World Water Forum College Grant Program
2007 Grant Proposals

College	UC Riverside (2)
Faculty	Dr. Mark Matsumoto
Project	Silica Removal from Inland Brackish Water

ORIGINAL

PROJECT TITLE: SILICA REMOVAL FROM INLAND BRACKISH WATER

1. Organizational and Project Information

A. Organization

Name:	University of California, Riverside
Address:	Department of Chemical & Environmental engineering University of California, Riverside Bourns College of Engineering Riverside, CA 92521-0144
Website:	www.engr.ucr.edu

Make checks payable to: UC Regents

B. Type of application: First Time – Local Project

C. Student Project Manager:

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D. Faculty Advisor

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2. Organizational Background

The College of Engineering at University of California, Riverside was established in July 1988. In 1995, the Chemical and Environmental Engineering programs received accreditation from Accreditation Board of Engineering and Technology (ABET). Due to close association of the research interests of Chemical and Environmental Engineering faculty and the overlap of curriculum of both programs, the two programs has been administratively joined together in to Department of Chemical and Environmental Engineering.

The overall objective of the department is to provide students with a foundation that allows them to develop the current technology to diverse interest areas within chemical and environmental engineering, as well as, to maintain a high quality educational and research programs that will be able to prepare them for research development and leadership position in industry and government.

3. Project Description

Despite its location along the edge of Pacific Ocean, Southern California is facing critical issues regarding freshwater. In recent years, the availability of freshwater resources in this region has become limited due to population growth and increasing industries; hence, there is a need to find other sources for the freshwater. One of the potentials for the water supply is the brackish water, which can be found at San Joaquin and Imperial Valley in California.[19] Brackish water usually has a total dissolved solid (TDS) concentration between 1,000 mg/L and 5,000 mg/L,[5] and at this concentration the water requires treatment prior to human consumption because the Environmental Protection Agency (EPA), total dissolved solids (TDS) standard is 500 mg/L.[16] Thus, desalination of brackish water becomes important. One of the current technologies that have been successful in order to solve this problem is reverse osmosis (RO) technology. Although RO technology has proven its effectiveness, it also has problems and one of its major challenges is the presence of silica. Dissolved silica lowers the amount of drinking water that is able to be extracted through desalination because concentrated silica fouls reverse osmosis (RO) membranes once it reaches a concentration of approximately 100 ppm.[2] The performance of the RO technology can be significantly reduced due to a decline in the overall water flux efficiency that is caused by the precipitation of the silicates on the surface of the RO membrane.[17] As a result, the operations cost of the RO process becomes expensive due to frequent replacement of the RO membrane.

MWD has a partnership agreement with Imperial Valley.[10] Since Imperial valleys has a large supply of brackish water (approximately 270,000 af/yr[8]), which contains many chemicals including silica, implementing the combined system of the ROSi team in the pre-treatment process will improve the life span of the RO membrane. The combined system of the ROSi team of the University of California, Riverside (UCR) is proposing an innovative system for silica removal from brackish water prior to desalination as a part of a pre-treatment process. By implementing this system before RO desalination, it is anticipated that the silica content of the brackish water can be reduced up to 90%, which indicates that there will be a significant improvement of the life span of the RO membrane.

As mentioned above, silica can cause scaling and fouling to the membranes. Imperial Valley has the silica content in the amount of 600 mg/L with the TDS concentration of 2000 mg/L.[8,9] If the combined system were to remove a 90% of the silica, the silica concentration of brackish water at Imperial Valley will be reduced to 60 mg/L. Therefore, theoretically, the life span of RO membrane should be able to improve by ten times, considering that the current life span of the RO membrane is about a year due to silica fouling.

Furthermore the water recovery using the RO process is between 75% and 85% due to the membrane scaling.[18] However, the combined system may be able to increase the water recovery since it depends on the coagulation of the calcium hydroxide and the activated alumina as the adsorbent. Therefore, if we could avoid the membrane scaling, the water recovery would be able to increase up to 90%, which means that it saves valuable water resources. As a result, the quantity of water supply for this region will be able to improve.

4. Project Management Team

ROSi or Removal Of Silica team from University of California, Riverside (UCR) is composed of three primary researchers: Brian Hawkinson, Dewi Nilasari, Tongzhou Wang. Their responsibilities are to find literature review about the technology, design and implement the experiments as well as analyze the results, and design a scale up of the chosen technology with its economic evaluation. Dr. Kawai Tam (Lecturer, CEE Department) and Dr. Matsumoto are the supervisor and advisor for the group. Nida Saleem and Paiman Zabul are the students of Environmental Engineering who help to conduct the experiments.

Project Management Team

	NAME	TITLE	ADDRESS	PHONE & EMAIL
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6.	Dr. Mark Matsumoto	Professor / Associate Dean	same as above	(951)827-3197 matsumot@engr.ucr.edu
7.	Dr. Kawai Tam	Lecturer	same as above	(951) 827-2498 ktam@engr.ucr.edu

5. Costs of Project

Total cost of the project

Description	Cost ($)
Chemicals	1,937
Equipments	7,154
Indirect Cost	909
Grant Funds Requested from MWD	**10,000**

Indirect costs will be capped at 10% of the total cost of the project, at $909. Because UCR requires 50% of the total costs to be for indirect costs, the difference between the required 50% and the cap of 10% will be considered the in-kind contribution equivalent, which is greater than 25% of the matching funds required for this MWD RFP. A total budget of $10,000 is requested for the successful completion of the silica removal from brackish water project. No additional sources of funding are available for this project. A detailed list of chemicals and equipment are provided in this proposal in Section 10.

6. Signature Block

	NAME	SIGNATURE	DATE
Faculty Project Manager	Mark Matsumoto		12/13/07
Student Project Manager	Tongzhou Wang		12/13/07
Member Agency Representative	Monique Navarette		

7. Innovation of conservation concept

Brackish water has become a reliable water source due to increasing demands of water consumption within the state of California. In recent years, reverse osmosis (RO) membrane process has become the major desalination application for brackish water purification since there is a high concentration of salts and other dissolve solids within brackish water. Although most RO membrane processes have high efficiencies for removing total dissolved solids, the major challenge in treating brackish water with a RO membrane process is the presence of silica. According to recent studies, silica has been the most problematic foulant/scalant for RO membrane processes, and the cost of replacing reverse osmosis membranes has become the main factor for maintaining a low cost water production method. This recurring problem of silica fouling in the treating of brackish water has led the ROSi or Removal Of Silica team from University of California, Riverside (UCR) to design a pre-treatment system for the reverse osmosis process.

The combined treatment system proposed by the ROSi team relies on the effectiveness of the coagulant calcium hydroxide, to precipitate out the silica and the activated alumina as the adsorbent. While calcium hydroxide (hydrated lime) is able to remove the silica up to 60% at 20°C and 99% at 75°C based on literature,[2] activated alumina (AA) can have silica removal efficiencies as high as 99.8% according to the literature.[3] However, it would not be a reasonable to heat brackish water up to 75 °C due to its high energy cost, nor use activated alumina alone since AA costs about $1500[1] per ton and can only be regenerated up to three lifespans.[3] Therefore, by decreasing energy input for calcium coagulation at a lower temperature prior to the activated alumina will enhance the lifespan of activated alumina, and the overall cost can be significantly decreased.

The current objective is to develop a bench-scale process that removes 90% of silica from brackish water by combining two methods: hydrated lime coagulant and activated alumina. The brackish water will be pumped into a continuously stirred tank reactor with addition of hydrated lime. Silica dissolves in water and forms monosilicic acid (a weak acid) H_4SiO_4 or $Si(OH)_4$. In basic solutions, $Si(OH)_4$ dissociates to become anionic species such as SiO^-, $Si(OH)_3^-$, $SiO_2(OH)_2^{2-}$ and $Si_4(OH)_{18}^{2-}$, etc.[2] Since calcium has a positive surface, it will attract anionic silica to adsorb onto its surface during the coagulation and flocculation steps. The overall chemical reactions of the coagulants with silica are described as the following steps:[7,12]

$$SiO_2 + H_2O \rightarrow H_4SiO_4$$
$$H_4SiO_4 \rightarrow SiO^- \text{ (anionic silica)} + OH^-$$
$$Ca(OH)_2 + \text{ anionic } SiO_2 \rightarrow \text{C-S-H (calcium silicate hydrate)}$$

After the flocculation step is completed, the water will be pumped into an activated alumina adsorption column, where the rest of the silica will be adsorbed onto the active sites of activated alumina. An activated alumina adsorption column can enhance the overall efficiency of silica removal. Effects of foreign anions in aqueous solutions such as SO_4^{2-}, F^-, NO_3^- and HCO_3^-, have also been investigated. The results have shown that the reaction rate of activated alumina with these anionic species were dependent on pH, temperature and inlet concentration of brackish water.[3] Based on this study, we believe that the reaction rate of silica on activated alumina may also depend on pH, temperature and inlet concentration of silica. Obtaining these results will enable us to build a mathematical model that correlates with each of the parameters (temperature, pH, silica concentration) to optimize the silica removal efficiency for a given source of brackish water.

8. Methodology

The following bench scale apparatus may be applied for combining both lime coagulation and activated alumina adsorption.

8.1 Brackish water composition

A simulated brackish water will be made with a TDS of 2.065 to 2.65 g/L by dissolving 1 gram of sodium chloride, 1 gram of sodium sulfate, and 0.065 to 0.13 grams (20 to 40 ppm of silica SiO_3) of sodium meta-silicate pentahydrate to 1 L of deionized (DI) water. Air will be bubbled through the solution for one hour. Hydrochloric acid will then be added in order to bring the brackish water solution to pH 8.

8.2.Coagulation and Flocculation:

The coagulation/flocculation process reactor will be made of glass and designed to hold 5 liters of brackish water. To complete the silica removal process, five sequential steps will be performed.

1) Brackish water will be heated to the desired experimental temperature (15°C, 20°C, 25°C, 30°C, 35°C and 40°C) using an immersion heater. The immersion heater will be connected to a Proportional-Integral-Derivative (PID) controller to monitor and maintain a constant temperature.
2) The calcium hydroxide is then injected into the system at the concentration of 50 mg/L to 250 mg/L
3) Complete mixing between the brackish water and calcium hydroxide are achieved using an installed high speed motor (250 rpm) with a vertical mixing turbine for 1-5 minutes.
4) The vertical turbine will also act as a flocculator when run at a low speed (5-25 rpm) for 20-40 minutes.
5) Large particles that precipitate during the flocculation step are allowed to settle for 20 minutes in order to determine the optimal condition for silica removal.

Table 1 summarizes the experimental design parameters for finding the optimal condition for silica removal using calcium hydroxide as the coagulant. This range of coagulants will be investigated since most inland brackish water contains 20-40 ppm of silica.

Table 1: Experimental design parameters

Type	Values
Amount of coagulant (mg/L)	50-250
Temperature (°C)	15°C - 40°C
Reaction or mixing time (min)	1-5

8.3.Adsorbent method

A column with the diameter of 5 cm and the height of 60 cm will be used for the activated alumina adsorbent method. The adsorbent method will be tested on its own as well as in combination with the coagulant method later on. A schematic of the activated alumina column is shown in Figure1. Granular Activated alumina (AA) are filled half way through the column, and the brackish water will be running from top to bottom of the column. The water will pump through the column at various flow rates [50-200 ml/min] and the water coming out from the column will be collected and analyzed using a colorimetric method as will be described in the silica analysis section.

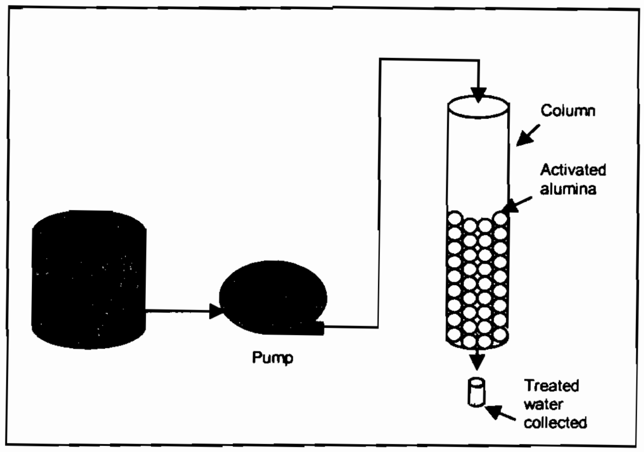

Figure 1: Activated Alumina (AA) column

8.4. Silica Analysis

Silica concentration of the treated brackish water will be determined using a colorimetric method based on the formation of a silicomolybdate complex. The complex solution will be reduced using metol and oxalic acid solutions to produce a blue color solution that is directly proportional to the silica concentration.[16] The absorbance of silica will be measured using a spectrophotometer (BioMini Shimadzu). In order to measure the absorbance of silica, the standard solution will be prepared by adding 1 ml of the molybdate solution to 2.5 ml of the standard solution. The solution will be mixed and incubated at 20°C for 20 minutes. Reducing reagent of 1.5 ml will be added to the previous solution, incubated at 20°C for 3 hours, and then the standard solutions are ready to be measured using the spectrophotometer at 812 nm. A standard curve of absorbance versus silica concentration will be produced.

The samples of treated brackish water will also be prepared the same way as the standard solutions by adding the same amount of molybdate solution to the samples and reducing reagent. The absorbance measurement of the samples will also be taken using the spectrophotometer at 812 nm. Using the silica standard curve, the silica concentration of the samples will be determined and the percentage of silica removal can be obtained using equation 1, with the initial silica concentration.

$$\frac{Silica_{initial} - Silica_{final}}{Silica_{initial}} \times 100\% = \%Silica_{removal} \qquad (1)$$

9. Potential applications beyond local communities

The needs of fresh water supplies become crucial in many regions of the world including United States. While some species have advantages of using brackish water for survival, the human population needs to treat this brackish water in order to consume it and to use it for everyday life especially for agriculture. Using reverse osmosis to treat the brackish water requires high pressure to push water molecules over a membrane through which salt molecules cannot pass. Though this method can be used to treat brackish water, the total operation cost has always been an issue due to membrane cleaning and high pressure, which requires a lot of energy. The other main concern is that the cost will be higher to communities due to increasing limited water sources.

In addition, in many countries, reverse osmosis technology have not been chosen as the first choice to solve their problem with the brackish water. Spain, for example, they have to use desalination with large-scale of purification plants due to membrane import from United States in order to meet their growing demands of clean water. Iraq has a similar problem to Spain. Although they use reverse osmosis and ion-exchange to treat the brackish water, they have to constantly import their membrane supplies from other countries since membrane scaling/fouling has been a major problem.

Silica removal from brackish water prior to desalination is another way to solve many problems regarding brackish water treatment in many regions of the world. The elongation of lifespan for reverse osmosis membranes by applying ROSi silica removal process may significantly reduce reverse osmosis membrane replacement in which leads to reduction in operation cost. Water production efficiency will also increase for desalination facilities. In addition, the amount of RO membrane wastes taken to landfill will significantly decrease on a global basis as well as creating a better environment for the future. It will allow reverse osmosis membrane technology to become cost effective for developing countries such as Iraq, Spain and rest of the world.

10. Budget

This project will be conducted in one of the research labs at UC Riverside. Table 2 indicates chemicals that are needed to make the brackish water, remove and analyze the silica. Table 3 specifies the equipment that we will need to perform the bench-scale experiment. It is estimated that this project will be able to be completed within four months with the following arrangement: ordering the chemicals and equipments, lab preparation and equipment set-up, and lab experimentations with calcium hydroxide and activated aluminum to remove the silica with the analysis of the silica in the treated brackish water.

Table 2: Cost estimation of chemicals needed for silica removal

Chemicals	Cost ($)
Calcium hydroxide, 500 g	$68
Aluminum sulfate, 100 g	$28
Activated alumina, 2.5 kg	$154
Sodium meta-silicate pentahydrate, 3 kg	$90
Ammonium paramolybdate, 500 g	$309
Anhydrous sodium sulfite, 500 g	$51
Metol (p-methyl aminophenol sulfate), 500 g	$112
Oxalic acid dihydrate, 500 g	$167
Sodium silicofluoride, 100 g	$959
Total	**$1,937**

Table 3: Equipment costs for bench-scale experiments

Equipments	Cost ($)
Flocculator	$640
Spectrophotometer	$2,999
Cuvette	$116
Fraction collector	$995
Tubing pump	$144
Glass reactor	$291
Water pump	$1,668
500 ml glass bottle	$300
Total	**$7,154**

11. Project Timeline

It is expected that the funding will be received on Spring 2008; hence, the experiment will start on April 1, 2008. It is estimated that this project will be able to complete within a year with the following arrangement: ordering the chemicals and equipments, lab preparation and equipment set-up, and lab experimentations with calcium hydroxide and aluminum sulfate to remove the silica with the analysis of the silica in the treated brackish water. Table 4 provides a projected timeline for our experiments.

Table 4: Project schedule for April 1, 2008 to April 30, 2009

Date	Description
4/1 – 5/30	Receipt of funds; Purchase the chemicals and equipments
6/2 – 6/30	Expect all the chemicals and equipments to be arrived at the latest
7/1 – 7/31	Lab set-up and make the necessary reagents for the analysis
8/1 – 8/29	Finding the optimum condition for silica removal using coagulation method only
9/01 - 9/30	Silica experiment with the activated alumina column only
10/1 – 10/31	Silica removal using the combined system
11/03 – 12/19	Report the results in written format
01/05 – 04/30	Preparation for MWD Expo featuring prototype & report

12. References

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