proven.

As described in the experimental results, the new synthesized compound, HGE-MGA, presented exceptional boron up-taking ability from boron-contained water solution. The compound formed a micelle structure in aqueous solution, so that the boron-bonded micelle compound could be separated easily with loose membranes such as nanofiltration or ultrafiltration membrane with low energy. Furthermore, the boron-absorbed compound could be regenerated by simply lowering the pH and recovering the compound by fine filtration.

Because of the exceptional material properties of HGE-MGA, boron-reduced water can be prepared using the synthesized compound. However, in order to enhance the industrial competitiveness of the compound and the purification

procedure for preparation of boron reduced water, the preparation cost of the material should be low and the regeneration procedure of the boron-bonded compound should be simple. In order to prepare the compound at a cost and with a simple regeneration procedure, more study on the materials, as well as the synthetic process, is required. Through these studies, the industrial competitiveness of the material and purification procedure can be improved.

In addition, the synthesized compound can be applied in different areas, such as removing pesticides from water. The functional moiety of the compound absorbs atrazine by chemical interaction. However, the concentration of the pesticide in water is extremely low. In order to remove the pesticide from water, the chemical interaction of the moiety and the pesticide needs to be increased. By high affinity of the functional moiety and the pesticide, low concentrations of the pesticide can be removed.

4. Literature Search

A review of relevant publications was conducted to identify special functional groups that bind the species of interest. Also, system designs for RO membrane processing system were conducted.

The review showed that the absorption of boron by chemicals occurs by formation of a chelate with boron and special functional moieties (Egneus, 1973; Diehl, 1937; Mezzenga, 2000; Ryschkewitsch, 1970; Bic, 2001; Simonnot, 2000; Inukai, 2004; Lesimple, 1991; Rodrigues-Lopez, 2004; Schilde, 1992; Kabaya, 2004). The special functional moieties that interacted with boron such as carboxylic group, amine group, and hydroxyl group are shown on figures 3, 4, and 5.

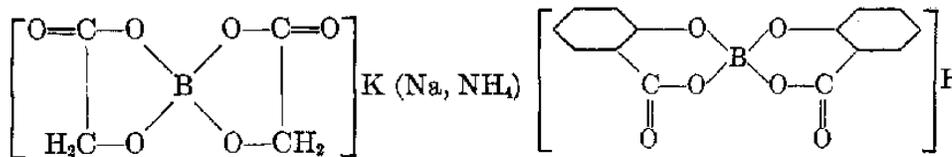


Figure 3. Chelation of boron with one acidic carboxylic group and one hydroxyl group (Boeseken, 1926, 1930, 1933; Rosenjeim, 1924; Wark, 1923).

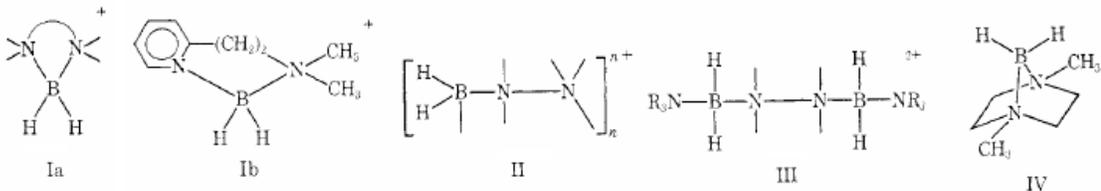


Figure 4. Chelation of boron with two acidic amine groups (Ryschkewitsch, 1970).

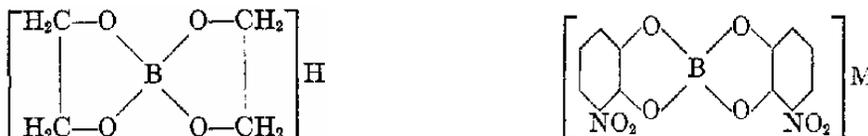


Figure 5. Chelation of boron with two acidic hydroxyls (Anadori, 1931; Boesken, 1936; Franke, 1931; Hermans, 1936).

The mutual effects of the interaction of polyhydroxy alcohols and boric acid have been known for a long time. In the presence of glycerol or mannitol, boric acid becomes a fairly strong monobasic acid and can be readily bound with the bases. Some articles demonstrated that the position of the hydroxyl groups had a great influence on the effectiveness; hydroxyl groups on neighboring carbon atoms and

in the same plane produced the maximum increase in the conductivities of boric acid solutions (Tomalia, 1990). Various glycols exerted different effects on the interaction with boric acid; 1,3-glycols showed a pronounced effect.

The initial observations were that the promising functional moieties for increased boron rejection could be obtained from hydroxyl groups, N-methyl glucamine (MGA). Literature review of preparation of the compounds composed of similar functional groups was conducted.

The compounds consisting of functional hydroxyl groups (MGA) can be synthesized via modification of peripheral groups of dendrimeric compound or reaction of MGA and others chemicals. The introduction of MGA on the dendrimeric compound having amine groups can be done by reaction with saccharides or lactones, as shown on figures 6 and 7.

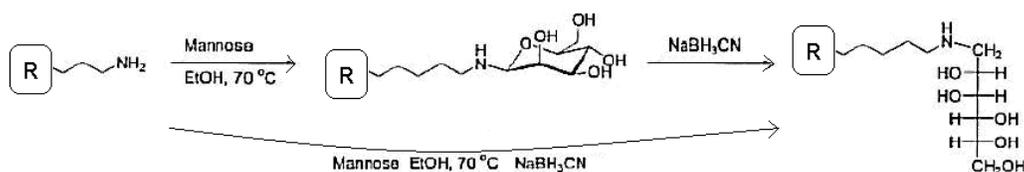


Figure 6. Reaction of amine and saccharides.

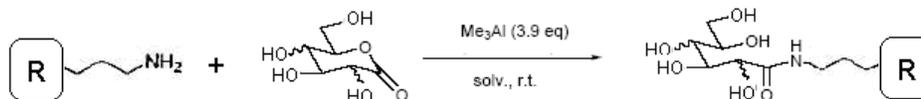


Figure 7. Reaction of amine and lactone.

As mentioned in the introduction, the compounds which form micelles also demonstrate nanoscale behavior with high density of functional groups on the surface of the structure. Preliminary evaluation of N-decanoyl-N-methylglucamine (DMG), composed of a long hydrophobic tail (decanoyl) and a hydrophilic hydroxyl functional group (methylglucamine), showed formation of micelles and promising boron rejection, without decline of permeation of flux. The compound so composed can be prepared by reaction of an amine with an epoxy. The reaction of glycidyl ether and amine is convenient and feasible method (Mezzenga, 2000). The reaction occurs by a ring opening mechanism in mild conditions without any catalyst and byproduct, as shown on figure 8.

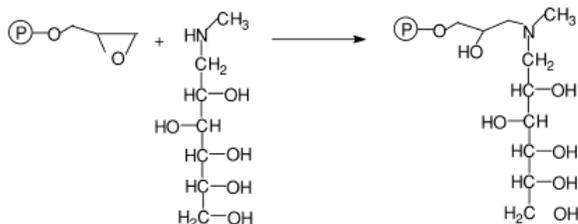


Figure 8. Reaction of glycidyl ether and amine.

The amphiphile structure can form a micelle structure in the aqueous solution as DMG. This amphiphilic chemical structure provides nanoscale micelles having a high density of hydrophilic functional groups at the surface of micelles. The micelle particles can be separated easily using an ultrafiltration membrane with low energy for regeneration.

Numerous studies on the design of RO membrane systems have been conducted (Melnik, 2005, Pastor, 2001; Sahin, 2002; Nadav, 1999; Almullaa, 2003; Redodo, 2003; Chua, 2003; Qm, 2005; Taniduchi, 2001; Sallangos, 2001; Magara, 1998; Prats, 2000; Glueckstem, 2003; Vial, 2003). Reduction of boron concentration using a reverse osmosis process presents a design challenge due to poor rejection of boron species by RO membranes at neutral and low feed pH. The low rejection rate is due to the lack of charges of the boric molecule. Increasing the pH of the feed water increases the ionization degree of the boric species, which improves the rejection rate. Increasing the boron rejection at elevated pH has been utilized in RO system processing of low-salinity water. Operation at elevated pH has been applied in processing first-pass RO permeate, especially in semiconductor industry reverse osmosis. For boron reduction in brackish water, the HERO (1) process has been developed, which, for some water compositions, enables high pH RO processing of water containing a significant quantity of calcium hardness and alkalinity. In high-salinity cases, such as seawater application, a two-pass system configuration is usually adopted. In such a design, the first pass is operated at low or neutral feed pH, but the second pass, which is permeate of the first pass, is reprocessed at an elevated feed pH. However, a simple two-pass configuration has a disadvantage of low overall recovery rate, potential scaling of second-pass RO units, and difficulty producing consistent permeate with very low boron concentration, which results in high water cost. Stringent boron specifications in number of large seawater systems being built recently resulted in development of new design configurations. These include multistage RO processing of first-pass permeate and incorporation of boron specific ion exchange units.

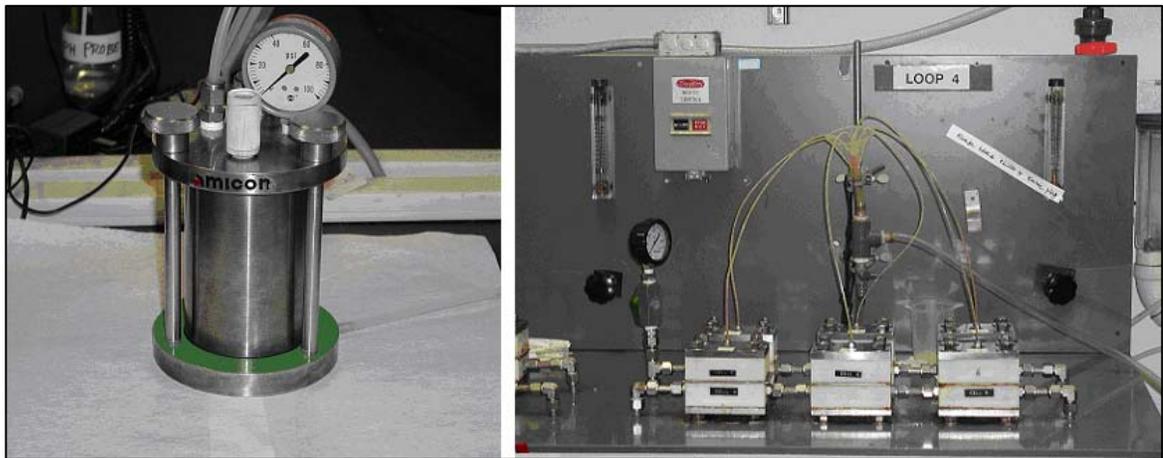
5. Experimental Results and Discussion

5.1 Evaluation Conditions

To evaluate the boron-absorption ability of developed materials from water, selected amounts of the new material were added to the feed water, which was composed of 10 ppm boron and 1,500 ppm sodium chloride. After adding the developed material in water, the solution was mixed for 4 hours to absorb the boron by the test material. After mixing, the boron-absorbed materials were removed using a membrane. Finally, the unabsorbed residue amount of boron in the filtrated solution was evaluated. The boron-absorption ability of the developed material was calculated by comparing the boron amount in the feed solution and the filtrated solution.

5.1.1 Filtration Device

The rejection of the boron-bonded materials from the water solution by filtration was conducted using a batch-type, single-pressure cell (A) and a circulating pressure filtration system (B), as shown on figure 9.



(A) (B)
Figure 9. Filtration cell and system for removing the boron bonded materials from water solution: (A) batch-type, single-pressure cell and (B) circulating pressure filtration system.

5.1.2 Filtration Membrane

The unabsorbed residual amount of boron in the mixed solution of boron, as well as the sodium chloride, was evaluated after removing all of the boron absorbed material. The boron-absorbing compound was filtrated from the solution with a membrane. The membrane should reject all of the boron-bonded material but pass the dissolved salts, including the free boron. The permeation of the boron-

bonded material through membrane contaminates the filtrated solution, which leads to high residue amount of boron and low boron absorption ability of the tested material. On the other hand, rejection of free boron by the membrane results in low residue amount of boron and high boron absorption ability of the evaluated material.

5.1.2.1 Characterization of ESPA2+ Brackish RO Membrane

To ensure no false readings from the filtering membrane, the membranes were tested with standard saline test solutions. The initial test was conducted using a sheet of ESPA2+ RO membrane, which is a composite aromatic polyamide membrane. The nominal performances of an ESPA2+ spiral-wound element are 99.6-percent salt rejection and a specific permeability of 0.23 gallons per square foot of membrane per day/pounds per square inch (gfd/psi).

As previously stated, boron rejection varies with the pH. Therefore, in order to know the variation of membrane properties, the membrane performance was evaluated at different pHs of feed solution. The test was conducted in the feed pH range of 5–9. Feed salinity was maintained at the level of about 3,000 microsiemens per centimeter (uS/cm), which is a typical standard test condition. The tests were conducted at two settings of feed pressure: 100 psi and 150 psi. This corresponds to two levels of flux rate, as shown on figure 10.

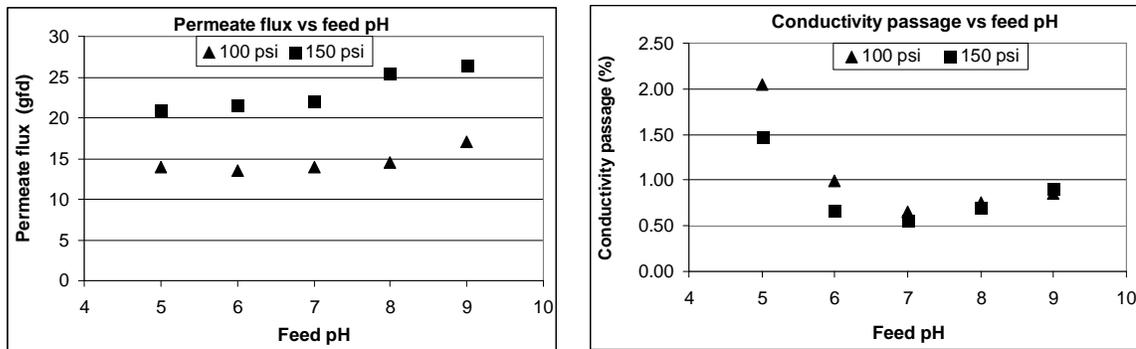


Figure 10. Permeate flux results of ESPA2+ membrane.

The flux and salt rejection of the membrane were changed as a function of pH at the same pressure. In the studied pH range, the flux of the RO membrane increased as the pH increased. The conductivity (salt passage) of the permeate decreased as the feed pH increased up to pH 7 but increased as the pH increased above this level.

The effect of pH on the boron passage of the ESPA2+ membrane is shown on figure 11 and on table 1. The results presented on figures 11 are the average of results from six test cells, as shown in table 1. The effect of feed pH on boron

passage is rather unexpected—in the lower pH range of 5–8. An increased passage of boric species with an increased feed pH is observed until feed pH 8. The subsequent decline of boron passage at feed pH 9 is expected due to increased ionization of boric species. It was decided to repeat this experiment to increase confidence in results before attempting to explain these phenomena.

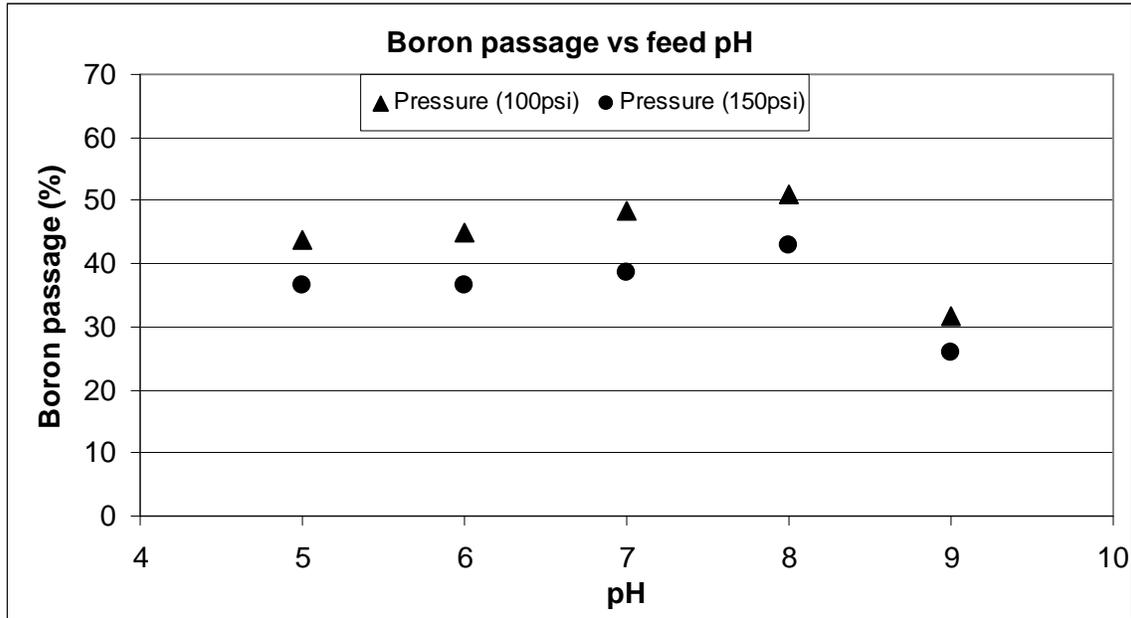


Figure 11. Boron passage of ESPA2+ membrane.

Table 1. pH Dependence of Boron Passage on ESPA2+ Membrane

Pressure (psig)	pH	Boron concentration (ppm)							
		Feed	Permeate						Ave
			Cell 1	Cell 2	Cell 3	Cell 4	Cell 5	Cell 6	
100	5	11.5	5.04	4.99	4.88	5.04	4.93	5.30	5.03
	6	11.7	5.40	5.26	5.20	5.25	5.05	5.46	5.27
	7	11.7	5.66	5.76	5.68	5.79	5.37	5.77	5.67
	8	11.3	5.89	5.68	5.74	5.80	5.57	5.96	5.77
	9	11.7	3.78	3.68	3.72	3.65	3.56	3.77	3.69
150	5	11.4	4.30	4.18	4.16	4.21	3.93	4.23	4.17
	6	11.5	4.40	4.22	4.20	4.19	3.94	4.34	4.22
	7	11.7	4.66	4.51	4.54	4.54	4.24	4.62	4.52
	8	11.8	5.12	4.99	4.77	5.24	4.96	5.34	5.07
	9	11.2	3.00	2.90	2.92	2.90	2.80	2.96	2.91

5.1.2.2 Characterization of ESNA2 Nanofiltration membrane

Initial tests of the high-permeability RO membranes, ESPA2+, showed that the membrane performance was affected by the pH of the feed water and operation pressure. In addition, there was some natural variability of permeability and

rejection of different testing membrane segments. This variability of baseline performance complicated the interpretation of test results that were conducted in presence of materials added for improvement of boron rejection.

A second set of tests were conducted with ESNA2 nanofiltration membranes. These NF membranes have very low rejection of sodium chloride and boron but high rejection of large molecules, such as sulfate and the organic materials added for adsorption of boron. Therefore, any improvement of boron rejection can be easily identified, since only adsorbed boron will be rejected by the ESNA2 membrane.

Tests were conducted to define water flux and rejection of boron, MgSO₄, and organic molecules by NF ESNA2 membranes. The organic molecules selected for rejection test were sucrose and polyethyleneimine (PEI) of two sizes (MW: 1,800 and 10,000 Daltons). The tests were conducted with six coupons at a feed pressure of 150 psi, and an average of the six coupons was taken as the representative values, as shown in table 2.

Table 2. Summary of Characterization of NF ESNA2 Membranes

Membrane type		ESNA2	ESNA2
Lot #		R 571404000	R 592802000
Permeate flux (gfd)		47.26	54.29
Rejection (%)	Boron	7.54	6.51
	MgSO ₄	99.01	99.29
	Sucrose	99.85	99.51
	PEI 1,800 MW (8,000 ppm)		99.88
	PEI 1,000 MW (8,000 ppm)		99.97

The results listed in table 2 indicate that the selected membrane had high passage of boron species. However, it had high rejection for MgSO₄, sucrose, and PEI, indicating it was a good membrane for filtering the boron-chelating compound.

5.2 Preliminary Evaluation of Dendrimeric Compounds

5.2.1 Preliminary Screening of Dendrimeric Compounds with ESPA2+ Membrane

The evaluation and selection of dendrimeric compounds for screening tests was conducted by Dr. Amane Michizuki and Dr. Sheng Li from Nitto Denko Technical Corporation. The compounds selected are designated as D1, D2, and D3. All three dendrimers belong to poly(amidoamine) compounds with different peripheral groups such as D1-NH₂, D2-OH, and D3-COONa. The configuration of dendrimers is provided on figure 12.

The results of testing are shown in table 3. D0 designates the reference test without the use of dendrimers. D1–D3 designates tests with dosings of 10 ppm of corresponding dendrimers.

The unmodified commercial dendrimeric compounds, including D1, D2, and D3, showed minimal increase in boron rejection. Before adding the materials, the ESPA2+ membrane showed 45.98 percent of boron rejection (D0). By adding the compounds, the boron rejection was improved by about 5 percent.

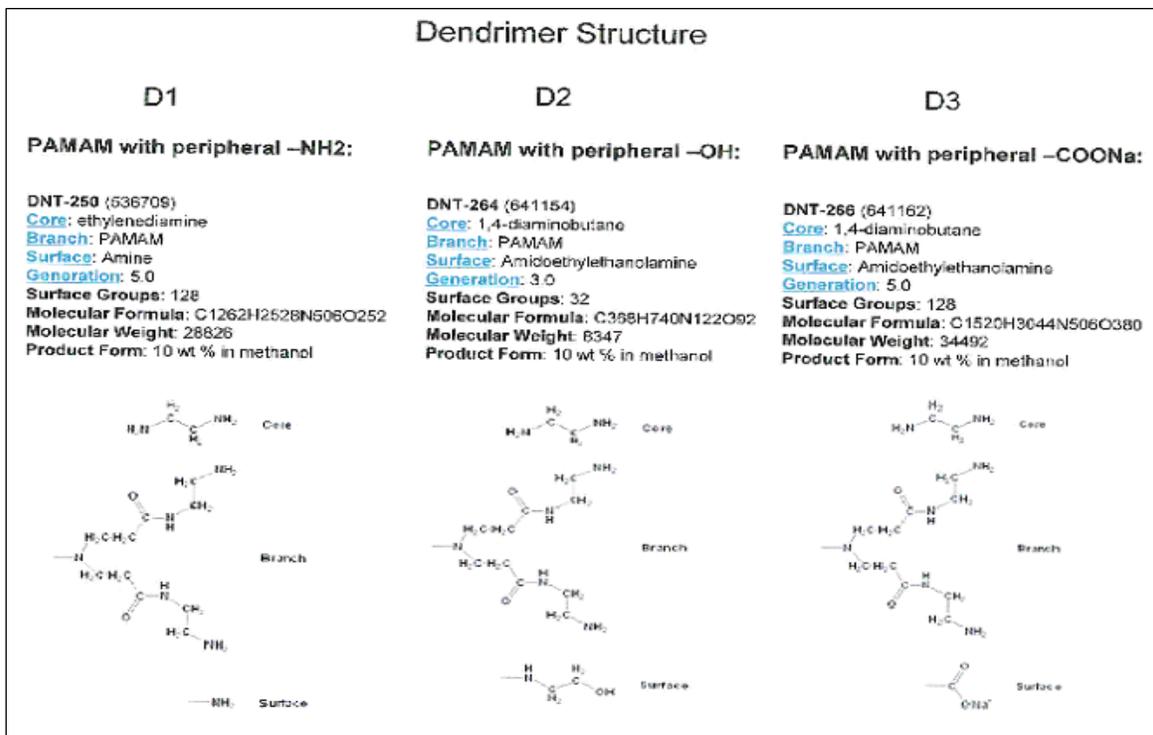


Figure 12. Dendrimer structure of D1, D2 and D3.

Table 3. Summary of Rejection Results in Presence of Dendrimers

Test ID	Peripheral groups	Feed pH	Conductivity rejection (%)	Boron rejection (%)
D0	-	7.9	97.51	45.98
D1	–NH ₂	6.7	97.70	50.25
D2	–OH	7.3	98.60	51.85
D3	–COONa	6.7	98.47	48.38

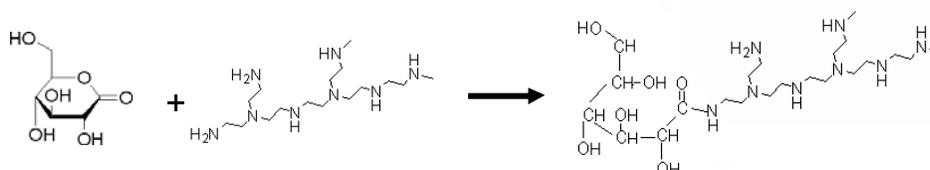
5.2.2 Preliminary Preparation of Dendrimeric Compounds

Review of relevant literature was conducted to find chemical compounds that would have a structure with good potential for selective boron bonding. Based on a literature survey, gluconolactone was selected for the preparation of the

hyperbranched polyethyleneimine having peripheral OH groups. The reaction mechanism and condition are shown on figure 13.

Several PEI-based compounds were prepared; the configurations of dendrimer and preparation conditions are provided on figure 14. 2D6 and 2D7 (2D8 and 2D9) are the same compound, but prepared twice under the same conditions.

Reaction mechanism: Ring opening reaction



Gluconolactone, Hyperbranched PEI (MW: 1,800 and 10,000)

Reaction process (Schmitzer, 1999)

- Solvent: Dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (anhydrous)
- Mole ratio: PEI(1st+2nd amine)/gluconolactone= 1/1.1
- Temperature: 40 °C
- Time: 8 hrs @ 40 °C and 14 hours @ room temperature
- Stirring in argon environment

Figure 13. Reaction of PEI and gluconolactone.

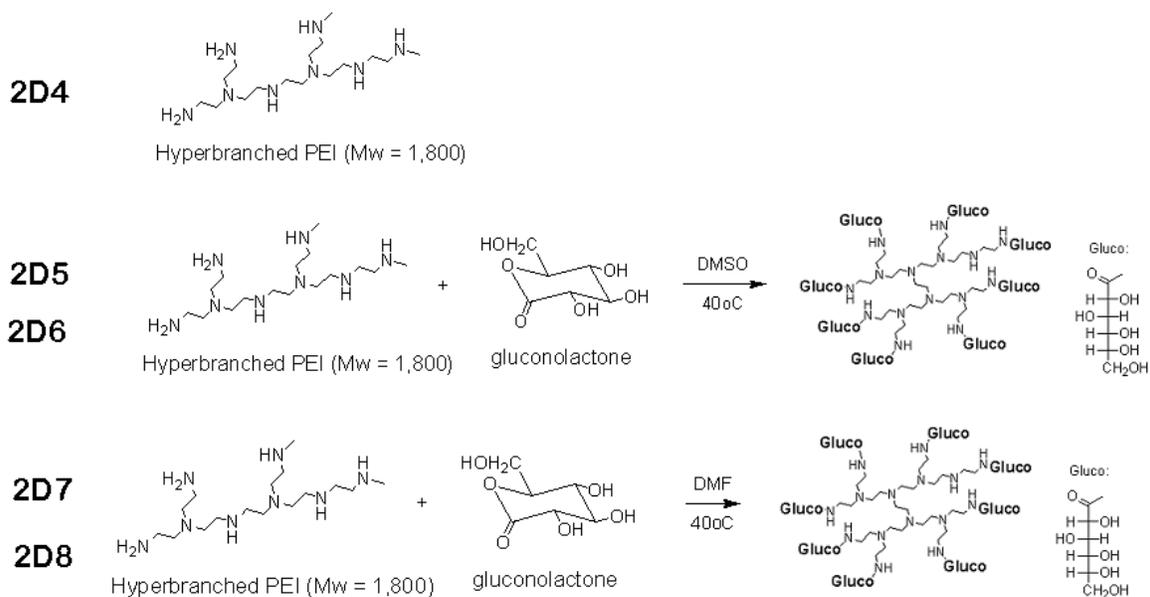


Figure 14. Reaction of PEI and gluconolactone.

Evaluation of the prepared compounds was conducted with ESPA2+ membrane at 150psi. The results are summarized in table 4. As a base line, the unmodified compound (2D4) was evaluated. The unmodified compound showed about 21% improvement of boron rejection. However, the modified compounds including 2D6, 2D7, 2D8 and 2D9 showed improved boron rejection, but not as much as the unmodified compound (2D4). This result implied that the boron absorption ability of the modified compound was not significant, likely due to the low concentration of the boron absorbing species. It was decided to study the effect of adding higher concentrations of the boron adsorbing compound.

Table 4. Boron rejection of PEI-Based Compound

Compounds	Sample ID	Concentration (ppm)	Boron rejection (%)		Rejection difference
			Without compound	With compound	
PEI (MW 1,800)	2D4	20	27.1	49.4	21.3
PEI – Glucose	2D6	20	35.8	45.6	9.7
PEI – Glucose	2D7	20	43.8	54.1	10.3
PEI – Glucose	2D8	20	42.3	49.7	7.4
PEI – Glucose	2D9	20	42.3	49.7	7.4

The effect of the boron-adsorbing compound was studied by changing the concentration from 80 to 8,000 ppm. Separation was made using the NF membrane (ESNA2), which showed low boron rejection without adding the evaluation compounds. The results of boron rejection at different concentrations of different MW PEIs (EI MW 1,800 and MW 10,000) are shown in table 5.

Table 5. Effect of PEI Concentration on the Boron Rejection

Compounds	Concentration (ppm)	Boron rejection (%)		Rejection difference
		Without PEI	With PEI	
PEI-1800 MW	80	1.8	3.6	1.8
PEI-1800 MW	400	2.7	5.5	2.8
PEI-1800 MW	800	0.9	13.2	12.3
PEI-1800 MW	8,000	0.0	40.7	40.7
PEI-10,000 MW	80	0.8	1.9	1.1
PEI-10,000 MW	400	1.5	1.9	0.4
PEI-10,000 MW	800	4.0	6.0	2.0

The results in table 5 indicate an increasing effect on boron rejection with an increasing concentration of PEI in solution. The improvement of boron rejection, especially by adding 8,000 ppm of PEI-1,800, was much improved. This result

implied that the concentration of the testing compound is important to clarify the properties of the modified compounds.

To evaluate the effect of molecular size of polyethyleneimine on boron rejection, tests were conducted with PEI-10,000 MW at the same conditions as conducted with PEI-1,800 MW. The results shown in table 4 are quite unexpected, as the overall boron rejection was negligible, and no significant effect of concentration on boron rejection has been observed. At this time, there is no plausible explanation of these results. Possible causes may include clustering large PEI-10,000 MW molecules as compared to PEI-1,800 MW. However, no direct evidence or literature information is available to support such assumption.

Various PEI-based compounds, such as different peripheral groups like $-NH_2$ (D1), $-OH$ (D2), and $-COONa$ (D3); different molecular weights, including MW 1,800 and 10,000; and modified compounds (D6, D7, D8, and D9), were evaluated. PEI-1,800 MW showed improved boron rejection. However, all other cases did not show significant improvement of boron rejection. Based on these results, further experiments were conducted to screen compounds showing high boron absorption.

5.3 Screening of Dendrimeric Compounds

5.3.1 Chlorhexidine

One amine compound, chlorhexidine, was screened for performance. The chemical structure of chlorhexidine, which is composed of biguanide, is

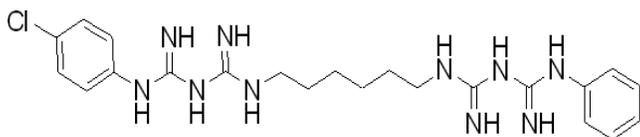


Figure 15. Chemical structure of chlorhexidine.

shown on figure 15. This compound is similar to PEI (figure 2). This chemical shows good solubility in water solution and excellent antiseptic properties.

This compound was evaluated using NF and RO membranes as shown in table 6. The boron rejection improvement of chlorhexidine was better than that of PEI. By adding chlorhexidine, the boron passage decreased about 43 percent and 26 percent for NF and RO membranes, respectively. However, the water flux by adding this compound decreased significantly. Water flux declined by about 67 percent and 66 percent for NF and RO membranes, respectively. The huge water flux decline is due to coating of chlorhexidine on the surface of the membrane. The chemical property of chlorhexidine is similar to the membrane barrier layer, resulting in high interaction between chlorhexidine and the barrier layer of membrane. High interaction results in attraction and fouling of the

membrane surface. The improvement of boron rejection also seems due to the low permeability of the added organic layer.

Table 6. Tests with Chlorhexidine Results

Membranes	Concentration (ppm)	Running time (min)	Results			
			Flux (gfd)	Flux decline (%)	Boron rejection (%)	Imp Boron Rejection (%)
NF membrane (ESNA 2)	8,000	Baseline	37.8	67.1	8.4	42.8
		152	12.4		51.2	
RO membrane (ESPA 2)		Baseline	23.2	65.8	63.2	26.2
		152	7.9		89.4	

5.3.2 N-decanoyl-N-methylglucamine (DMG)

Another compound composed of hydroxyl groups, N-decanoyl-N-methylglucamine was screened. DMG consists of hydrophilic functional groups and a long hydrophobic tail.

The hydrophilic functional group consists of one amine group and a multitude of 1,3-hydroxyl groups, as shown on figure 16. This chemical is dissolved in water solution but makes micelle structure at concentrations above 3,000 ppm at pH 8.0.

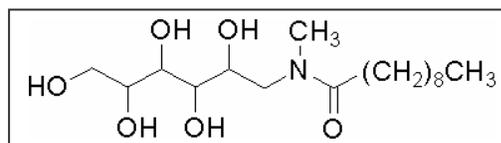


Figure 16. Chemical structure of N-decanoyl-N-methylglucamine.

Tests with DMG were conducted initially at a concentration of 8,000 ppm (table 7) and then in concentration range of 22–80,00 ppm (table 8). The evaluation conditions are the same with other compounds: 8,000 ppm DMA, 10 ppm boron, 1,500 ppm sodium chloride, pH 8.0, and pressure 150 psi. For DMA evaluation, the ESNA2 NF membrane was again used. Initial testing at concentration of 8,000 ppm was conducted twice with the same evaluation conditions using different membrane coupons. The results are shown in table 7.

Table 7. Results of Evaluation of DMA at 8,000 ppm

Membranes	Concentration (ppm)	Running time (min)	Results			
			Flux (gfd)			
NF membrane (ESNA 2)	8,000	Base line	71	-7~-14	6.9	89~92
		1st test	76.0		95.5	
		2nd test	81.0		98.5	

By adding the compound, the membrane flux did not decrease. However, the boron rejection was greatly improved. Almost 90 percent of 10-ppm boron was absorbed by 8,000-ppm DMG.

Following positive test results with DMG at concentration of 8,000 ppm that showed promising increase of boron rejection without decline of permeate flux, tests were run at various DMG concentrations. The results are summarized in table 8.

Table 8. Summary of Boron Rejection Results with Different DMG Concentrations

Membrane (Lot #)	N-Decanoyl-N-methylglucamine (DMG)	Flux (gfd)	Boron rejection (%)
ESNA 2 (R 592802000)	22 ppm (1:1)	94.0	0.0
	55 ppm (1:5)	76.0	4.3
	220 ppm (1:10)	67.0	2.6
	2,200 ppm (1:100)	86.0	77.9
	8,000 ppm (1:363)	81.0	98.5

The results with DMG were very promising. The rejection of boron was increased without any significant decrease of permeate flux. Since DMG shows higher interaction with water than the barrier layer of the membranes, the flux decline of membrane is negligible. The results imply that the compound does not foul the surface of membrane but strongly absorbs boron from water solution. The improvement of boron rejection was due to the absorption of boron by the compound and the high rejection of this complex by the membrane.

To confirm that similar results can be achieved with RO membranes, DMG was evaluated with dense RO membranes as a function of concentration of DMG and the performance results as shown in table 9 and figure 17.

Table 9. DMG Performance Using Dense RO Membrane

Membrane	Concentration (ppm)	Stoichiometric ratio	Flux (gfd)	Boron rejection (%)
ESPA 2 (RO membrane)	0	Baseline	22.0	35.2
	100	1:4.5	29.0	50.5
	200	1:9	28.0	54.2
	2,000	1:90	24.0	91.0

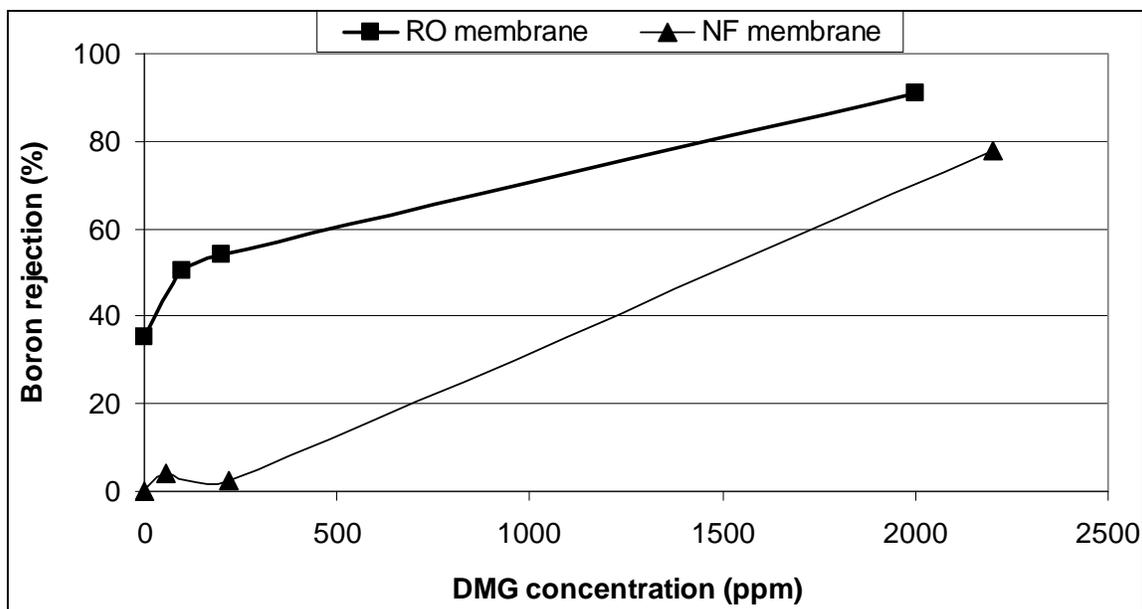


Figure 17. Comparison of DMG performance with different filtering membranes. Note that the performance was evaluated with 11 ppm boron at pH 8.0.

As shown in table 9 and figure 17, DMG also showed improved boron removal capacity for the tighter RO membrane. The tighter membrane showed better boron rejection than the NF membrane. This result is due to the combined effect of the membrane properties and the larger size of the organic-boron complex. The tighter RO membrane itself showed better boron rejection than the NF membrane (see 0 DMG concentration). The tight membrane can reject more free Boron and the Boron bonded material than the NF membrane, resulting in higher Boron rejection.

The results of valuable compound screening show that the compound composed of one amine and lots of hydroxyl groups presents exceptional boron absorption ability without any significant decrease of permeate flux.

Based on the compound screening result, the compound composed of one amine group and lots of hydroxyl groups was selected for removing boron from water. However, application of DMG in membrane area is very difficult because the price of commercial DMG is very expensive. Therefore, the synthesis of a compound having amine and hydroxyl groups was designed and prepared for evaluation.

5.4 Preparation of Dendrimeric Compounds

5.4.1 Molecular Design of New Compounds

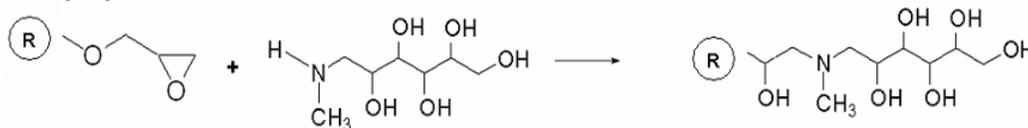
As mentioned above, compounds having amphiphile chemical structure form a micelle structure in aqueous solution. The micelle structure provides many benefits in this application, such as high functional density at the surface of the particles, high surface area because of nanoscale, and easy separation for isolation and regeneration of the compound.

To synthesize the compounds showing good boron absorption ability, ring opening reaction of glycidyl ether and amine, as depicted on figure 8, was selected. N-methyl-D-glucamine (MGA) having one amine and 1,3-hydroxyl groups was chosen as the functional group of the compound. Secondary amine of MGA can react with glycidyl ether easily.

The reactivity of glycidyl ether strongly depends on the electrophilic property as well as on the flexibility of the chemical structure. The compounds with flexible linkage in the chemical structure show good reactivity with the first or second amine. Glycidyl ether compounds such as diglycidyl ether of bisphenol A (DGEBA) reacts with primary amine at room temperature without any catalyst or special reaction conditions.

Based on the information for the synthetic methods and desirable chemical structure of the compound, molecular designs for several compounds were conducted, as shown in figures 18 and 19:

A. Amphiphile structure



(R) : Aliphatic or Aromatic

Figure 18. Reaction of glycidyl ether and N-methyl-glucamine.

B. High functional density

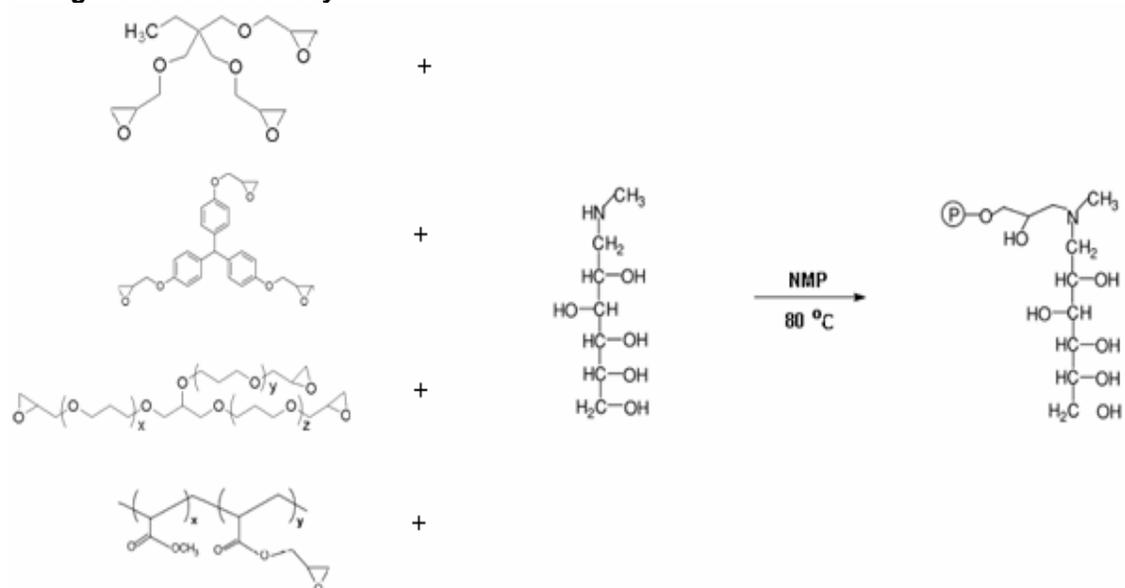


Figure 19. Reaction of multi-glycidyl ether and N-methyl-glucamine.

5.4.2 Synthesis of a New Compound

A new compound having amphiphilic property was synthesized with aliphatic glycidyl ether (glycidyl hexadecyl ether, HGE) and MGA. The prices of both commercial chemicals are low, and the synthesis reaction for the designed compounds is relatively simple. Thus, the designed compounds can be prepared at low cost. The amphiphile is composed of a hydrophobic part with a 16-methylene chain and a hydrophilic part having 6 hydroxyl groups, one amine and one ether. The reaction mechanism and conditions are shown on figure 20.

The reaction was successfully conducted with HGE and MGA in a solvent of anhydrous 1-methyl-2-pyrrolidinone (NMP) under nitrogen atmosphere at 80 °C for 4 hours. The reaction was reactively simple, but the isolation and purification of the synthesized product was difficult because the monomer and the product showed similar solubility.

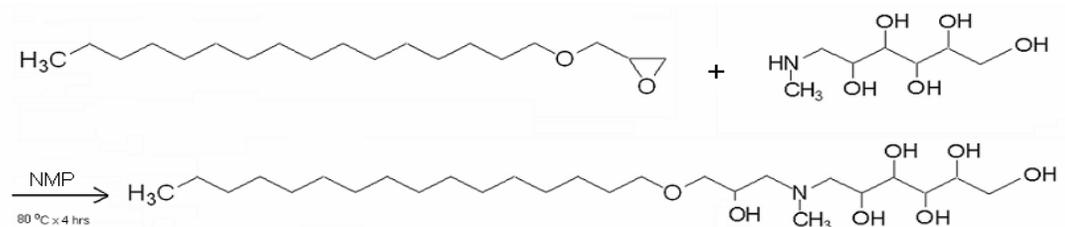


Figure 20. Reaction mechanism and conditions of glycidyl hexadecyl ether and N-methyl-glucamine.

In order to isolate and purify the synthesized material, a systematic solvent study for monomers and the product was carried out as shown in table 10. Because the two monomers have opposite hydrophilic properties, they showed very different solubility. On the other hand, since MGA monomer and the synthesized product have many hydroxyl groups, they exhibited similar dissolving behavior in solvent. By systematic study of the various solvents, one solvent system of 20 percent water and 80 percent acetone was selected for isolation and purification of the product. The solvent system presented good solvent properties for both monomers, but nonsolvent properties for the synthesized product. After three times washing and purification by stirring for 1 day, the final product was vacuum-dried at room temperature and used for testing and evaluation.

Table 10. Solvents for Monomers and the Synthesized Product

Solvents	Monomers		Product (HGE-MGA)
	Glycidyl hexadecyl ether (HGE)	N-Methyl-D-glucamine (MGA)	
Diethyl ether	Soluble	Insoluble	Insoluble
Acetone	Soluble	Insoluble	Insoluble
Butanol	Soluble	Insoluble	Soluble
Isopropyl alcohol	Soluble	Insoluble	Insoluble
Ethanol	Soluble	Insoluble	Insoluble
Methanol	Soluble	Soluble	Soluble
Water	Insoluble	Soluble	Insoluble
Water/Acetone = 20/80	Soluble	Soluble	Insoluble

5.4.3 Evaluation of the Synthesized Compound

5.4.3.1 Concentration of HGE-MGA

The performance of the synthesized compound prepared by the reaction of HGE and MGA was evaluated using an NF membrane. The evaluation conditions were the same as for the above materials, such as adding the testing compound in 10 ppm boron and 1,500 ppm sodium chloride water solution at pH 8.0. The filtration was conducted at 150psi for the NF membrane and 800 psi for the RO membrane. HGE-MGA is insoluble in water and forms a micelle structure. Below 3,000 ppm, the aqueous solution is in a milky state. However, at above 3,000 ppm, the micelle size became bigger by aggregation of the material and the bigger micelles were precipitated. The performance of the new compound as the material concentration is presented in table 11 and figure 21.

Table 11. The Performance of HGE-MGA

Concentration (ppm)	Stoichiometric ratio	Solution state	Flux (gfd)	Boron rejection (%)
0	Base line	Clean	125.6	2.83
300	1:10	Milky	142.0	28.68
1,500	1:50	Milky	73.7	80.19
3,000	1:100	Precipitation	43.7	98.43
4,500	1:150	Precipitation	78.1	99.98

The new synthesized compound exhibited excellent boron rejection as shown in table 11. The boron rejection increased dramatically and reached almost 100 percent at 3,000 ppm of the synthesized compound using the NF membrane. Furthermore, because the new material formed micelles at 3,000 ppm, the micelle can be separated using a loose membrane with low energy. This separation process can provide benefits for recovery system of the boron-bonded material.

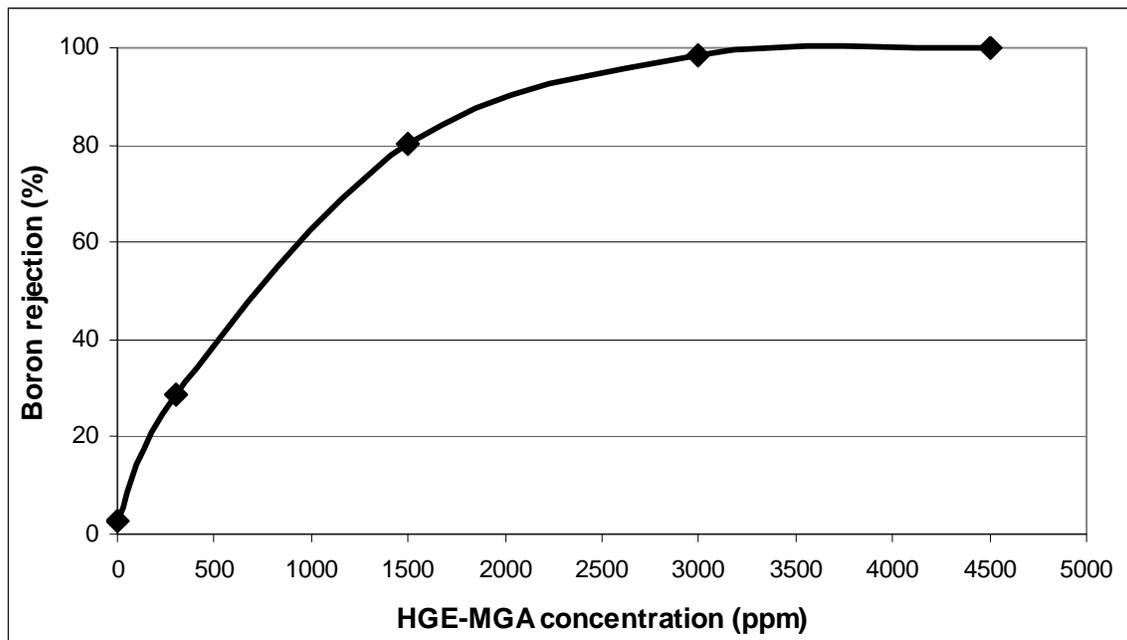


Figure 21. Boron rejection as the HGE-MGA concentration. Note that the rejection was evaluated with 11 ppm Boron at pH 8.0 using NF (ESNA2) membrane at 100 psi pressure.

5.4.3.2 Salinity of HGE-MGA

As explained in the introduction, the ionization of boric acid is different at different salinities. The ionization of boric acid increases with increased salinity, which results in different interaction with the boron-absorption compound and membrane. The effect of salinity of the feed solution on the absorption of boron by the HGE-MGA was tested in different concentrations of sodium chloride, including 4,500 and 1,500 ppm. The results are shown in table 12.

Table 12. Boron Rejection by Adding HGE-MGA in Different Salinities

Sodium chloride concentration (ppm)	HGE-MGA concentration (ppm)	Flux (gfd)	Boron rejection (%)
1,500	Base line	81.9	-
	3,000	90.1	96.3
4,500	Base line	54.6	-
	3,000	62.8	94.9

The evaluation was conducted under the same conditions, such as 3,000 ppm of HGE-MGA and pH 8.0 using NF membrane at 150psi. The boron rejection at high salinity is basically the same as that at lower salinity. The difference of boron rejection is in the range of experiment error. The effect of salinity on the boron rejection is negligible. This result seems due to an excess concentration of the HGE-MGA, compared to the concentration of boron. The high concentration of the HGE-MGA offsets the ionization effect of boric acid at different salinities.

5.4.3.3 Effect of Solution pH

The bonding behavior of boron and the new synthesized compound was studied at different pHs. Boron can make a chelate with oxygen of the hydroxyl group by sharing the lone electron pair of oxygen. For stabilization of the chelation, boron needs to be bonded with more than two lone electron pairs and a maximum of four lone electron pairs of oxygen. However, the interaction of boron and the lone electron pair of oxygen might go down under the high concentration of electrophilic materials such as hydrogen ion. Hydrogen ion is an electrophilic material, which can interact with the moieties having lone electron pairs. The decrease with pH means increasing the concentration of hydrogen ion. Therefore, the interaction of boron with lone electron pairs of oxygen can be affected by pH. Because boron/oxygen and proton/oxygen is a competitive reaction, the lone electron pairs of oxygen might be occupied by hydrogen ion at low pH (high concentration of hydrogen ion). In other words, as pH decreases, the possibility of interaction between boron and oxygen of the hydroxyl group decreases.

To confirm the interaction of boron and oxygen of the hydroxyl group, the boron rejection was evaluated at different pHs; the results are shown in table 13 and

figure 22. As expected, boron rejection decreases with the decrease in pH of the aqueous solution. Notably, boron rejection goes down dramatically below pH 4 and reaches almost no boron rejection at pH 2. The result implies that the lone electron pairs of oxygen of the hydroxyl group were already occupied because of the high hydrogen ion density at low pH so that boron cannot interact with the lone electron pair of oxygen. This result also means that the chelation of boron and oxygen of hydroxyl group is very unstable at low pH. This result demonstrates that the boron-bonding material can be regenerated in acidic solution.

Table 13. The Effect of pH on the Boron Rejection of the New Synthesized Material

Membrane	pH	Concentration (ppm)	Flux (gfd)	Boron rejection (%)
ESNA 2 (NF membrane)	2.0	3,000	8	1.9
	4.0	3,000	10	84.7
	6.0	3,000	11	95.7
	8.0	3,000	90	96.3

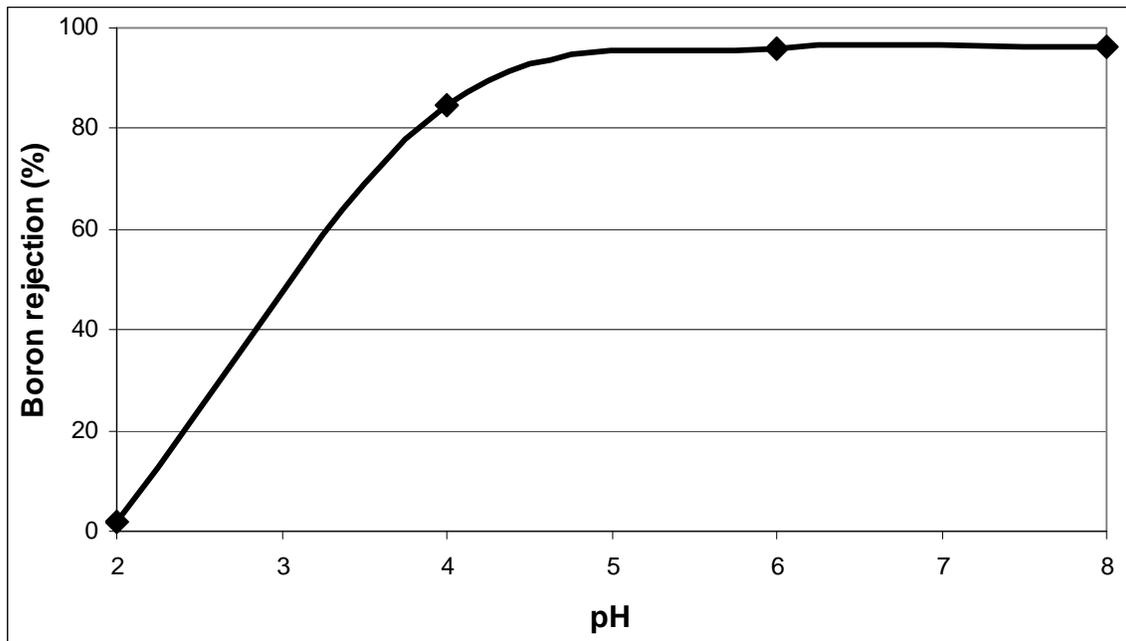


Figure 22. The effect of pH on the boron rejection of the synthesized compound. Note that the evaluation was conducted with 11 ppm boron at 3,000 ppm of the material using NF (ESNA2) membrane at 100 psi pressure.

5.4.3.4 Filtration of Boron-Bonded Compound

The new compound forms micelles in water solution. As mentioned above, the size of the micelle depends on the concentration of the material. Above the critical micelle concentration (CMC, 2000ppm), the micelles were generated.

The filtration of the micelles was conducted by NF membranes. However, if the micelles are large enough to use a UF membrane, the separation of the boron-bonded compound can be conducted with low energy cost. The filtration rate of a UF membrane is about 6 times that of an NF membrane at the same operation pressure.

The boron-bonded compound was separated using a UF membrane. The molecular weight cut-off (MWCO) of the membrane is 10,000 Daltons. The flux and rejection of the boron bonded compound are shown in table 14 and figure 23.

Table 14. The Effect of pH on the Boron Rejection of the New Synthesized Material

Membrane	Run time (minutes)	Flux (gfd)		Compound rejection (%)	Boron rejection (%)
		Baseline	3,000ppm		
Polyethersulfone 10k (UF membrane)	5	51.9	49.2	99	96
	10	46.4	49.2		
	15	49.2	46.4		
	20	49.2	49.2		

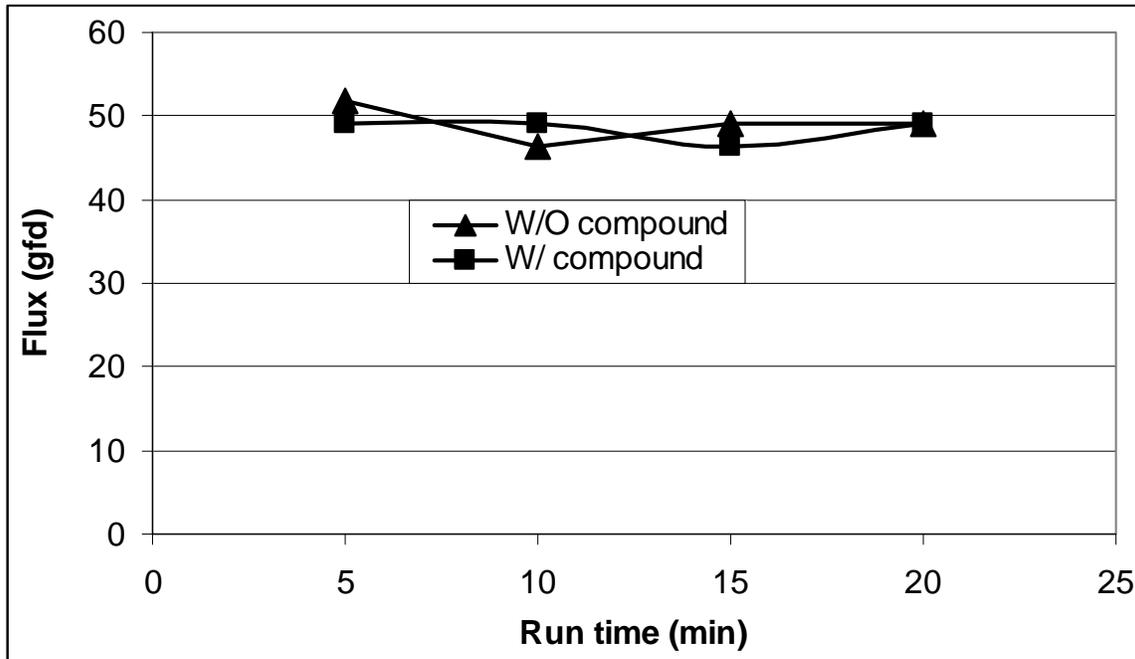


Figure 23. The flux variation of the UF membrane for separation of the synthesized micelle compound. Note that the evaluation was conducted with 10 ppm boron at 3,000 ppm of the compound using a UF (PES 10k) membrane at pH 8.0 and 25 psi.

The UF membrane showed no flux decline during the separation. Furthermore, the rejection of the boron bonded compound and boron was 99 percent and 96 percent, respectively. The results demonstrate that the UF membrane entirely rejects the boron-bonded compound without any decline of water flux. It also demonstrates that boron rejection occurs by absorption of boron on the compound. So, boron can be removed from water by the compound and then reclaimed with a UF (MWCO 10,000) membrane operating at low pressure and low energy consumption.

5.4.3.5 Regeneration of Boron-Bonded Compound

As mention in above, the boron rejection in this system was accomplished by absorption of boron on the developed compound, and then the boron-bonded compound was filtrated using a UF membrane. Therefore, the boron absorption ability of the compound will be decreased by absorption of boron until saturation of the compound with boron. The boron-saturated compound cannot absorb any more boron. To restore the boron absorption ability of the boron-bonded compound, the boron bonded with the compound must be released.

To regenerate the boron-bonded compound, boron saturation and regeneration test were conducted. The results are shown in figure 24 and table 15.

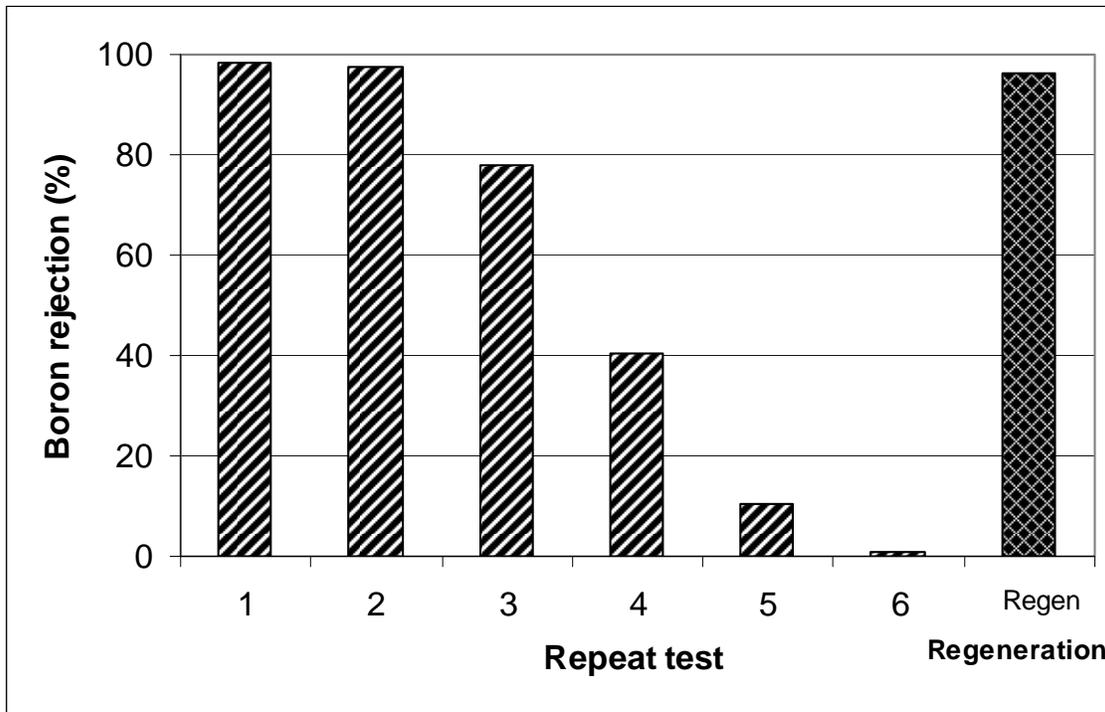


Figure 24. Repeat test of boron rejection and regeneration of the boron-bonded compound. Note that the evaluation was conducted with 10 ppm boron at 3,000 ppm of the compound at pH 8.0.

Table 15. Repeat Test of Boron Absorption and Regeneration of Boron-Bonded Compound

HGE-MGA (3,000 ppm)	Repeat test						Regeneration
	1st	2nd	3rd	4th	5th	6th	
Boron rejection (%)	98.2	97.6	78.0	40.3	10.5	0.9	96.2

Because an excess amount of the compound was added to the water solution to ensure removal of all the boron, the compound still has many free active functional moieties. To test saturation of the compound with boron, the repeat test of boron absorption was conducted by separating the tested compound and then again using the tested compound without regeneration. Figure 24 and table 15 show that the compound was becoming saturated with boron during the fifth repeat test. The compound did not absorb boron by the sixth adsorption test.

Regeneration of the boron-saturated compound was conducted in 1N HCl solution. After 3 hours stirring, the compound was filtered and then used for evaluation by adding in 10 ppm boron and 1,500 ppm sodium chloride solution. The pH of the solution was fixed at pH 8.0. Figure 24 and table 15 show the boron rejection of the regenerated compound. Before regeneration of the compound, boron rejection was almost 0 percent. However, after regeneration of the compound, boron rejection was 96 percent. This boron rejection is close to the initial boron rejection. The results demonstrate that the boron-bonded compound can be regenerated in acid solution easily.

5.5 System Configuration for Application of Compound

Application of the compound will require development of a system configuration that will combine effective application with recovery of the compound at the end of separation process. The absorption and desorption of boron by the developed compound can be controlled by adjusting the pH solution. At present, two system configurations are being evaluated.

As shown on figure 25, configuration 1 is a two-pass permeate processing system. The compound is added to permeate of the first-pass RO unit prior to processing by the second-pass UF unit. The UF unit could be used instead of the second-pass RO unit because the boron-bonded compound is sufficiently rejected by UF membranes. The UF unit can operate at higher flux and lower feed pressure than the second-pass RO unit. The UF membrane permeate is clean water, free from boron, but the rejected water contains the boron-bonded compound. As shown on figure 25, the compound recovery is accomplished by treating second-pass UF concentrate with another UF unit after pH adjustment to break the dendrimer and

boron bond. In the compound recovery UF unit, the filtrate will contain a high concentration of boron and the concentrate stream will contain a high concentration of the compound. One difficulty for application of this procedure is the solubility of the compound at low pH. Because of increased solubility of the compound in low pH, the separation flux of the second UF unit is low.

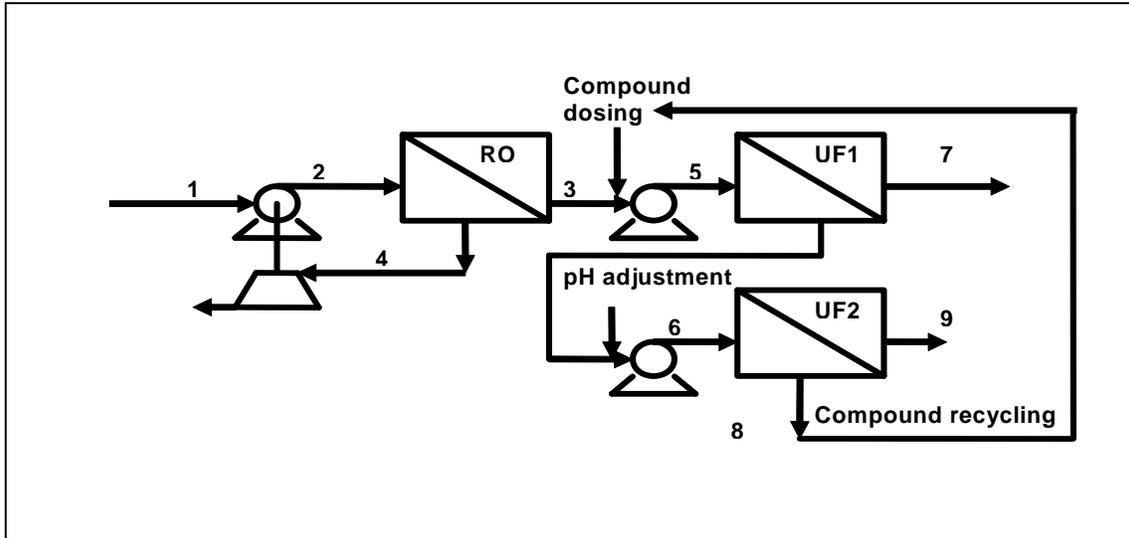


Figure 25. Schematic diagram of configuration 1 for applications of the compound.

Configuration 2 is shown on figure 26. In this configuration, the compound is added to the feed of the first-pass RO unit. This will increase rejection level of boron to the required level. The recovery of the compound from the concentrate stream is somehow more problematic than in the previous configuration. Here again, the compound-loaded stream, after pH adjustment, is processed by the UF unit. A majority of the compound should end up in the UF concentrate stream. This could be reused provided that the UF unit can operate at a very high recovery rate to reduce amount of contaminants that will be added with the compound to the feed of the first-pass RO unit. These issues would have to be evaluated further to determine the overall feasibility of the process.

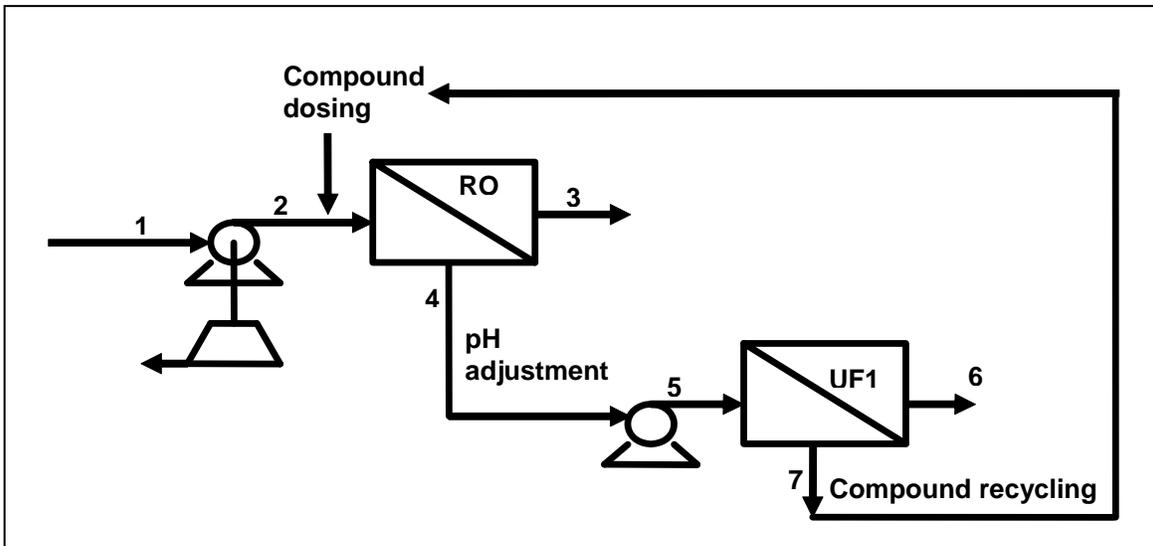


Figure 26. Schematic diagram of configuration 2 for applications of the compound.

5.6 Economic Analysis

Boron rejection, even for the best seawater commercial membranes, is only 92–93 percent. Therefore, in RO projects where boron concentration in the permeate is specified at the level below 1 ppm, a partial or complete two-pass system is necessary. The boron rejection of brackish membrane at neutral pH is even much lower, in the range of 50–70 percent. Therefore, prior to second-pass processing, the pH of the second-pass feed has to be increased to about 10 to ionize boric species and to increase boron removal. Economics of this process could be improved either by increasing boron rejection to reduce the number of passes or by decreasing the amount of caustic needed.

The economic evaluation data is included in the appendix. Based on the boron rejection improvement by adding 10 ppm MGA, water costs were evaluated. The evaluation conditions are as follows:

- Recovery rate: 50%
- Average permeate flux rate: 8.5 gfd
- Native feed water: pH 8.0
- Boron concentration in feed water: 5 ppm
- Seawater temperature: 21 °C (57–69 degrees Fahrenheit (14–21 °C))
- Efficiencies of pumps: 86% percent
- Power recovery turbines (ERT): 86 percent
- Electric motors: 94 percent

- Cost of caustic: \$700/ton
- Cost of scale inhibitor: \$3,000/ton
- Scale inhibitor dosing: 2 ppm

Table 16 shows the water cost for each case, including normal RO with complete two-pass system, one-pass system at high pH, and the newly evaluated system by adding MGA in the feed water. The calculation was conducted using Hydranautics' IMSDesign software.

Table 16. Economic Evaluation of Water Cost for Different Configuration and Conditions

System		Normal two-pass system	One-pass system at high pH	New developed system
		SWC5 + ESPA2	SWC5 at high pH	SWC5 + MGA
Membranes				
Boron concentration after 3 years (ppm)		0.786	0.787	0.787
Product (million gallons per day)		5	5	5
Initial investment (\$millions)		25	22	22
# of membranes		2,200	1,472	1,472
Membrane price (\$)		487	500	550
pH (feed 8.0)		8.0 + 8.90	8.71	8.26
NaOH (ppm)		1.8	9.7	2.5
Antiscalant (ppm)		2	2	1
Boron pass decline (%)		0.0	38.2	32.7
Flux decline (%)		0.0	0.45	8.0
Cost (\$/kgal)	Capital cost	0.06	0.05	0.05
	Energy cost	1.02	0.80	0.82
	Chemical cost	0.05	0.10	0.04
	Membrane cost	0.13	0.09	0.10
	Maintenance	0.46	0.40	0.40
	Water cost	1.73	1.45	1.41

In the case of the normal process, which consists of a two-pass system with two RO membranes (seawater RO membrane (SWC5) and brackish RO membrane (ESPA2)), the evaluated water cost is \$1.73 per thousand gallons (\$/kgal). The increased cost is due to the use of two separation systems and the high pH in the second pass. The capital, energy, and membrane costs are relatively high.

However, the requirement of boron passage (less than 1 ppm after 3 years) can be achieved using a one-pass system by increasing in pH of feed water. To avoid using a second-pass system, the seawater feed pH has to be increased to ionize boric species and increase boron removal. Since this results in a one-pass system, the capital, energy, and membrane costs are less than for the two-pass system. The evaluated water cost using a one-pass system at high pH is 1.45 \$/kgal. The chemical cost is high because caustic as well as an anti-scaling agent are required.

In addition, the use of concentrated caustic, which is a toxic material, will require special handling.

The newly designed system only requires adding 10 ppm MGA in feed water. The boron passage requirement can be achieved by using just a one-pass system and normal pH. The evaluated water cost is 1.41 \$/kgal. The new designed system presents the lowest evaluated water cost compared to the other RO system designs.

6. References

- Almullaa, A., M. Eid, P. Côté, and J. Coburn, 2003. *Desalination* 153, 237–243.
- Anadori, M., 1931. *Gam. chim. ital.* 61, 215.
- Arkas, M., D. Tsiourvas, and C.M. Paleos, 2003. *Chem. Mater.* 15, 2844–2847.
- Bertrand, S., I. Lemaire, and E. Wittman, 1997. “Performance of nanofiltration plant on hard and highly sulphated water during two years of operation,” *Desalination* 113, 227–281.
- Bhattacharyya, A. and D. Butterfield (editors), 2003. *New Insight into Science and Technology: Polymeric and Biofunctional Membranes*. Elsevier, New York, New York.
- Biçak, N., N. Bulutçu, B.F. Şenkal, and M. Gazi, 2001. *Reactive and Functional Polymers* 47, 175–184.
- Boeseken, J., H.D. Muller, and R.T. Japhongjouw, 1926. *Rec. trav. chim.* 46, 919.
- Boeseken, J., 1930. *Rec. trav. chim.* 40.
- Boeseken, J., K. Vermaas, and A.T. Kuchlin, 1930. *Rec. trav. chim.*, 49, 711.
- Boeseken, J., 1933. *Rec. trav. chim.* 38.
- Boeseken, J., G. Sloof, J. Hoeffelman, and H.E. Hirsch, 1933. *Rec. trav. chim.* 62, 881.
- Boeseken, J., K. Vermaas, W.H. Zaater, and J.L. Leefers, 1936. *Rec. trav. chim.* 64, 853.
- Bosman, A.W., H.M. Janssen, and E.W. Meijer, 1999. *Chem. Rev.* 99, 1665–1688.
- Bush, M., et al., 2003. “Boron removal in seawater desalination,” Proceedings of IDA Conference, Bahamas, September.
- Chua, K. T., M.N.A. Hawlader, and A. Malek, 2003. *Desalination* 159, 225–243.
- Cohen, S. M., S. Petoud, and K. N. Raymond, 2001. *Chem. Eur. J.* 7(1), 272–279.

- Diallo, M., S. Christie, P. Swaminathan, J. Johnson, and W. Goddard, 2005. "Dendrimer enhanced ultrafiltration. Recovery of Cu(II) from aqueous solution using PAMAM dendrimers with ethylene diamine core and terminal NH₂ groups," *Environmental Science and Technology*, Vol. 39, No. 5, 1366–1377.
- Diehl, H., 1937. *Chem. Review* 21, 39–111.
- Egneus B. and L. Uppstrom, 1973. *Analytica Chimica Acta* 66:21, 1–229.
- Faigon, M., et al., 2003. "Pressure center and boron removal in Ashkelon desalination plant," Proceedings of IDA Conference, Bahamas, September.
- Fischer, M. and F. Vögtle, 1999. *Angew. Chem. Int. Ed.* 38, 884–905.
- Franke W. and G. Brathuhn, 1931. *Ann.* 487, 20.
- Fréchet, J.M., 1994. *J. Science* 263, 1710–1715.
- Fu, P., H. Ruiz, J. Lozier, K. Thompson, and C. Spangenberg, 1995. "A pilot study on groundwater natural organics removal by low pressure membranes," *Desalination* 102, 47–56.
- Glueckstern, P. and M. Priel, 2003. *Desalination* 156, 219–228.
- Grayson, S.M. and J.M. Fréchet, 2001. *J. Chem. Rev.* 101, 3819–3867.
- Hermans, P.H., 1925, *anorg. allgem. Chem.* 142, 83.
- Hermans, P.H., 1936. *J. Chem. Soc.* 68, 1668; 1991.
- Inukai, Y., Y. Tanaka, T. Matsuda, N. Mihara, K. Yamada, N. Nambu, O. Itoh, T. Doi, Y. Kaida, and S. Yasuda, 2004. *Analytica Chimica Acta* 511, 261–265.
- Kabay, N., I. Yılmaz, S. Yamac, S. Samatya, M. Yuksel, U. Yuksel, M. Arda, M. Sağlama, T. Iwanaga, and K. Hirowatari, 2004. *Reactive and Functional Polymers* 60, 163–170.
- Lesimple, P.D. and C.H. Bigg, 1991. *Synthesis*, 306.
- Magara, Y., A. Tabata, M. Kohki, M. Kawasaki, and M. Hirose, 1998. *Desalination* 118, 25–34.
- Majoral, J.P. and A.M. Caminade, 1999. *Chem. Rev.* 99, 845–880.

- Melnyk, L., V. Goncharuk, I. Butnyk, and E. Tsapiuk, 2005. *Desalination* 185, 147–157.
- Mezzenga, R., L. Boogh, J-A. E. Månson, and B. Pettersson, 2000. *Macromolecules* 33, 4373–4379.
- Nadav, N, 1999. *Desalination*, 124, 131–135.
- Newkome, G.R., C.N. Moorefield, and F. Vögtle, 1996. *Dendritic Molecules: Concepts, Syntheses and Perspectives*. VCH: Weinheim, Germany.
- Pastor, M.R., A.F. Ruiz, M.F. Chillón, and D.P. Rico, 2001. *Desalination* 140, 145–152.
- Pistilis, G. and A. Malliaris, 2002. *Langmuir* 18, 246–251.
- Prats, D., M.F. Chillon-Arias, and M. Rodriguez-Pastor, 2000. *Desalination* 128, 269–273.
- Qin, J-J., M.H. Oo, M.N. Wai, and Y-M. Cao, 2005. *Desalination* 172, 151–156.
- Redondo, J., M. Busch, and J-P De Witte, 2003. *Desalination* 156, 229–238.
- Rether, A. and M. Schuster, 2003. *Reactive and Functional Polymers*, 57, 13–21.
- Rodrigues-Lopez, G., M.D. Marcos, R. Martinez-Manez, F. Sancenon, J. Soto, L.A. Villaescusa, D. Beltrain, and P. Amoros, 2004. *Chem. Commun.*, 2198–2199.
- Rosenjeim A. and H. Vermbhren, 1924. *Ber.* 67, 1337.
- Ryschkewitsch G. E. and T. E. Sullivan, 1970. *Inorganic Chemistry*, Vol. 9, No. 4, April, 899–904.
- Sahin, S., 2002. *Desalination* 143, 35–43.
- Sallangos, O. and P. Moss, 2001. *Desalination* 139, 125–129.
- Schilde U. and E. Uhlemann, 1992. *Reactive Polymers* 18, 155–158.
- Schmitzer, A. 1999. *Lamgmuir* 15, 4397–4403.
- Simonnot, M-O., C. Casrel, M. Nicolai, C. Rosin, M. Sardin, and H. Jauffret, 2000. *Water Research*, Vol. 34, No. 1, 109–116.
- Stumm, W. W. and J. Morgan, 1981. *Aquatic Chemistry*, John Wiley & Sons.

- Tanford, 1974. *Proc. Nat. Acad. Sci.*, 71(5), 1811–1815.
- Taniguchi, M., M. Kurihara, S. Kimura, 2001. *Journal of Membrane Science* 183, 249–257.
- Tomalia, D.A., A.M. Naylor, and W.A. Goddard III, 1990. *Angew. Chem., Int. Ed. Engl.* 29, 138–175.
- Tomalia, D.A., D.M. Hedstrand, L.R. Wilson, 1990. *Encyclopedia of Polymer Science and Engineering, Index Volume*. Wiley: New York, New York, 46–92.
- Tomalia, D.A. and H.D. Durst, 1993. *Topics Curr. Chem.* 165, 193–313.
- Ventresque, C., G. Turner, and G. Bablon, “Nanofiltration: from prototype to full scale,” *Journal AWWA*, Vol 89, Issue 10, October, 65–76.
- Vial, D., G. Doussaua, and R. Galindob, 2003. *Desalination* 156, 43–50.
- Wark, I.W., 1923. *J. Chem. Soc.* 123, 1815.
- Wilf, M., and C. Bartels, 2005. “Optimization of seawater RO system design,” *Desalination* 173(1), 1–12.
- Xu, Y-H. and D-Y. Zhao, 2005. *Environ. Sci. Technol.*, 39, 2369–2375.

SI Metric Conversion Table

SI metric	U.S. unit
gallon per day (GPD)	3.785 liters/day (LPD)
thousand gallons (kgal)	3785.4 liters
pound/inch ² (psi)	6 894.757 N/m ²
1 degree Celsius	33.8 degrees Fahrenheit
gfd (gallon feet per day)	0.34822 L/m ² .day

Appendix

Economic Analysis

1. Regular Two-Pass System

Hydranautics Membrane Solutions Design Software, v. 2006

TWO PASS

RO program licensed to:

Calculation created by: x

Project name: SeaWater-Pacific

Permeate flow: 5555555.6 5000000.0 gpd
0 4

HP Pump flow: 7716.0 3858.0 gpm Raw water flow: 10555526.1 gpd

Recommended pump press.: 807.0 psi

Feed pressure: 778.0 215.3 psi Permeate recovery: 50.0 90.0 %

Feedwater Temperature: 21.0 C(70F) Total system recovery: 47.4 %

Feed water pH: 8.0 8.9 Element age: 3.0 years

Chem dose, ppm, ppm 0.0 1.8 Flux decline % per year: 7.0 3.0

Acidified feed CO2: 1.62 0.0 Salt passage increase, %/yr: 10.0 3.0

Average flux rate: 8.5 22.0 gfd Feed type: Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel Feed gpm	Conc gpm	Flux gfd	Beta	Conc.&Throt. Pressures psi	psi	Element Type	Elem. Nb.	Array
1-1	3858.0	37.8	18.9	8.5	1.04	757.7	0.0	SWC5	1632	204x8
2-1	2532.8	83.9	28.8	24.8	1.18	155.4	0.0	ESPA2	368	46x8
2-2	939.4	53.0	15.4	16.9	1.22	122.5	0.0	ESPA2	200	25x8

Ion	Raw water		Feed water		Permeate		Concentrate	
	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3
Ca	351.0	875.3	333.8	832.3	0.001	0.0	666.9	1663.2
Mg	1780.0	7325.1	1692.6	6965.6	0.007	0.0	3382.2	13918.4
Na	9880.0	21478.3	9429.6	20499.1	0.906	2.0	18776.4	40818.1
K	597.0	765.4	570.4	731.3	0.084	0.1	1134.5	1454.5
NH4	0.0	0.0	0.0	0.0	0.000	0.0	0.0	0.0
Ba	0.003	0.0	0.003	0.0	0.000	0.0	0.006	0.0
Sr	10.600	12.1	10.080	11.5	0.000	0.0	20.141	23.0
CO3	2.6	4.3	2.6	4.3	0.000	0.0	5.1	8.5
HCO3	137.9	113.0	133.0	109.0	0.074	0.1	264.1	216.4
SO4	2572.0	2679.2	2446.0	2547.9	0.013	0.0	4887.1	5090.7
Cl	18161.0	25615.0	17325.1	24435.9	1.442	2.0	34511.5	48676.4
F	2.1	5.5	2.0	5.3	0.001	0.0	4.3	10.5
NO3	0.2	0.2	0.2	0.2	0.001	0.0	0.4	0.3
B	5.00		5.04		0.786		8.75	
SiO2	2.9		2.8		0.00		5.5	
TDS	33502.3		31953.1		3.32		63666.5	
pH	8.0		8.0		7.3		8.3	

	Raw water	Feed water	Concentrate
CaSO4 / Ksp * 100:	18%	16%	39%
SrSO4 / Ksp * 100:	33%	31%	73%
BaSO4 / Ksp * 100:	12%	12%	27%
SiO2 saturation:	2%	2%	4%
Langelier Saturation Index	0.89	0.86	1.69
Stiff & Davis Saturation Index	-0.03	-0.05	0.68
Ionic strength	0.70	0.67	1.33
Osmotic pressure	349.8 psi	333.7 psi	664.8 psi

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.

Hydranautics (USA) Ph:(760)901-2500 Fax:(760)901-2578 info@hydranautics.com

Hydranautics (Europe) Ph: 31 5465 88355 Fax: 31 5465 73288 (30/53)

TWC PASS

RO program licensed to:

Calculation created by: x

Project name: SeaWater-Pacific

Permeate flow: 5555555.6 5000000.0 gpd
0 4

HP Pump flow: 7716.0 3858.0 gpm Raw water flow: 10555526.1 gpd

Recommended pump press.: 807.0 psi

Feed pressure: 778.0 215.3 psi Permeate recovery: 50.0 90.0 %

Feedwater Temperature: 21.0 C(70F) Total system recovery: 47.4 %

Feed water pH: 8.0 8.9 Element age: 3.0 years

Chem dose, ppm, ppm 0.0 1.8 Flux decline % per year: 7.0 3.0

Acidified feed CO2: 1.62 0.0 Salt passage increase, %/yr: 10.0 3.0

Average flux rate: 8.5 22.0 gfd Feed type: Seawater - open intake

Stage	Perm. Flow	Flow/Vessel		Flux	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
	gpm	gpm	gpm	gfd		psi	psi			
1-1	3858.0	37.8	18.9	8.5	1.03	757.7	0.0	SWC5	1632	204x8
2-1	2532.8	83.9	28.8	24.8	1.18	155.4	0.0	ESPA2	368	46x8
2-2	939.4	53.0	15.4	16.9	1.23	122.5	0.0	ESPA2	200	25x8

CALCULATION OF POWER REQUIREMENT

	Main	Pass 2
Feed pressure, psi	778.0	215.3
Concentrate pressure, psi	757.7	122.5
Permeate flow,gpd	5555555.6	5000000.0
Recovery ratio, %	50.0	90.0
Pump efficiency, %	86.0	86.0
Motor efficiency, %	94.0	94.0
ERT efficiency, %	86.0	
ERT backpressure, psi	0.0	
Pumping energy, kwhr/kgal	12.80	
Pumping power, hp	5014.8	
Recovered power, hp	1438.2	
Power requirement, hp	3576.6	

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.
 Hydranautics (USA) Ph:(760)901-2500 Fax:(760)901-2578 info@hydranautics.com
 Hydranautics (Europe) Ph: 31 5465 88355 Fax: 31 5465 73288 (30/53)

TWO PASS

RO program licensed to:

Calculation created by:

Project name:

x
SeaWater-Pacific

Permeate flow:

5555555.6 5000000.0 gpd
0 4

HP Pump flow:

7716.0 3858.0 gpm

Raw water flow:

10555526.1 gpd

Recommended pump press.:

807.0 psi

Feed pressure:

778.0 215.3 psi

Permeate recovery:

50.0 90.0 %

Feedwater Temperature:

21.0 C(70F)

Total system recovery:

47.4 %

Feed water pH:

8.0 8.9

Element age:

3.0 years

Chem dose, ppm, ppm

0.0 1.8

Flux decline % per year:

7.0 3.0

Acidified feed CO2:

1.62 0.0

Salt passage increase, %/yr:

10.0 3.0

Average flux rate:

8.5 22.0 gfd

Feed type:

Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel		Flux gfd	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
		Feed gpm	Conc gpm			psi	psi			
1-1	3858.0	37.8	18.9	8.5	1.03	757.7	0.0	SWC5	1632	204x8
2-1	2532.8	83.9	28.8	24.8	1.18	155.4	0.0	ESPA2	368	46x8
2-2	939.4	53.0	15.4	16.9	1.23	122.5	0.0	ESPA2	200	25x8

CALCULATION OF INVESTMENT AND WATER COST

Plant capacity, gpd	5000000.0
Plant life, years	20.0
Investment, \$	\$25,000,000.00
Membrane life, years	5.0
Interest rate, %	5.0
Membrane cost, \$/element	\$487.00
Plant factor, %	90.0
Number of elements	2200
Power cost, \$/kWhr	0.080
Inhibitor cost, \$/kg	3.00
Power consumption, kWhr/kgal	12.80
Inhibitor dosing, ppm	2.0
Maintenance (as % of investment)	3.0
Acid cost, \$/kg	0.70
Acid dosing, ppm	1.8

Calculation Results:

Capital cost, \$/kgal	\$0.06
Power cost, \$/kgal	\$1.02
Chemicals cost, \$/kgal	\$0.05
Membrane replacement cost, \$/kgal	\$0.13
Maintenance, \$/kgal	\$0.46
Total water cost, \$/kgal	\$1.73

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.

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2. One-Pass System with High pH

Hydranautics Membrane Solutions Design Software, v. 2006

One pass with high pH

RO program licensed to:
 Calculation created by: x
 Project name: SeaWater-Pacific

Permeate flow: 5000000.0 gpd
 0
 HP Pump flow: 6944.4 gpm
 Raw water flow: 10000000.0 gpd
 Recommended pump press.: 849.7 psi
 Feed pressure: 814.7 psi
 Permeate recovery: 50.0 %
 Feedwater Temperature: 21.0 C(70F)
 Feed water pH: 8.7
 Element age: 3.0 years
 Chem dose, ppm (100%): 9.7 NaOH
 Flux decline % per year: 7.0
 Acidified feed CO2: 0.29
 Salt passage increase, %/yr: 10.0
 Average flux rate: 8.5 gfd
 Feed type: Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel		Flux gfd	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
		Feed gpm	Conc gpm			psi	psi			
1-1	3472.2	37.7	18.9	8.5	1.04	794.5	0.0	SWC5-PHS	1472	184x8

Ion	Raw water		Feed water		Permeate		Concentrate	
	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3
Ca	351.0	875.3	351.0	875.3	0.785	2.0	701.2	1748.7
Mg	1780.0	7325.1	1780.0	7325.1	3.983	16.4	3556.0	14633.8
Na	9880.0	21478.3	9885.6	21490.4	105.902	230.2	19665.3	42750.7
K	597.0	765.4	597.0	765.4	7.988	10.2	1186.0	1520.5
NH4	0.0	0.0	0.0	0.0	0.000	0.0	0.0	0.0
Ba	0.003	0.0	0.003	0.0	0.000	0.0	0.006	0.0
Sr	10.600	12.1	10.600	12.1	0.024	0.0	21.176	24.2
CO3	2.6	4.3	16.0	26.7	0.016	0.0	32.1	53.4
HCO3	137.9	113.0	126.1	103.3	2.213	1.8	249.9	204.9
SO4	2572.0	2679.2	2572.0	2679.2	6.296	6.6	5137.7	5351.8
Cl	18161.0	25615.0	18161.0	25615.0	177.476	250.3	36144.5	50979.6
F	2.1	5.5	2.1	5.5	0.041	0.1	4.2	10.9
NO3	0.2	0.2	0.2	0.2	0.014	0.0	0.4	0.3
B	5.00		5.00				9.21	
SiO2	2.9		2.9		0.02		5.8	
TDS	33502.3		33509.5		305.5		66713.5	
pH	8.0		8.7		7.1		9.0	

	Raw water	Feed water	Concentrate
CaSO4 / Ksp * 100:	18%	18%	<2%
SrSO4 / Ksp * 100:	33%	33%	78%
BaSO4 / Ksp * 100:	12%	12%	29%
SiO2 saturation:	2%	2%	4%
Langelier Saturation Index	0.89	1.65	2.49
Stiff & Davis Saturation Index	-0.03	0.72	1.48
Ionic strength	0.70	0.70	1.39
Osmotic pressure	349.8 psi	349.9 psi	696.4 psi

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.
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BASIC DESIGN

RO program licensed to:

Calculation created by: x

Project name: SeaWater-Pacific

Permeate flow: 5000000.0 gpd

HP Pump flow: 6944.4 gpm

Raw water flow: 10000000.0 gpd

Recommended pump press.: 849.7 psi

Feed pressure: 814.7 psi

Permeate recovery: 50.0 %

Feedwater Temperature: 21.0 C(70F)

Feed water pH: 8.7

Element age: 3.0 years

Chem dose, ppm (100%): 9.7 NaOH

Flux decline % per year: 7.0

Acidified feed CO2: 0.29

Salt passage increase, %/yr: 10.0

Average flux rate: 8.5 gfd

Feed type: Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel		Flux gfd	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
		Feed gpm	Conc gpm			psi	psi			
1-1	3472.2	37.7	18.9	8.5	1.03	794.5	0.0	SWC5-PHS	1472	184x8

CALCULATION OF POWER REQUIREMENT

	Main Pump
Feed pressure, psi	814.7
Concentrate pressure, psi	794.5
Permeate flow,gpd	5000000.0
Recovery ratio, %	50.0
Pump efficiency, %	86.0
Motor efficiency, %	94.0
ERT efficiency, %	86.0
ERT backpressure, ps	0.0
Pumping energy, kwhr/kgal	10.06
Pumping power, hp	4167.2
Recovered power, hp	1357.2
Power requirement, hp	2809.9

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.
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BASIC DESIGN

RO program licensed to:

Calculation created by: x

Project name: SeaWater-Pacific

Permeate flow: 5000000.0 gpd
0

HP Pump flow: 6944.4 gpm Raw water flow: 10000000.0 gpd

Recommended pump press.: 849.7 psi

Feed pressure: 814.7 psi

Feedwater Temperature: 21.0 C(70F)

Feed water pH: 8.7

Chem dose, ppm (100%): 9.7 NaOH

Acidified feed CO2: 0.29

Average flux rate: 8.5 gfd

Permeate recovery: 50.0 %

Element age: 3.0 years

Flux decline % per year: 7.0

Salt passage increase, %/yr: 10.0

Feed type: Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel		Flux gfd	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
		Feed gpm	Conc gpm			psi	psi			
1-1	3472.2	37.7	18.9	8.5	1.03	794.5	0.0	SWC5-PHS	1472	184x8

CALCULATION OF INVESTMENT AND WATER COST

Plant capacity, gpd	5000000.0
Plant life, years	20.0
Investment, \$	\$22,000,000.00
Membrane life, years	5.0
Interest rate, %	5.0
Membrane cost, \$/element	\$500.00
Plant factor, %	90.0
Number of elements	1472
Power cost, \$/kWhr	0.080
Inhibitor cost, \$/kg	3.00
Power consumption, kWhr/kgel	10.06
Inhibitor dosing, ppm	2.0
Maintenance (as % of investment)	3.0
Acid cost, \$/kg	0.70
Acid dosing, ppm	9.7

Calculation Results:

Capital cost, \$/kgal	\$0.05
Power cost, \$/kgal	\$0.80
Chemicals cost, \$/kgal	\$0.10
Membrane replacement cost, \$/kgal	\$0.09
Maintenance, \$/kgal	\$0.40
Total water cost, \$/kgal	\$1.45

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.

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3. New Developed System with MGA Added

Hydranautics Membrane Solutions Design Software, v. 2006

New system with MGA

RO program licensed to:

Calculation created by:

Project name:

x
SeaWater-Pacific

Permeate flow:

5000000.0 gpd

HP Pump flow:

6944.4 gpm

Raw water flow:

10000000.0 gpd

Recommended pump press.:

867.0 psi

Feed pressure:

830.4 psi

Permeate recovery:

50.0 %

Feedwater Temperature:

21.0 C(70F)

Feed water pH:

8.3

Element age:

3.0 years

Chem dose, ppm (100%):

2.5 NaOH

Flux decline % per year:

7.0

Acidified feed CO2:

0.87

Salt passage increase, %/yr:

10.0

Average flux rate:

8.5 gfd

Feed type:

Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel Feed gpm	Conc gpm	Flux gfd	Beta	Conc.&Throt. Pressures psi	psi	Element Type	Elem. No.	Array
1-1	3472.2	37.7	18.9	8.5	1.04	810.0	0.0	SWC5-MGA1S	1472	184x8

Ion	Raw water		Feed water		Permeate		Concentrate	
	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3	mg/l	CaCO3
Ca	351.0	875.3	351.0	875.3	0.722	1.8	701.3	1748.8
Mg	1780.0	7325.1	1780.0	7325.1	3.663	15.1	3556.3	14635.1
Na	9880.0	21478.3	9881.4	21481.4	97.376	211.7	19665.5	42751.1
K	597.0	765.4	597.0	765.4	7.349	9.4	1188.7	1521.3
NH4	0.0	0.0	0.0	0.0	0.000	0.0	0.0	0.0
Ba	0.003	0.0	0.003	0.0	0.000	0.0	0.006	0.0
Sr	10.600	12.1	10.600	12.1	0.022	0.0	21.178	24.2
CO3	2.6	4.3	6.1	10.2	0.006	0.0	12.2	20.4
HCO3	137.9	113.0	135.4	111.0	2.184	1.8	268.5	220.1
SO4	2572.0	2679.2	2572.0	2679.2	5.786	6.0	5138.2	5352.3
Cl	18161.0	25615.0	18161.0	25615.0	163.121	230.1	36158.9	50999.8
F	2.1	5.5	2.1	5.5	0.038	0.1	4.2	11.0
NO3	0.2	0.2	0.2	0.2	0.013	0.0	0.4	0.3
B	5.00		5.00		0.787		8.83	
SiO2	2.9		2.9		0.02		5.8	
TDS	33502.3		33504.7		261.5		66728.0	
pH	8.0		8.3		6.6		8.5	

	Raw water	Feed water	Concentrate
CaSO4 / Ksp * 100:	18%	18%	42%
SrSO4 / Ksp * 100:	33%	33%	78%
BaSO4 / Ksp * 100:	12%	12%	29%
SiO2 saturation:	2%	2%	4%
Langlier Saturation Index	0.89	1.17	2.01
Stiff & Davis Saturation Index	-0.03	0.24	1.00
Ionic strength	0.70	0.70	1.39
Osmotic pressure	349.8 psi	349.8 psi	696.6 psi

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.

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BASIC DESIGN

RO program licensed to:

Calculation created by:

Project name:

x
SeaWater-Pacific

Permeate flow:

5000000.0 gpd
0

HP Pump flow:

6944.4 gpm

Raw water flow:

10000000.0 gpd

Recommended pump press.:

867.0 psi

Feed pressure:

830.4 psi

Permeate recovery:

50.0 %

Feedwater Temperature:

21.0 C(70F)

Feed water pH:

8.3

Element age:

3.0 years

Chem dose, ppm (100%):

2.5 NaOH

Flux decline % per year:

7.0

Acidified feed CO2:

0.87

Salt passage increase, %/yr:

10.0

Average flux rate:

8.5 gfd

Feed type:

Seawater - open intake

Stage	Perm. Flow gpm	Flow/Vessel Feed gpm	Conc gpm	Flux gfd	Beta	Conc.&Throt. Pressures psi psi	Element Type	Elem. No.	Array
1-1	3472.2	37.7	18.9	8.5	1.04	810.0 0.0	SWC5-MGA1S	1472	184x8

CALCULATION OF POWER REQUIREMENT

	Main Pump
Feed pressure, psi	830.4
Concentrate pressure, psi	810.0
Permeate flow,gpd	5000000.0
Recovery ratio, %	50.0
Pump efficiency, %	86.0
Motor efficiency, %	94.0
ERT efficiency, %	86.0
ERT backpressure, ps	0.0
Pumping energy, kwhr/kgal	10.25
Pumping power, hp	4247.5
Recovered power, hp	1383.7
Power requirement, hp	2863.8

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.

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BASIC DESIGN

RO program licensed to:				Permeate flow:		5000000.0		gpd		
Calculation created by:		x		Raw water flow:		10000000.0		gpd		
Project name:		SeaWater-Pacific		Permeate recovery:		50.0		%		
HP Pump flow:		6944.4		Element age:		3.0		years		
Recommended pump press.:		867.0		Flux decline % per year:		7.0				
Feed pressure:		830.4		Salt passage increase, %/yr:		10.0				
Feedwater Temperature:		21.0		Feed type:		Seawater - open intake				
Feed water pH:		8.3								
Chem dose, ppm (100%):		2.5								
Acidified feed CO2:		0.87								
Average flux rate:		8.5								
Stage	Perm. Flow	Flow/Vessel		Flux	Beta	Conc.&Throt. Pressures		Element Type	Elem. No.	Array
	gpm	Feed	Conc	gfd		psi	psi			
1-1	3472.2	37.7	18.9	8.5	1.04	810.0	0.0	SWC5-MGA1S	1472	184x8

CALCULATION OF INVESTMENT AND WATER COST

Plant capacity, gpd	5000000.0
Plant life, years	20.0
Investment, \$	\$22,000,000.00
Membrane life, years	5.0
Interest rate, %	5.0
Membrane cost, \$/element	\$550.00
Plant factor, %	90.0
Number of elements	1472
Power cost, \$/kWhr	0.080
Inhibitor cost, \$/kg	3.00
Power consumption, kWhr/kgal	10.25
Inhibitor dosing, ppm	1.0
Maintenance (as % of investment)	3.0
Acid cost, \$/kg	0.70
Acid dosing, ppm	2.5
Calculation Results:	
Capital cost, \$/kgal	\$0.05
Power cost, \$/kgal	\$0.82
Chemicals cost, \$/kgal	\$0.04
Membrane replacement cost, \$/kgal	\$0.10
Maintenance, \$/kgal	\$0.40
Total water cost, \$/kgal	\$1.41

These calculations are based on nominal element performance when operated on a feed water of acceptable quality. No guarantee of system performance is expressed or implied unless provided in writing by Hydranautics.
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