

Engineering Data Sheet

7334

Subject: Silica Contamination Removal from Spent Fuel Pools and Refueling Water Storage Tanks at Nuclear PWR Power Generation Plants

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The Problem

Zircaloy surface cladding of fuel rods in reactor cores is susceptible to silica based scaling which increases the potential for premature fuel failure. The silica scale behaves as thermal insulation, which gradually permits the tubes to overheat. The sources of silica contamination are twofold:

1. Boric acid addition. Boric acid from U.S. Borax contains a rather small concentration of silica. This source of silica contamination is minor. A Spanish company has recently introduced silica-free boric acid to U.S. markets through a New York City based representative.
2. Spent fuel racks are constructed from borosilicates. Over time silica will gradually leach from the racks. Silica from fuel racks is thought to be the major source of silica contamination.

3. The referred to silica contamination is present in both dissolved and colloidal forms. Dissolved silica is referred to as "reactive silica" whereas non-reactive silica is referred to as colloidal. Reactive silica can be determined quantitatively from 0.4 to 25.0 mg/L through the formation of the yellow molybdosilicate complex. The majority of the silica contamination found in the spent fuel pools (SFP) and refueling water storage tanks (RWST) is in the form of dissolved or reactive silica. Fuel fabricators routinely specify a maximum silica concentration of 1.0 mg/L in RWST and SFP to prevent the harmful formation of silica based scale.

Feed and Bleed

The traditional method used to reduce silica to levels lower than 1.0 mg/L consists of bleeding the contaminated water while simultaneously feeding borated demineralized make-up water. This is generally called a "feed and bleed" (F&B) system. For example, if the initial silica concentration (S_{iO}) is 6.0 mg/L in a 500,000 gallon tank (V_T) and the desired final silica concentration (S_{iF}) is 0.5 mg/L, the volume of continuously recirculated complete mix water that requires processing (V_P) is calculated as follows:

$$\frac{V_P}{V_T} = -\ln \frac{S_{iF}}{S_{iO}}$$

$$\frac{V_P}{V_T} = -\ln \frac{0.5}{6.0}$$

$$= 2.48$$

$$V_P = 2.48 \times 500,000 = 1,240,000 \text{ gallons}$$

If the required concentration of the boron moderator is, say, 2,200 mg/L, the total cost (excluding labor and overhead) of the example F&B system is:

A. Boron

$$= \frac{1,240,000 \times 8.34 \times 2,200}{1,000,000} = 22,752 \text{ lbs.}$$

$$1.0 \text{ lb. boron} = 5.72 \text{ lbs. of boric acid}$$

Cost of nuclear grade boric acid ~ \$2,000.00/ton (or about \$1.00/lb.)

$$22,752 \times 5.72 \times \$1.00 = \mathbf{\$130,141.00}$$

B. Estimated cost of make-up demin water @ 0.10/gallon = **\$124,000.00**

C. Estimated cost of rad waste liquid disposal @ 0.25 per gallon = **\$310,000.00**

Total F&B estimated project costs:

A.	130,141.00
B.	+ \$124,000.00
C.	+ \$310,000.00
Total	\$564,141.00

A Solution: Over 1/2 of the above F&B costs can be saved on a project of the example volume by using a modern reverse osmosis membrane type silica cleaning system. For most PWR plants the cleaning can be accomplished in just a few weeks (24 hours per day) at water processing rates which can vary from 30 to 150 gpm. During cleaning, the RWST and/or SFP can remain on line thereby permitting silica removal during normal power generation while eliminating a major task during an outage. Silica cleaning should, in fact, be scheduled prior to an outage so that clean water is available for fuel changeout. Such a system may be purchased outright, rented/leased with or without an operator(s), or made available with operators on a simple performance contract basis from a nuclear services company. Under this approach contract payments are made against specified reductions of silica concentration.

The purpose of this publication is to thoroughly familiarize PWR chemists and operators with the technology that achieves significant reductions in silica removal costs.

Reverse osmosis treatment systems are capable of separating colloidal and aqueous phase soluble constituents by exerting hydraulic pressure across the membrane. As a result, water and other small molecules pass through the membrane (called permeate) while larger molecules are rejected (called concentrate or reject).

In applying this technology to SFP and RWST cleaning, an ideal membrane would permit expensive demin water with its valuable boron content to permeate 100% while rejecting 100% of the silica. Not surprisingly, ideal membranes do not exist. Several membranes do exist which exhibit varying degrees of boron permeation/silica rejection depending on membrane material of construction, operating pressure, operating temperature, membrane rate of permeation (called flux), system TDS levels, stages of treatment, and other variables.

Contaminants Removed

In addition to silica, SFP and RWST waters can contain hot dissolved and colloidal isotopes such as $\text{Ag}^{110\text{m}}$, Co^{58} , Co^{60} , Cs^{137} , Mn^{54} , Sb^{124} , Sb^{125} , T_3 , and Xe^{133} . Less than mg/L amounts of Cl^- , F^- , Al^{+++} , Ca^{++} , Mg^{++} , and Na^+ can be present along with suspended solids in the 0 to 2 mg/L range.

Except for tritium, which passes through untouched, the vast majority of the suspended solids and hot debris are removed and retained by both pre-membrane microfiltration cartridges as well as post-membrane dead-end ultrafiltration. Divalent cations are 100% rejected to the rad waste treatment plant. Monovalent cations and anions are rejected proportional to their respective sizes. Difficult to remove fluorides, for example, are rejected about 50% in a properly designed membrane silica cleaning system.

The excellent rejection of charged ions is attributable to the common ion effect. The greater the concentration of boron,

the greater the rejection of other charged ions also attempting to permeate the membrane matrix. To the extent that contamination is present as non-charged ions or molecules, rejection will occur relative to their respective atomic/molecular weights. The greater the weight the greater the rejection. Non-charged isotopes with a molecular weight greater than 200 will be 100% rejected. Smaller isotopes will begin permeating relative to their size.

A membrane treatment system is therefore capable of doing an excellent job in removing other unwanted constituents in the SFP and RWST waters. The radiation level of the effluent from a membrane silica cleaning system can be kept below 10^{-4}mCi/mL to control the load on the power plant's liquid rad waste treatment facility.

Membrane Treatment

In every membrane treatment system, there exist three flow streams called:

1. Feed flow or feed stream (F),
2. Permeate or product flow (P), and
3. Concentrate or reject flow (CR).

Frequently, membrane treatment applications require more than a single stage of treatment. In a multiple stage membrane treatment design, the reject flow from the first stage becomes the feed flow to the second stage, and so forth. When more than a single stage of membrane treatment is used, the total design is then referred to as a treatment system.

Process Terms and Treatment Costs

The recovery (R) of a treatment system is the ratio of the permeate rate (Q_P) divided by feed rate (Q_F), or:

$$R = \frac{Q_P}{Q_F}$$

For example, if the feed flow is 53.0 gpm and the permeate is 50.0 gpm, the recovery would be expressed as:

$$R = \frac{50.0}{53.0} \\ = 0.9434 \text{ or } 94.34\%$$

The rejection (λ) of a treatment system is a quantitative measurement of its ability to separate a particular ion, molecule, or substance. It is expressed as:

$$\lambda = 1 - \frac{C_P}{C_F}$$

where

C_P is concentration of ion in permeate and,

C_F is concentration of ion in feed

For example, if the concentrations of silica contamination in the feed and permeate are 6.0 mg/L and 1.40 mg/L, respectively, the system rejection ($S_{i\lambda}$) is:

$$S_{i\lambda} = 1 - \frac{C_P}{C_F} \\ = 1 - \frac{1.40}{6.0}$$

$$= 1 - 0.2333$$

$$= 0.7666 \text{ or } 76.66\%$$

Since the rejection of silica is less than 100%, the processing volume of a membrane silica cleaning system is greater than the F&B system. The volume of continuously recirculated complete mix water that requires processing is calculated as follows:

$$\frac{V_P}{V_T} = \left[-\ln \frac{Si_F}{Si_O} \right] \left[\frac{1}{1-R(1-Si_i)} \right]$$

by substituting the example values,

$$\frac{V_P}{V_T} = \left[-\ln \frac{0.5}{6.0} \right] \left[\frac{1}{1-0.9434(1-0.7666)} \right]$$

$$= (2.48)(1.2824)$$

$$= 3.180$$

$$V_P = 3.180 \times 500,000 = 1,590,000 \text{ gallons (vs. } 1,240,000)$$

Processing Time

To determine the length of time required T_P to accomplish silica removal, the processing volume is divided by the feed rate. The calculations are as follows:

$$T_P = \frac{V_P}{Q_F}$$

$$= \frac{1,590,000}{53}$$

$$= 30,000 \text{ min} = 500 \text{ hours} = 20.8 \text{ days}$$

Boron Costs

If, for example, the membrane silica cleaning system rejection of boron is 10.77%, the amount of boron lost is calculated as follows:

$$\lambda = 1 - \frac{C_P}{C_F}$$

$$10.77 = 1 - \frac{C_P}{2,200}$$

$$C_P = 1,963 \text{ mg/L}$$

Pounds of boron processed is calculated as follows:

$$\frac{1,590,000 \times 8.34 \times 1,963}{1,000,000} = 29,173 \text{ lbs.}$$

Pounds of boron in permeate is calculated as follows:

$$\frac{1,590,000 \times 0.9434 \times 8.34 \times 1,963}{1,000,000} = 24,557 \text{ lbs.}$$

$$29,173 - 24,557 = 4,616 \text{ lbs. boron lost}$$

$$4,616 \times 5.72 \times \$1.00 = \$26,403.52$$

At the example recovery (R) of 94.34%, (1 - R) or 5.66% of V_P or 89,994 gallons will be lost over the duration of the cleaning. The concentration of boron (B_C) in the concentrate effluent is calculated as follows:

$$B_C = \frac{4,616 \times 1,000,000}{89,994 \times 8.34}$$

$$= 6,150 \text{ mg/L}$$

The minimum water solubility of boron is 4,405 mg/L, which occurs at 0°C. Therefore there is no danger of boron salting out of solution at the example conditions. Membrane silica cleaning systems can inadvertently be designed to cause boron salt-out with system failure soon to follow. Appendix A shows boron solubilities.

Demineralized Water Costs

The cost of the demineralized water lost is calculated as follows:

$$89,994 \times \$0.10 = \$8,999.40$$

Disposal Costs

The lost water must, of course, be disposed of as at a disposal cost of \$0.25/gallon. The cost is calculated as follows:

$$89,994 \times \$0.25 = \$22,498.50$$

Membrane System Savings

All above comparison costs are tabulated as follows:

Table I; Cost Comparison		
Cost Item	F&B System	Membrane System
Boric acid	\$130,141.00	\$26,403.52
Demin water	\$124,000.00	\$8,999.40
Rad waste disposal	\$310,000.00	\$22,498.50
Equipment rental/lease amortized purchase service contract	N/A	\$238,500.00*
Totals	\$564,141.00	\$296,401.42
Estimated savings	N/A	\$267,739.58

* Based on an estimated \$0.150 per gallon treated under a service contract.

Factors Which Influence Savings: The actual savings potential at a specific PWR facility are dependent on:

1. The volume of water to be cleaned. Greater volumes increase the relative savings because project mobilization and demobilization expenses per gallon treated are decreased.
2. The concentration of boron to be maintained. The higher the concentration the greater the relative savings.
3. The initial silica concentration. The higher the concentration the slightly less the relative savings.
4. The final silica concentration. Relative savings are slightly less the lower the concentration.
5. The expertise on the part of the entity performing the task.
6. The net rate of cleaning. Increased rates slightly increase the relative savings because operator expenses per gallon treated are decreased.

Membrane Silica Cleaning Design Considerations

The information disclosed herein is cutting edge technology. Successful silica cleaning project experience within the marketplace is extremely limited. Several companies are now aware of the potential for membrane silica cleaning but do not yet possess the required expertise to design a reliable system. In order for a membrane system to work well it must be correctly and exactly designed. If so designed, its performance will be exemplary. If not, severe operating problems could prevent accomplishment of the silica cleaning objectives within the time and cost parameters established for the project. Therefore, critical membrane design factors will be discussed to enable independent review of the proposed cleaning machine/equipment in order to permit the prospective user the opportunity of satisfying itself and/or its consultants respecting the adequacy of the membrane system design.

Pre-membrane filtration: In order to condition the SFP and RWST waters to membrane cleaning, pre-membrane microfiltration is necessary for two reasons:

1. To prevent larger sized radioactive debris from accumulating within the membrane-cleaning machine. Microfiltration utilizing a nominal one (1) micron polypropylene based cartridge filter is recommended. As the activity of the cartridge filter reaches a predetermined level, or upon reaching a predetermined pressure drop across the vessel, whichever first occurs, the cartridges are removed and replaced. Changing out cartridge filters is far less costly and takes less time to accomplish than changing out the membranes.
2. Since membranes can become fouled with excessive suspended solids, their effective removal is essential. Removal of ten (10) micron sized particles is usually thought of as a minimum requirement. Removal of particles to one (1) micron assures that the membranes will not

become fouled or otherwise adversely affected by the presence of suspended solids in the feed.

Colloidal silica and colloidal heavy metal isotopes readily pass through one (1) micron filtration. Their removals are next discussed.

Post-membrane dead-end filtration: After third stage reverse osmosis treatment, the reject stream is permeated through an ultrafiltration membrane. If the membrane has a nominal 0.1 micron pore size (we recommend 0.04 microns), some colloidal silica will be retained and essentially all of the radioactive metal isotopes will be captured. The permeate will contain dissolved silica, colloidal silica, anions, cations, and boric acid. Its activity will be $<10^{-4}$ mCi/mL. No ultrafiltration membrane reject water is discharged.

Post-membrane permeate filtration: To absolutely prevent the introduction of foreign particles into the permeate return a twenty (20) micron cartridge filter is used. It is highly unlikely that a membrane would rupture or fracture and thereby generate suspended solids. Since this event is theoretically possible, the use of a preventive cartridge filter represents but prudent engineering practice.

Membrane selection and system design: The selection of a correct membrane coupled with the system design are both of paramount importance and must be considered together. The concurrent objectives of every silica-cleaning project are to:

1. Maximize system recovery thereby minimizing the:
 - A. Loss of boron
 - B. Load on the liquid rad waste treatment facility
2. Maximize silica rejection thereby minimizing:
 - A. Processing volume
 - B. Processing time
 - C. Loss of boron

When considered together a specific design can easily result in:

1. Excessive boron in the concentrate resulting in the precipitation of the excess beyond its solubility limit and, or
2. Excessive silica in the concentrate resulting in the precipitation of the excess beyond its solubility limit.

Both above conditions are absolutely fatal to the silica removal project after only a short operating period. By carefully following the several examples cited herein, each membrane silica cleaning system can be independently evaluated from a technical purview to establish the theoretical adequacy of its design. Only those designs that measure up should be considered for the silica-cleaning project at hand. Additionally, the boron make-up requirements during the cleaning should also be established during the management review period in order to determine the existence of or potential for operating problems.

System evaluation: For an exercise example, let's say the specific membrane proposed has silica and boron

rejections of 87.0% and 25.0%, respectively. Let's further say that the system design consists of three (3) stages in a classical 4:2:1 array. Such a system is shown in the appendix (see Figure 1). If the liquid temperature is, let's say, 20°C and the pH_{CR} of the concentrate discharge is 4.5, the example design conditions can be summarized in Table II.

Table II; Design Conditions	
Items	Values
Membrane silica rejection ($S_{i\lambda}$)/stage	87.0%
Membrane boron rejection (B_{λ})/stage	25.0%
System recovery (R)	94.34%
Feed rate (Q_F)	53.0 gpm
Permeate rate (Q_P)	50.0 gpm
Tank volume (V_T)	500,000 gallons
Processing volume (V_P)	1,590,000 gallons
Boron concentration (B_O)	2,200 mg/L
Initial silica concentration (S_{iO})	6.0 mg/L
Final silica concentration (S_{iF})	0.5 mg/L
Temperature (T)	20°C
pH_{CR}	4.5

Silica removed: At a feed rate of 53.0 gpm, a total of 76,320 gallons/day of water will be processed. At a recovery of 94.34%, 72,000 gallons will be permeated and the balance of 4,320 gallons will be discharged to rad waste treatment. The total amount of silica in the feed equals:

$$\frac{6.0 \times 76,320 \times 8.34}{1,000,000}$$

or 3.8191 lbs.

Since the first stage contains 4/7 of the membranes, the first stage permeate = 4/7 of 72,000 or 41,143 gallons. At a membrane silica rejection of 87.0% per stage, the first stage permeate will contain:

$$\frac{(1 - 0.870) \times 6.0 \times 41,143 \times 8.34}{1,000,000}$$

or 0.2676 lbs. silica

3.8191 minus 0.2676 equals 3.5515 lbs. silica remaining in the first stage concentrate (same as second stage feed). Subtracting the first stage permeate volume of 41,143 gallons from 76,143 gallons processed equals 35,177 gallons for second stage treatment. The 3.5515 lbs. silica remaining translate into a silica concentration of:

$$\frac{35,177 \times 8.34 \times (S_{i_{mg/L}})}{1,000,000} = 3.5515$$

or 12.11 mg/L

Since the second stage contains 2/7 of the membranes, the second stage permeate equals 2/7 of 72,000 or 20,571

gallons. At a membrane silica rejection of 87.0% per stage, the second stage permeate will contain:

$$\frac{(1 - 0.870) \times 12.11 \times 20,571 \times 8.34}{1,000,000}$$

or 0.2701 lbs. silica

3.5515 minus 0.2701 equals 3.2814 lbs. silica remaining in the second stage concentrate (same as third stage feed). Subtracting the second stage permeate volume of 20,571 gallons from 35,177 gallons processed equals 14,606 gallons for third stage treatment. The 3.2814 lbs. silica remaining translate into a silica concentration of:

$$\frac{14,606 \times 8.34 \times (S_{i_{mg/L}})}{1,000,000} = 3.2814$$

or 26.94 mg/L

Since the third stage contains 1/7 of the membranes, the third stage permeate = 1/7 of 72,000 or 10,286 gallons. At a membrane silica rejection of 87.0% per stage, the third stage permeate will contain:

$$\frac{(1 - 0.870) \times 26.94 \times 10,286 \times 8.34}{1,000,000}$$

or 0.3004 lbs. silica

3.2814 minus 0.3004 equals 2.9810 lbs. silica remaining in the third stage concentrate (same as ultrafiltration feed). Subtracting the third stage permeate volume of 10,286 gallons from 14,606 gallons processed equals 4,320 gallons for discharge through ultrafiltration dead-end filtration. The 2.9810 lbs. silica remaining translate into a silica concentration of:

$$\frac{4,320 \times 8.34 \times (S_{i_{mg/L}})}{1,000,000} = 2.9810$$

or 82.74 mg/L

Permeate Silica Concentration

Total silica in the permeate = 0.2676 + 0.2701 + 0.3004 = 0.8381 lbs. The 0.8381 lbs. of total silica in the permeate translate into a concentration of:

$$\frac{72,000 \times 8.34 \times (S_{i_{mg/L}})}{1,000,000} = 0.8381$$

or 1.40 mg/L

System Silica Rejection

System silica rejection is found by:

$$\begin{aligned} \lambda &= 1 - \frac{C_P}{C_F} \\ &= 1 - \frac{1.4}{6.0} \\ &= 0.7666 \text{ or } 76.66\% \end{aligned}$$

Maximum System Recovery

The maximum recovery (R_{MAX}) of a membrane silica cleaning system is limited by the maximum concentration or saturation point of silica ($SiO_{2\ MAX}$) in the concentrate or reject flow. Therefore, as the silica concentration in the

feed ($\text{SiO}_2_{\text{FEED}}$) decreases the recovery may be increased. Increasing the recovery throughout the cleaning period slightly decreases the processing time but significantly decreases the loss of boron and demin water. The maximum recovery achievable at a specific feedwater silica concentration may be calculated as follows:

$$R_{\text{MAX}} = \left[1 - \frac{\text{SiO}_2_{\text{FEED}}}{\text{SiO}_2_{\text{MAX}}} \right] \times 100$$

where $\text{SiO}_2_{\text{MAX}} = \text{SiO}_2$ correction factor $\times (4.39T - 3.66)$

Table III; SiO_2 Correction Factor	
Concentrate or Reject pH	Correction Factor
4.0 to 6.5	$3.48 \times \text{pH}_{\text{CR}}^{(-0.667)}$
6.5 to 7.8	1.00
7.8 to 10.0	$1.24 \times 10^{-5} \text{pH}_{\text{CR}}^{(5.45)}$

For the example:

$$\begin{aligned} \text{SiO}_2 \text{ correction factor} &= 3.48 \times 4.5^{(-0.667)} \\ &= 1.276 \end{aligned}$$

$$\begin{aligned} \text{SiO}_2_{\text{MAX}} &= 1.276 \times (4.39T - 3.66) \\ &= 107.36 \text{ mg/L which is } > 82.74 \text{ mg/L and } \therefore \text{ OK} \end{aligned}$$

substituting,

$$\begin{aligned} R_{\text{MAX}} &= \left[1 - \frac{6.0}{107.36} \right] \times 100 \\ &= 94.41\% \text{ which is } > 94.34\% \text{ and } \therefore \text{ OK} \end{aligned}$$

Other Tests: If the initial silica concentration were 9.0 rather than 6.0 mg/L,

$$R_{\text{MAX}} = 91.62\% \text{ which is } < 94.34\% \text{ and } \therefore \text{ NOT OK}$$

also, if the temperature were lowered to 10°C ,

$$\text{SiO}_2_{\text{MAX}} = 51.35 \text{ mg/L which is } < 82.74 \text{ mg/L and } \therefore \text{ NOT OK}$$

or likewise, if the permeate were increased from 50.0 to 51.0 gpm, the recovery increases to 96.22% which is $> 94.34\%$ and \therefore NOT OK

Boron Removed

At a feed rate of 53.0 gpm, a total of 76,320 gallons per day of water will be processed. At a recovery of 94.34%, 72,000 gallons will be permeated and the balance of 4,320 gallons will be discharged to rad waste treatment. The total amount of boron in the feed equals:

$$\frac{2,200 \times 73,320 \times 8.34}{1,000,000}$$

or 1,400 lbs.

Since the first stage contains 4/7 of the membranes, the first stage permeate = 4/7 of 72,000 or 41,143 gallons. At a membrane boron rejection of 25.0% per stage, the first stage permeate will contain:

$$\frac{(1 - 0.250) \times 2,200 \times 41,143 \times 8.34}{1,000,000}$$

or 566.2 lbs. boron

1,400 minus 566.2 equals 833.8 lbs. boron remaining in the first stage concentrate (same as second stage feed). Subtracting the first stage permeate volume of 41,143 gallons from 76,143 gallons processed equals 35,177 gallons for second stage treatment. The 833.8 lbs. boron remaining translate into a boron concentration of:

$$\frac{35,177 \times 8.34 \times (B_{\text{mg/L}})}{1,000,000} = 833.8$$

or 2,842 mg/L

Since the second stage contains 2/7 of the membranes, the second stage permeate = 2/7 of 72,000 or 20,571 gallons. At a membrane boron rejection of 25.0% per stage, the second stage permeate will contain:

$$\frac{(1 - 0.250) \times 2,842 \times 20,571 \times 8.34}{1,000,000}$$

or 365.7 lbs. boron

833.8 minus 365.7 equals 468.1 lbs. boron remaining in the second stage concentrate (same as third stage feed). Subtracting the second stage permeate volume of 20,571 gallons from 35,177 gallons processed equals 14,606 gallons for third stage treatment. The 468.1 lbs. boron remaining translate into a boron concentration of:

$$\frac{14,606 \times 8.34 \times (B_{\text{mg/L}})}{1,000,000} = 468.1$$

or 3,843 mg/L

Since the third stage contains 1/7 of the membranes, the third stage permeate = 1/7 of 72,000 or 10,286 gallons. At a membrane boron rejection of 25.0% per stage, the third stage permeate will contain:

$$\frac{(1 - 0.250) \times 3,843 \times 10,286 \times 8.34}{1,000,000}$$

or 247.3 lbs. boron

468.1 minus 247.3 equals 220.8 lbs. boron remaining in the third stage concentrate (same as ultrafiltration feed). Subtracting the third stage permeate volume of 10,286 gallons from 14,606 gallons processed equals 4,320 gallons for discharge through ultrafiltration dead-end filtration. The 220.8 lbs. boron remaining translate into a boron concentration of:

$$\frac{4,320 \times 8.34 \times (B_{\text{mg/L}})}{1,000,000} = 220.8$$

or 6,128 mg/L

At 20°C , Appendix A shows the solubility of boron @ 8,251 mg/L, well above the above boron concentration. If, however, the silica cleaning were carried out at 10°C , the above boron concentration would exceed the boron solubility of 6,101 mg/L at this temperature. Therefore solubilities of the final membrane concentrate must be

closely monitored to prevent the occurrence of boron supersaturation with concurrent boric acid precipitation.

Permeate Boron Concentration

Total boron in the permeate = 566.2 + 365.7 + 247.3 = 1,179 lbs. The 1,179 lbs. of total boron in the permeate translate into a concentration of:

$$\frac{72,000 \times 8.34 \times (B_{\text{mg/L}})}{1,000,000} = 1,179$$

or 1,963 mg/L

System Boron Rejection

System boron rejection is found by:

$$\begin{aligned} \lambda &= 1 - \frac{C_P}{C_F} \\ &= 1 - \frac{1,963}{2,200} \\ &= 0.1077 \text{ or } 10.77\% \end{aligned}$$

Compliance with Tech Specs

The initial total boron content of the tank being cleaned is found by:

$$\frac{500,000 \times 8.34 \times 2,200}{1,000,000} = 9,174 \text{ lbs.}$$

after one day's processing without boron addition, the boron remaining is given by:

$$9,174 - 220.8 = 8,953.2 \text{ lbs.}$$

likewise, the remaining tank volume without water addition is given by:

$$500,000 - 4,320 = 495,680 \text{ gallons}$$

the resulting boron concentration is found by:

$$\frac{495,680 \times 8.34 \times (B_{\text{mg/L}})}{1,000,000} = 8,953.2 \text{ lbs.}$$

or 2,166 mg/L which must \geq tech specs

Additionally, the above loss of water will result in a specific lowering of the tank liquid level. The new level must also \geq tech specs.

Borated demin water make-up requirements are determined by the above operational characteristics. Should processing or recovery rates be changed during the cleaning period, corresponding water/boron make-up rates/amounts must also be changed accordingly.

General System Design Considerations

The permeation rates of silica and boric acid are extremely similar. To accomplish their separation requires the selection of a membrane with exact but differing rejections of each component. At a pH of less than 8, silica predominantly exists as dissolved silica and silicic acid. If present at a concentration exceeding its saturation point, the formation of a silica gel is rapid and certain.

In the example analyzed, the individual membrane rejections/stage were 87% silica and 25% boron for a difference of 62%. A different membrane might have corresponding rejections of 97% and 35%, respectively. The difference is still 62% but if used in the same system as the example, excessive silica concentrations in the final membrane concentrate would require significant lowering of the recovery rate or silica supersaturation would occur.

Likewise, if the membranes exhibited rejections of 77% and 15%, respectively, the difference is still 62% but if used in the same system as the example, a much longer processing time would be necessary due to the lesser silica rejection. The longer the processing time the greater the boron loss. Consequently, the selection of the membranes and system design selected have a direct impact on the boron solute lost as well as its demin water solvent.

In like manner, the difference in the system rejection rates of the two constituents was 77.66% - 10.77% or 65.89%. This difference is realistic of membranes available today. However, the difference of 65.89% when considered alone does not necessarily translate into an acceptable silica cleaning system. It all depends on the specific rejections of the membranes selected.

Some membrane system designers may incorporate recirculation flow to improve the separation process. Recirculation flow increases the recovery of boron simultaneous with an ever-increasing concentration of silica in the concentrate. Eventually the silica will exceed its saturation point resulting in silica precipitation. Therefore every system which uses recirculation in its design must be purged periodically to eliminate the build-up of silica. Recirculation flow therefore represents inferior system design.

The recovery of any membrane silica cleaning system is limited by the silica concentration in the feed as well as the temperature of the raw water. The higher the silica and the colder the water the less the theoretical recovery. Throughout the cleaning period the actual recovery can be increased proportional to the declining silica concentration. In the vast majority of instances, recoveries of 90 to 95% are realistic and achievable.

Every membrane has a minimum concentrate flow/permeate flow ratio in order to minimize membrane fouling. In addition, each membrane has a maximum flux rate (rate of permeation) that it can achieve. Exceeding the membrane manufacturer's specifications usually results in rapid failure once in use. To increase the performance reliability of any membrane silica cleaning system, a design that exceeds the membrane manufacturer's specifications by a comfortable margin is synonymous with greater projected system reliability.

During a silica cleaning project, other treatment equipment such as acid washed activated carbon adsorption to remove organics or cobalt burst debris, mixed bed demineralizers to reduce or eliminate the load on the rad waste disposal facilities, or selective ion exchangers can

be added to achieve additional objectives at but nominal costs.

Safety Considerations

A silica-cleaning project must undergo a safety evaluation review before implementation. To permit such a review a comprehensive General Operating Procedure must be developed for the cleaning task. Respecting Regulatory Guide 1.143, if a services company accomplishes the cleaning on an as-required basis, non-compliance therewith is permitted since the cleaning system requires but a temporary installation and is vendor supplied; and further, the cleaning system is neither a test nor an experiment since its interfaces are defined and established such that no experimenting is necessary.

Cleaning systems can be furnished with microprocessor controls and instrumentation. If so furnished the cleaning

system operator(s) can monitor and control routine operations from a remote location by utilizing a phone modem communication link. An additional monitor can be furnished to enable the chemistry laboratory to simultaneously monitor the cleaning system's flow rates, pressures, conductivity levels, pH, and temperature thereby providing back-up observation of operating conditions. The general operating procedure will reflect windows of operating parameters to identify permissive limits of the above variables.

Summary: The above example permits a rather thorough review and evaluation of any membrane silica cleaning system. A good understanding of this technology by the PWR facility is absolutely essential as a prerequisite to a consideration of its application. Although the facts will change from project to project, the principles of evaluation remain constant.

About the Company

WaterSmart Environmental, Inc. is a manufacturer of highly engineered water purification components and systems. The company designs and builds a wide variety of water treatment equipment including packaged water and wastewater treatment plants, UltraPac™ aerobic package plants, OAT™ Process anaerobic digesters with associated energy production, aerators, filters, PuriSep™ oil/water and solids/liquid separators, RainDrain™ perimeter trench sand filters for stormwater runoff, dissolved air flotation separators, air strippers, complete skid assembled aqueous waste treatment plants, FilterFresh™ skid mounted potable water production plants, skid mounted wastewater treatment systems for laundromats, laundries, and car/truck

wash facilities with water reclamation and reuse, softeners, demineralizers, activated carbon treatment equipment, and water purifiers for domestic and international markets.

The **Energy and Power Management Division** of the company designs and provides *Energy Management Control Systems* for large office buildings, malls, hospitals, and similar facilities. Reduction of combined or total energy costs by 30% or more can frequently be achieved.

WaterSmart Environmental, Inc. takes great pride in supplying treatment equipment and energy management control systems that work *as represented* and *as required* for each application undertaken.

Appendix A

BORIC ACID SOLUBILITIES IN WATER					
<i>Temperature</i>		<i>Wt. % H₃BO₃*</i>	<i>Parts H₃BO₃ per 100 Parts H₂O by Weight</i>	<i>Parts H₃BO₃ per U.S. Gallon of Water by Weight</i>	<i>H₃BO₃ mg/L (ppm)</i>
°C	°F				
0.0	32.0	2.52	2.59	0.216 (03.5 oz)	4,405
5.0	41.0	2.98	3.07	0.256 (04.1 oz)	5,209
10.0	50.0	3.49	3.62	0.302 (04.8 oz)	6,101
15.0	59.0	4.08	4.25	0.355 (05.7 oz)	7,132
20.0	68.0	4.72	4.95	0.413 (06.6 oz)	8,251
25.0	77.0	5.46	5.78	0.481 (07.7 oz)	9,544
30.0	86.0	6.23	6.64	0.552 (08.8 oz)	10,890
35.0	95.0	7.12	7.67	0.636 (10.2 oz)	12,445
40.0	104.0	8.08	8.79	0.728 (11.6 oz)	14,124
45.0	113.0	9.12	10.02	0.830 (13.3 oz)	15,942
50.0	122.0	10.27	11.45	0.994 (15.1 oz)	17,952
55.0	131.0	11.55	13.06	1.074 (17.3 oz)	20,189
60.0	140.0	12.97	14.90	1.223 (19.7 oz)	22,672
65.0	149.0	14.42	16.85	1.379 (22.2 oz)	25,206
70.0	158.0	15.75	18.69	1.526 (24.5 oz)	27,531
75.0	167.0	17.41	21.08	1.715 (27.6 oz)	30,433
80.0	176.0	19.10	23.61	1.914 (30.8 oz)	33,387
85.0	185.0	21.01	26.60	2.151 (34.6 oz)	36,725
90.0	194.0	23.27	30.33	2.444 (39.3 oz)	40,676
95.0	203.0	25.22	33.73	2.707 (43.5 oz)	44,085
100.0	212.0	27.53	37.99	3.039 (48.9 oz)	48,122
103.3	217.9	29.27	41.38	3.301 (53.1 oz)	51,164

*1 wt. % of H₃BO₃ = 1,748 mg/L (ppm) boron.

Appendix B

ABBREVIATIONS	
<i>Symbol</i>	<i>Description</i>
λ	System Rejection Percentage
B _λ	Boron Rejection/Membrane Stage
B _{mg/l}	Boron Concentration
B _O	Initial Boron Concentration
C	Concentration
C _F	Feed Concentration
C _P	Permeate Concentration
CR	Concentrate Or Reject Flow
F	Feed flow Or Feed Stream
F&B	Feed And Bleed
P	Permeate Or Product Flow
Q _F	Feed Rate Of Flow
Q _P	Permeate Rate Of Flow

ABBREVIATIONS	
<i>Symbol</i>	<i>Description</i>
R	Recovery
R _{MAX}	Maximum Recovery
Si _λ	Silica Rejection/Membrane Stage
Si _F	Final Silica Concentration
Si _{mg/l}	Silica Concentration
Si _O	Initial Silica Concentration
SiO ₂ FEED	Silica Concentration In Feed
SiO ₂ MAX	Maximum Silica Concentration
T	Temperature In °C
T _P	Processing Time
V _P	Processing Volume
V _T	Tank Volume

Appendix C

Sample Request for Quotation for Silica Cleaning Service

Provide silica-cleaning equipment/machine with operator(s) to remove silica and other contaminants while reclaiming boric acid from the water in:

Tank Name	Tank Volume	Initial Silica mg/L	Final Silica mg/L	Boron Content mg/L	Tank Liquid Temp. °C	Minimum Recovery Required
						95%
						95%

Notes:

- Silica to be measured by purchaser's laboratory instrument using ASTM analysis method part 31 D 859 for measuring reactive silica in water.
- Liquid radiological waste rejection rate shall not exceed 5% of the processed rate.
- Total waste volume shall not exceed 15% of the tank volume. A penalty of 1% of the contract price for each percent above 15% of the tank volume will be incurred for the excessive generation of liquid rad waste.
- Radioactivity of reject water must be removed by ultrafiltration or other purchaser approved methods to achieve less than 10^{-4} microcuries/mL for colloidal metals. The spent ultrafilters (or other method) will be changed out by the vendor/contractor and disposed of by purchaser.
- Contractor must identify in its silica cleaning system proposal the membrane rejections for silica and boron as follows:

A. Silica: ___% minimum

B. Boron: ___% maximum

Membrane rejections outside of specific levels represent inferior cleaning system designs and will not be considered.

Purchaser will be responsible for monitoring and maintaining boron concentration(s) within the technical specification limits.

Billing program shall be based on the purification cleanup half life of silica. Payments to be divided into four equal

increments based on the number of purification half-lives it takes to achieve silica reduction to concentrations equal to the above-specified limit.

Bidders shall include with their proposal a P&ID of the silica cleaning equipment proposed along with membrane specifications in sufficient detail to permit the purchaser to independently evaluate the design as to its adequacy to perform the required task. The purchaser's review does not relieve the vendor/contractor of its performance obligations hereunder, as the purchaser will review only, not change the proposed design.

Award will be made to the bidder whose proposal is judged to be in the best interests of the purchaser. Price and technical merit will both be considered in arriving at this determination. Purchaser reserves the right to accept or reject any proposal as well as to decline award entirely.

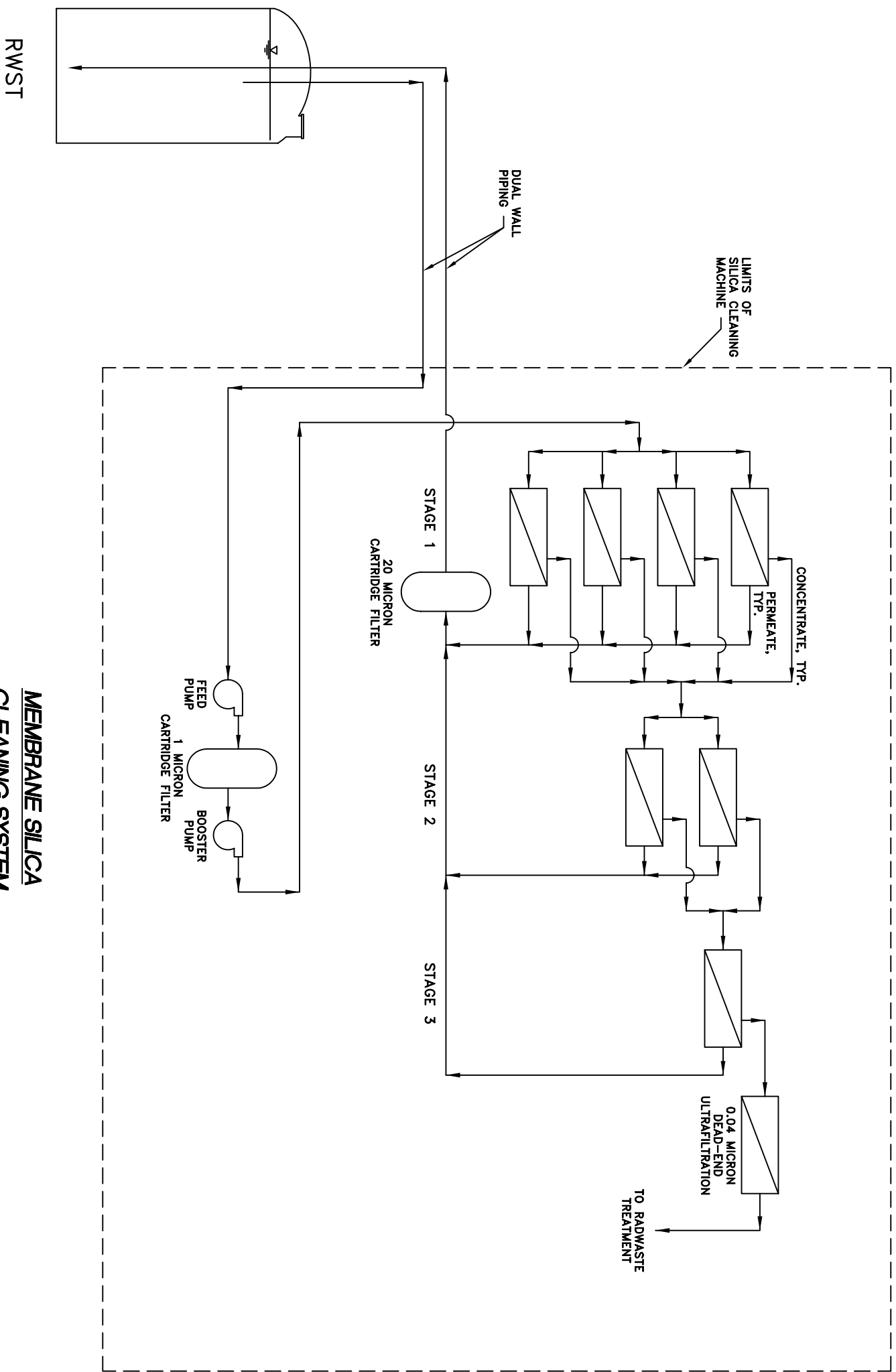
A comprehensive general operating procedure must be submitted to the purchaser for its safety review and comment. This procedure must be approved by the purchaser prior to initiating the silica cleaning program.

This project is classified as non-safety related.

End of RFQ

(Under note 5 supra, the minimum membrane Silica rejection that will work is 75% whereas the maximum Boron membrane rejection is 30%. Cleaning systems offering membrane rejections outside of these specific parameters represent inadequate design and should therefore be considered technically unacceptable.)





**MEMBRANE SILICA
CLEANING SYSTEM**

FIGURE 1

REV.	DATE	DESCRIPTION	BY	CHK	DATE	SCALE	DRAWN	CHECKED	ENG. NO.
						NONE			S-1100
					3/18/93				

DO NOT SCALE DRAWING. USE DIMENSIONS ONLY.

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**NUCLEAR PWR POWER
GENERATION PLANT**

PROCESS FLOW DIAGRAM