

Defining the Concentrate Disposal Problem & Identifying Potential Solutions

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In designing and engineering water treatment plants, preliminary steps include, but are not limited to, finding a high-quality water source that is capable of being treated by technologies known to be effective in removing the contaminants in the source water. This is an extremely important step that will keep costs low.

More often than not, saltwater is overlooked when high-quality source water is sought; however, the Guiding Vision for the USBR/Sandia National Laboratories document *Desalination and Water Purification Technology Roadmap – A Report of the Executive Committee* predicts that by 2020 “desalination and water purification technologies will contribute significantly to ensuring a safe, sustainable, affordable and adequate water supply for the United States.”

There are currently several barriers for utilities to overcome in order to implement desalination successfully. Utilities interested in using desalination technologies as a long-term water supply option must be concerned about the low productivity, regulatory issues with concentrate management, and high energy costs.

Current technology limits the efficiency of membrane solutions and the pumps that drive them; approximately 20 percent of desalination-treated brackish water and up to 50 percent of desalinated seawater is lost via concentrate. This low productivity, combined with high energy consumption rates and the lack of desalination disposal techniques, are recognized as primary hurdles to widespread adoption of desalination technologies; however, the management of concentrate to increase recovery would seem to hold promise. In addition, treatment of concentrate would also appear to remove regulatory hurdles associated with water quality, which currently restricts the ability of utilities from pursuing such resources as saltwater for potable water.

The *Desalination and Water Purification Technology Roadmap – A Report of the Executive Committee* report suggests five technology areas where additional research is required in order to create the next generation of desalination technologies:

- 1) membrane technologies
- 2) thermal technologies
- 3) alternative technologies
- 4) concentrate management
- 5) reuse/recycling

This article will focus on the water quality of concentrate created by various water sources and membrane processes, and the disposal of the concentrate generated by each. The disposal of concentrate is generally a limiting issue for many utility applications. These limitations focus on three areas: pH, density, and toxicity of the concentrate.

The pH of most concentrate is lower than most surface waters when it leaves the membranes. Low-pH waters can add toxicity to marine environments. In many situations, the high density caused by the concentration of dissolved solids may potentially create benthic impacts.

For example, with a seawater source, an efficient treatment process will generate concentrate that is double the typical marine concentration of total dissolved solids of 36 parts per thousand (ppt). Even for fresh and slightly brackish water sources, high total dissolved solids and salts are toxic to grass, crops, and landscaping.

The ionic constituents within the concentrate may also be a problem. Mickley (2000) and FDEP (1995) identified the likely cause of whole effluent toxicity tests using concentrate as an ion imbalance in the concentrate because membranes remove the majority of the ions within the water and therefore the concentration of ions is not in its correct proportion when compared to the body or receiving water. As a result, concentrate has been shown to be acutely toxic to freshwater and marine organisms.

Calcium, fluoride and potassium are the ions which appeared likely to cause problems. In order to resolve the concentrate disposal problem, solutions to each of these problems must be generated. Certain solutions have been proposed as a result of the efforts of students and faculty at the University of Miami and Florida Atlantic University.

Current Membrane & Concentrate Management Practices

The quality of the raw water is an important factor to consider when determining the efficiency of a membrane system. For example, the design of the North Collier and Hollywood facilities included three-stage nanofiltration to enhance recovery of surficial groundwater with high color, organics, and hardness to 92+ percent. This is a signif-

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icant improvement over two-stage systems (Miramar, Pompano Beach, Boca Raton) that recover only 85 percent of the feed water, since it conserves water while minimizing the volume of concentrate. Use of low-pressure reverse osmosis is projected to achieve up to 97-percent recovery.

There are a number of current concentrate disposal options, but in any given setting, they may be limited or poorly understood. Current methods for concentrate disposal in the United States include deep-well injection, direct and indirect outfalls into the ocean or surface water bodies, and use as a supplement to irrigation.

With deep-well injection, problems could occur if the concentrate reaches water-supply aquifers. Utilities that practice deep well-disposal include Collier County; Marco Island; Cape Coral; Mt. Pleasant, South Carolina; Vero Beach; Pompano Beach; Plantation; Jupiter; Miramar; and North Miami Beach, among others.

Where disposal of the concentrate is easily accomplished with injection wells, there is less need to resolve the concentrate “problem”; however, where injection wells are not available, the reduction in the volume of concentrate helps with water conservation goals but may exacerbate the disposal issue.

Direct and indirect outfall into the ocean is problematic because of potential water-quality impacts and benthic toxicity. Indirect disposal includes sending the concentrate to a wastewater treatment plant (WWTP) outfall to be mixed with treated effluent and discharged via ocean outfall, as is practiced in

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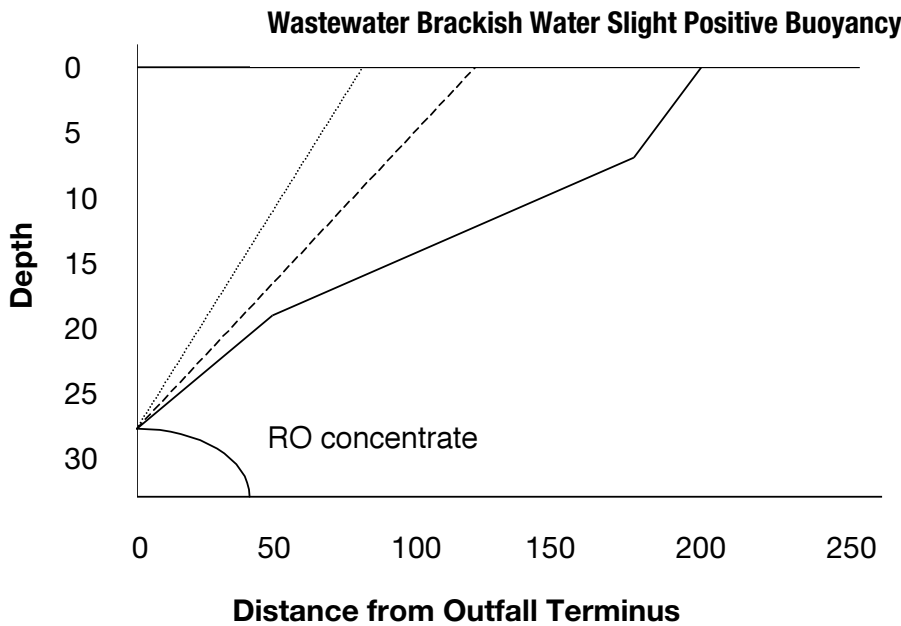


Figure 1. Fate of various waters in marine environments

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Hollywood and Tampa Bay. Direct disposal to surface water is practiced in Venice. In either case, the effluent must be monitored in the regulatory mixing zones and the initial dilution zones. Another option involves using concentrate for groundwater recharge and/or irrigation (e.g. Venice and Fort Myers).

In each of these cases, the toxicity issue is raised.

Defining the Concentrate Management Barriers

As noted, reducing the volume of concentrate is a major conservation initiative in water-limited environments, but it may only increase problems with water quality. The ultimate disposal problem remains because the concentrate, regardless of quantity, is still acutely toxic to marine and freshwater organisms. Complicating matters is that concentrate is characterized as an industrial waste by regulatory agencies.

Toxicity is associated with three parameters: pH, total dissolved solids (TDS), and ion imbalance. The pH issue is the result of acid addition to prevent scaling of calcium carbonate. Excessive TDS concentrations will have benthic impacts due to density differences with potential receiving waters.

Figure 1 shows how discharges to marine waters act upon discharge, based upon CORMIX modeling (Del Bene et al. 1997). Figure 1 demonstrates that as the density of the concentrate increases, the nearfield benthic impacts become important as the potential for dilution in surface waters is lost by the denser liquid. Even for fresh and slightly

brackish water applications, elevated TDS levels are toxic to grass, crops and landscaping and are regulated as such; therefore, their application to terrestrial practices is limited.

To understand the toxicity effects from ion imbalances, four water sources were analyzed to collect information assessing relative concentrations. Estimates of finished water and concentrate were made using Reverse Osmosis System Analysis (ROSA) to predict concentrate water quality from four sources:

- ◆ Hard, fresh Biscayne aquifer water, which is similar to that used in Mickley (2000).
- ◆ Recycled Biscayne aquifer water, which may provide the most potential for solutions.
- ◆ Brackish Floridan water (TDS = 2400 mg/L).
- ◆ Seawater.

The first three were sampled from the city of Hollywood's existing nanofiltration and low-pressure reverse-osmosis treatment skids. Table 1 outlines the projected water-quality characteristics and concentrate quality predicted, using the ROSA software and the potential for treatment needs and toxicity involving disposal of the ultimate concentrate solution.

Mickley (2000) predicted toxicity by analyzing concentrate water-quality deviations from seawater in an AWWA Research Foundation Study, *Major Ion Toxicity in Membrane Concentrate*, which showed that calcium, fluoride, and potassium were all probable causes of toxicity. A similar analysis was performed and summarized in Table 2 for water samples taken in Hollywood.

The results indicate that fluoride and calcium are likely causes of toxicity in the Floridan Aquifer, Biscayne Aquifer, and recycled Biscayne waters. Bicarbonate, sulfate, and magnesium may also contribute to toxicity due to ion imbalance, but at lower relative levels. Findings indicated that calcium, fluoride, and potassium levels in the reverse-osmosis brine were consistent with those present in natural seawater, while magnesium and bicarbonate were relatively low.

Also referenced in Mickley (2000) was the *Protocols for determining Major-Seawater-Ion Toxicity in Membrane-Technology Water-Treatment Concentrate*, written by the Florida Department of Environmental Protection (1995); however, there are differences between the water in the AWWARF study and potential reverse-osmosis seawater brine because the AWWA study was completed on nanofiltered freshwater, and not on reverse-osmosis filtered saltwater.

Potential Solutions to Concentrate Management

Concentrate management solutions are

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Parameter	FL RO Raw	FL RO	Fr. MS Raw	Fr MS	MS Recycle	MS Recycle	Seawater	SW RO Conc
	Water	Concentrate	Water	Concentrate	Water	Concentrate		Concentrate
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
TDS	4953	24462	547	3477	3478	13745	30893	60386
Sr	n/a	n/a	n/a	n/a	n/a	n/a	6.6	12.6
F	1.47	7.13	0.2	0.5	0.5	1.95	0.6	1.33
HCO3	159	158	288.0	974.0	974.0	887	123.5	78.2
Ca	180	911	95.0	618.0	618.0	2434	360	686
SO4	550	3306	46.0	1448.0	1448.0	8341	2381	4716
Mg	150	759	23.0	200.0	200.0	966	1136	217
K	n/a	n/a	n/a	n/a	n/a	n/a	349	664
Cl	2461	12161	70.0	155.0	155.0	849	17002	32292
Na	1401	6910	222.0	74.0	74.0	236	9463	21642
Ammonia	0.64	3.1	2.0	5.1	5.1	21	1.3	2.9

Table 1. Comparison of raw water and concentrate water quality for different water types in Hollywood, Florida

Parameter	Seawater		Bicayne Concentrate			Recycled Bicayne Concentrate			Floirdan Concentrate			Seawater		
	Concentration	Percent	Percent	Percent	Deviation	Percent	Percent	Deviation	Percent	Percent	Deviation	Percent	Percent	Deviation
					fr. Seawater			fr. Seawater			fr. Seawater			fr. Seawater
TDS	30893		3478			13745			24462			60386		
Sr	6.6	0.021										12.6	0.02	0.98
F	0.6	0.002	0.22	0.006	3.26	1.95	0.01	7.30	7.13	0.03	15.01	1.33	0.00	1.13
HCO ₃	123.5	0.400	974	28.005	70.05	887	6.45	16.14	153	0.63	1.56	78.2	0.13	0.32
Ca	360	1.165	618	17.769	15.25	2434	17.71	15.20	911	3.72	3.20	686	1.14	0.97
SO ₄	2381	7.707	1448	41.633	5.40	8341	60.68	7.87	3306	13.51	1.75	4716	7.81	1.01
Mg	1136	3.677	200	5.750	1.56	966	7.03	1.91	759	3.10	0.84	217	0.36	0.10
K	349	1.130		0.000								664	1.10	0.97
Cl	17002	55.035	155	4.457	0.08	849	6.18	0.11	12161	49.71	0.90	32292	53.48	0.97
Na	9463	30.632	74	2.128	0.07	236	1.72	0.06	6910	28.25	0.92	21642	35.84	1.17
pH			7.07			5.97			6			0		

Note 1: Values close to 1.0 in "Deviation from Seawater" mean that their values are extremely close to the values present in typical seawater.

Note 2: Numbers in blue indicate where the ionic ration deviates significantly from seawater which means there is likely to be toxicity to marine organisms if the water is discharged to water bodies.

Table 2. Comparison between natural seawater and membrane-filtered concentrates

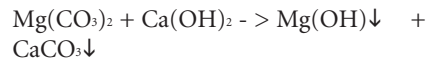
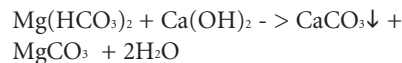
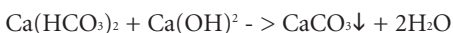


Figure 2 Initial Water Quality of Hollywood Nanofiltered Concentrate

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different for each of the potential problems: pH, toxicity and density. The adjustment of pH is simply a chemical reaction requiring the addition of caustic soda or some similar basic solution. The pH "problem" is therefore easily solved with existing technology and protocols.

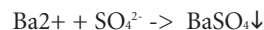
The removal of toxicity is more difficult. Table 2 is a starting point for understanding the type of treatment that would be required. In nanofiltration, the ions that significantly deviate from ion balance are calcium, magnesium, bicarbonate, sulfates, and fluoride. Testing by students indicated that lime and soda ash additions were effective in dealing with small volumes of concentrate from small nanofiltration plants for precipitating three of these constituents (calcium, magnesium and bicarbonate), as follows:



Sulfates and fluoride remain unbalanced. Sulfates are stable and thus do not precipitate easily except in the presence of barium chloride. Testing at the University of Miami demonstrated that the barium chloride could remove all of the sulfates, but the concentration of chlorides generated was significant. In addition, bicarbonates interfere with the reaction (hence, lime addition was pursued first to precipitate carbonate species).

After softening, the water pH was 9.3. In the presence of CO₃²⁻, the barium chloride will preferentially form BaCO₃, whereas barium chloride settles optimally below a pH of 7; therefore, HCl was added to lower the pH to 6.5, since at a pH of 6.5 there is almost no carbonate present and settling of BaSO₄ is encouraged.

Figure 2 shows the concentrate treated. Figures 3 and 4 show what happens after the BaCl₂ is added. The BaCl₂ dissociates in solution to form BaSO₄, which forms a colloidal suspension that does not settle easily – it took nearly two hours to achieve settling, and re-suspension occurred quickly. Here are the chemical reactions that occur:



Membrane filtration is required to remove the remaining residual. To get rid of all the sulfates, enough BaCl was added (3.013 g/L) so that the resulting chlorides added with BaCl were approximately 531 mg/L, exceeding the recommended criteria

Raw Water (meq/L)	Added Chemicals (meq/L)		
	BaCl ₂	Na ₂ CO ₃	Ca(OH) ₂
SO ₄ ²⁻ : 22.5	22.5		
Ca ²⁺ : 45.7		26.3	
HCO ₃ ⁻ : 19.4			19.4
Total (theoretic)	22.5	26.3	19.4
Total (actual)	23	27	21.5

Table 3 – Experiment 1

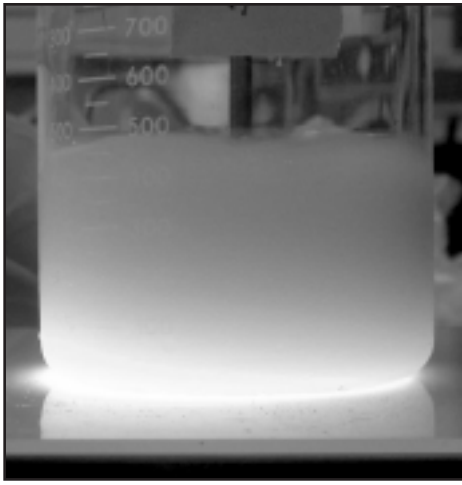


Figure 3 – Initial mixing after Barium Chloride was added, pH = 6.5

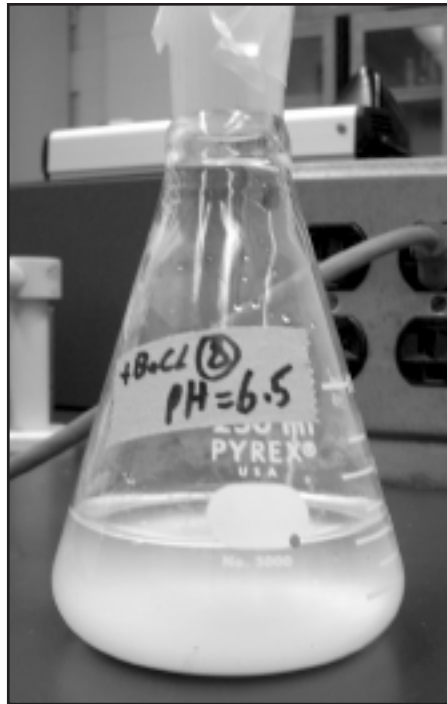


Figure 4 – Initial BaSO₄ Settling with Ph = 6.5

for chloride of 200 mg/L. The final sulfate concentration was 0.73 mg/L.

Tables 3 and 4 outline two experiments for removal of the sulfates.

Fluoride is more likely to remain in solution. The fluoride concentration in the brackish Floridan wells is even more problematic than other sources. One possible option is the use of a wet scrubber at the beginning of the process.

Aeration softening is a proven, though little-recognized, technology for precipitating calcium hardness from water (Chiao and Westerhoff 2002; Zhang et al. 2000). Aeration without chemical addition precipitates calcium carbonate as calcite, to the range of 20 mg/L Ca²⁺ or less, as a result of the carbonate equilibrium established with CO₂ in the air.

The amount of precipitation of calcite from a raw concentrate containing, as calcium carbonate, 1000 mg/L Ca²⁺, 500 mg/L Mg²⁺, and 1500 mg/L HCO₃⁻, can be predicted. Calcium fluoride is unlikely to precipitate as the practical calcium fluoride solubility of 7.6 mg/L, though it may precipitate in other concentrates.

Lime can be used to enhance removal by driving the pH upward to encourage the remaining calcium to react with the remaining carbonate and some fluoride ions to spur deposition. Results of equilibrium modeling indicate that fluoride can be removed in the aeration softening process from some concentrates through the addition of lime to precipitate calcium fluoride, but the amount may not be enough to eliminate the toxicity, while the calcium sulfate ($K_{sp} = 2 \times 10^{-4}$) solubility is 490 mg/L, which still retains the imbalance.

Due to solubility considerations, conventional coagulation and chemical precipitation methods with lime or alum are not expected to reduce fluoride levels to accept-

able levels (Qasim et al. 2000); therefore, chemical solutions appear to be limited.

A non-chemical solution does exist. Fluoride removal theoretically can be accomplished with activated aluminum. A mineral-mediated aeration process is under development at the University of Miami (Englehardt et al. 2002; Englehardt et al. submitted; Meeroff et al. submitted). This process provides detoxification related to the presence of toxic metallic cations and oxy-anions, and toxic organics.

The process involves aeration in the presence of natural mineral filter media containing zero-valent iron, and is naturally compatible with aeration softening. It appears to be effective with multi-valent ions (sulfates, metals, calcium and magnesium), but less so with monovalent ions like fluoride.

Activated alumina adsorption is being tested at Florida Atlantic University to check the veracity of Tokunaga et al (1993) assertions that activated alumina is a method of reducing fluoride to below drinking-water standards at optimum conditions. The fluoride adsorption capacity activated alumina media is 6-8 kg/m³ in a packed bed column with a minimum five-to-six-minute empty-bed contact time (Choi and Chen 1979).

Once the toxicity issue is resolved, the final hurdle is density. Unfortunately, seawater desalination concentrate is more dense than seawater; an engineering solution is required to effect a change.

Such a proposal would be limited to high-flow water bodies, where the density change can be diluted rapidly, minimizing benthic impacts. Figure 8 shows such a proposed process.

A diffuser would be installed in a cut to

dilute the concentrate. For instance, for a 50-percent efficient desalination (or seawater) process, the concentration of the brine is approximately 60 ppt, which is almost twice as much as the concentration of typical seawater.

Since the majority of aquatic life lives near the bottom of channels and streams, significant dilution is necessary so that the emerging concentrate does not just fall and spread out across the bottom, killing this marine life. To assure that aquatic life is not harmed, the concentrate would be disposed into the channel only during periods when large amounts of flow take place.

If the concentrate effluent is released into the channel only after a high tide, while the tides are flowing into the ocean, velocities are higher and better dilution and dispersion occurs. The major limitation with using high tide is that it happens only for six-hour periods, twice a day. During those six-hour periods, only four hours contain high velocities; therefore, because the concentrate is constantly being produced, approximately two-thirds of it must be stored during low-tide and low-velocity periods. If the day is divided into four-hour stages (six periods), four of these periods must be storage periods, while everything is discharged during two periods.

This is what the Tampa Bay Water desalination project attempted to achieve when mixing with the thermal discharge from a power plant. The requirements are either a wastewater outfall with limited total dissolved solids (limited to southeast Florida), where there are power plants with thermal discharges (very limited) or where there are large cuts with fast-moving outgoing tides (coastal regions only). The latter will require hydraulic engineering expertise and large sites (for storage of concentrate) to be effective.

Conclusions

The use of membrane technology will continue to expand as the demand for limited water resources continues to increase rapidly. Currently, membrane technology is restricted in most communities because of water recovery and concentrate disposal limitations. Some form of treatment is required.

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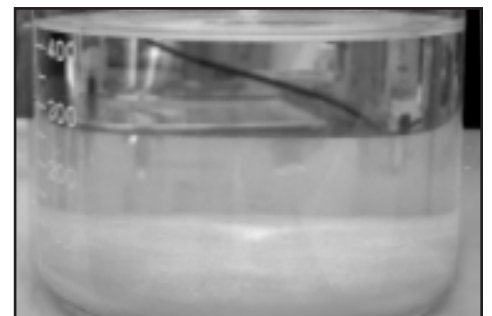


Figure 5 - Results after two hours

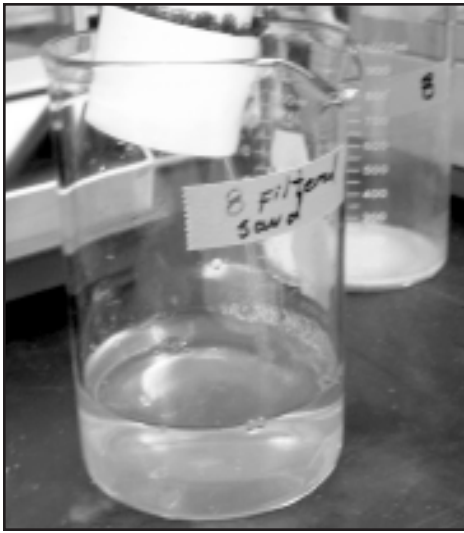


Figure 6 - After filtration by sand

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The addition of lime would effectively remove the magnesium and calcium hardness, but not the sulfate of fluoride toxicity. Aeration would likewise remove hardness and alkalinity, but not sulfates and fluoride. Fluoride and sulfates may be more appropriately removed with mineral mediated or ion exchange processes. Once the ion imbalance issue can be resolved, it would appear that the density issue will require specialized hydraulic engineering solutions, meaning that the places where desalination can occur will be limited and should be planned now for the future.

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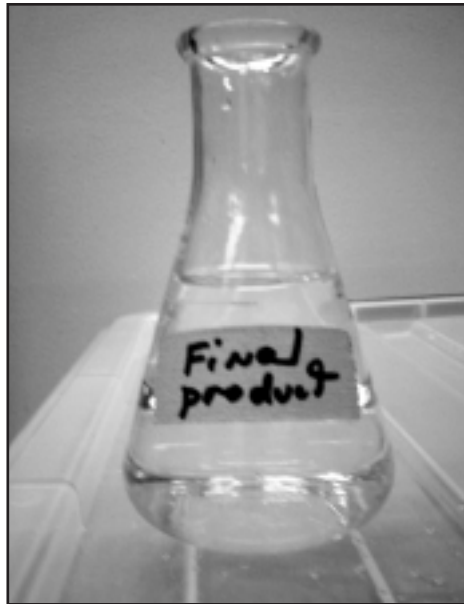


Figure 7 - After membrane filtration

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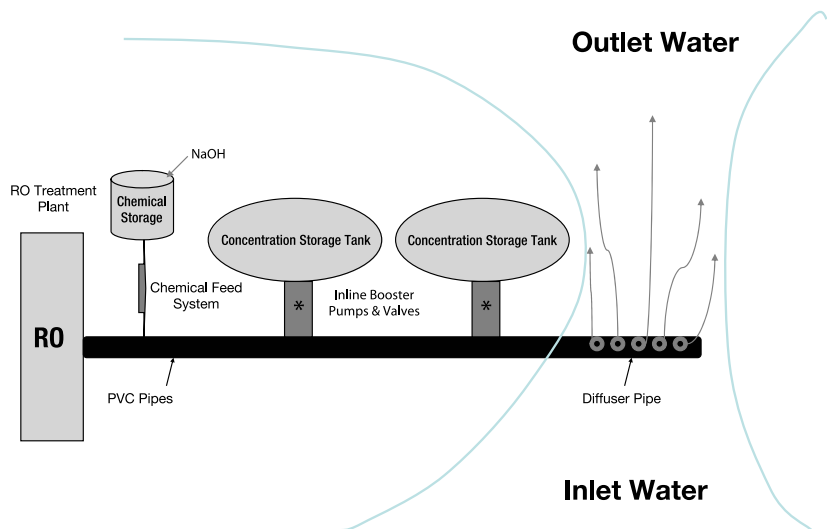


Figure 8 – Inlet discharge to minimize density effects