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Final Report

Innovative Reclamation of Membrane Concentrates: Conceptual Evaluation of Combining Two Innovative Technologies

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EXECUTIVE SUMMARY

Background

RO systems used for desalination generate brine concentrate waste streams that typically are at least 15 to 20 percent of volume treated. Thus, there is a need to develop technologies that facilitate recovery of membrane concentrates thereby reducing the volume of waste to be discharged. The principal characteristics of membrane brines are high concentrations of hardness, total dissolved solids (TDS), and possibly trace metals, most of which can be removed by precipitative softening processes.

Batchelor and his colleagues originally developed a noval softening process called the Ultra-High Lime (UHL) process to remove scalents (Ca^{2+}, Mg^{2+}, PO_4^{3-} and SiO_2) from recycled cooling water (Batchelor et al., 1984; 1991). Subsequently, Batchelor's group modified the UHL process to include the addition of alumina (UHLA process) to remove sulfate and chloride from recycled cooling water as aluminate salts. These processes use more lime and operate at a higher pH (near 12.0) than conventional lime softening process. Although the UHL/UHLA are attractive processes to recover membrane concentrates, they will create substantial amounts of sludge that will require disposal.

Pellet Softening (Graveland et al 1983; Li et al 2004) is a precipitative softening process that is used by some water systems to minimize the sludge handling/disposal issues associated with conventional lime softening process. The pellet softening process uses a fluidized bed of grains (typically sand) on which crystallization of calcium carbonate and, to a lesser extent, magnesium hydroxide (or possibly magnesium carbonate) precipitates occurs. The resulting pellets can be beneficially used; e.g., as a soil amendment or road fill. If the UHL/UHLA process is carried out in a pellet softening fluidized bed and pellets can be successfully formed, then sludge volume will be reduced and the resulting pellets may be beneficially used.

Objective

This objective of the study was to perform

- an estimation of RO treatment facility in SCE service area,
- a **conceptual evaluation** of performing the UHLA process in a pellet softening fluidized bed configuration, and
- evaluation of the overall impact (increase in water yield/unit power used, decrease in wastewater discharge) of the proposed technology to the RO facilities in SCE service area.

Methodology

An estimation of number of membrane treatment facilities in the project area was obtained from various sources including surveys, reports, policy documents, meeting minutes, web searches and personal communications with various water and wastewater agencies, water and wastewater agency associations, the Bureau of Reclamation, the USGS, California Department of Health Services, California Energy Commission, vendors of membrane technologies, and Kennedy/Jenks staff.

The conceptual evaluation of combining the UHLA and pellet softening processes was performed using the data from Kennedy/Jenks' recent pilot study at the City of Oxnard facility. In this pilot study Kennedy/Jenks evaluated i) a UHLA process to remove hardness and sulfate from RO reject stream of a groundwater source, and ii) a pellet softening process to remove hardness from the groundwater. This pilot study, however, did not directly evaluate performance of UHLA process in a pellet softening fluidized bed configuration.

Results

Survey of Membrane Units

A survey of RO facilities in the project area indicated that, there are 16 reclamation facilities, 8 desalination facilities, 26 brackish water facilities, 5 larger municipal water treatment facilities (serving more than 500 people), and 19 smaller municipal water treatment facilities (serving less than 500 people) in SCE service area. The design flow rates for 54 out of the 74 facilities were obtained. The total flow rate for the facilities with known flow rates is about 315 MGD. The overall treatment capacity of these facilities varied from 0.1 to 90 MGD. For the remaining facilities, assuming an average flow rate of 2 MGD for the larger systems and 0.25 MGD for the smaller system, the total water treated by membrane processes in the project area is about 330 MGD. Significant variations were observed in the water quality characteristics of groundwater sources using RO treatment. For example, with the exception of one saline source (average TDS of 42,000 mg/l and average hardness of 7,100 mg/l), the average and maximum raw water TDS values were 1,050 and 3,650 mg/l, respectively, and the average and maximum hardness were 490 and 1,630 mg/l as $CaCO_3$.

Conceptual Evaluation of Combining UHLA and Pellet Softening Technologies

The conceptual evaluation of performing UHLA softening process in a pellet softening fluidized bed configuration was performed based on a recent Kennedy/Jenks pilot project to treat brackish groundwater for the City of Oxnard. The Oxnard pilot study included evaluation of a large diameter RO process, UHLA treatment to remove hardness and sulfate from the RO reject stream, pellet softener process for hardness removal from the brackish groundwater. Among the various issues evaluated included i) characteristics and stability of the pellets during lime precipitation, ii) field verification of laboratory and computer model findings of the UHLA process, iii) potential for crystallization of UHLA sludge on the pellets, and iv) volume of sludge produced from pellet processing.

The UHLA process was evaluated using an upflow solids-contact clarifier (Claricone™), manufactured by CBI Walker, Plainfield, IL. The results from the pilot studies were compared with those predicted using a speciation model (Phreeqc) to evaluate the performance. During the initial tests, only lime was fed into the clarifier to precipitate i) calcium hardness (to carbonate limit) at pH 9.6, and ii) calcium (to the carbonate limit) and magnesium hardness at pH 10.8. Hardness removal from these studies was consistent with the model predictions, suggesting that the pilot units were operated under optimum conditions. Subsequently, lime, sodium aluminate and caustic were added to facilitate precipitation of calcium sulfoaluminate from the RO reject stream. The clarifier was operated for a brief period at a target pH ~ 11.8 (actual range of 11.8 to 12.4). The calcium and magnesium removal from this process was consistent with the model prediction, however, the sulfate and aluminum removal were significantly lower than that predicted by the model. This suggested that optimum conditions for effective calcium sulfoaluminate precipitation were not achieved in the process. The resulting levels of sulfate (1,700 mg/l) and aluminum (40 mg/l) in the treated effluent were significantly higher than desired for further treatment of this stream with RO. Hence, more studies need to be performed to identify the reasons for the deviations in the results prior to considering the use of these precipitation reactions for reclamation of the brine stream.

Unlike the UHLA process, which was performed using the RO reject stream, the pellet softening process was performed using untreated groundwater. Following four chemical feed strategies were used:, i) caustic feed at pH 9.6 to remove calcium hardness, ii) caustic feed at pH 10.8 to remove calcium and some magnesium hardness, iii) lime feed at pH 9.6 to remove calcium hardness, and iv) lime, barium and sodium carbonate (soda ash) feed at pH 9.6 to remove sulfate (as barium sulfate) in addition to calcium hardness. The performance of the process was evaluated by monitoring headloss across the reactor to track pellet growth. Results indicated that the pellet softener performed best under caustic feed conditions and pH favoring precipitation of calcium hardness alone (pH 9.6). Increasing the pH to 10.8 did not result in magnesium removal, as most magnesium precipitates (most likely magnesium hydroxide) carried over into the pellet softener effluent. Calcium hardness removal in tests using lime alone was limited by carbonate hardness and difficulties in controlling lime feed. The one test with addition of barium and soda ash was inconclusive regarding additional removal of calcium and sulfate. These results indicated that, the operating conditions for UHLA precipitation (pH ~11.8) might not be conducive for crystallization of the magnesium hydroxide precipitates on the pellets. Further studies are required to evaluate these findings.

Summary

In conclusion, uncertainties involved in the precipitation chemistry and operation requirements of the two technologies must be resolved to facilitate successful conceptual evaluation of combining these two processes. Further studies are required to understand the precipitation/crystallization of these solids, chemical dosing and operational requirements. The overall impact of combining these two technologies in SCE service area could not be performed due to lack of the above information.

SECTION 1: INTRODUCTION

Background

Membrane treatment (Reverse Osmosis, nanofiltration) technologies are widely used in California for treating brackish water, desalination of seawater, and recovery and reuse of wastewaters. While membrane processes facilitate augmentation of water resources they are very energy intensive and generate large volumes of waste streams. For example, RO processes typically require 1,600 KWh (~ 125 PSi operating pressure) to treat 1 MG of brackish (TDS ~ 1,000 mg/l) groundwater. Seawater (TDS ~ 35,000 mg/l) desalination requires approximately 12,000 KWh to treat MG water. These are significantly higher than the energy required by conventional water and wastewater treatment processes. Secondly, membrane processes generate a large volume of high concentration waste streams. Approximately 10 to 25% of the raw water is rejected as waste stream during RO treatment. Discharge of brackish wastewater into sewer system is prohibited in several parts of California. In Southern California, brackish wastewaters in Los Angeles, Orange, Riverside and San Bernardino counties must be discharged only into brine lines (e.g. Santa Ana Regional Interceptor (SARI)) for ultimate ocean discharge. Proximity to and available discharge capacities in the brine lines render the installation of RO plants uneconomical in these Counties.

Improving Membrane Processes Using Ultra High Lime Processes

In order to improve the energy efficiency of the RO process (yield/KWh), and to minimize the amount of waste stream generated, a technology is required to recover and reuse the brine stream from the RO process. The Ultra High Lime (UHL) process developed by Batchelor and his colleagues appears to be one such technology. This innovative process was originally developed to remove various scalents (Ca^{2+}, Mg^{2+}, PO_4^{3-} and SiO_2) from recycled cooling water (Batchelor, et al., 1984; 1991) by addition of lime at elevated pH levels.

Although this process is somewhat similar to lime softening process, it uses more lime and operates at a higher pH (near 12.0) than conventional lime softening. Recently, Batchelor's group has modified the UHL process to include the addition of aluminum (UHLA Process) to remove sulfate and chloride from recycled cooling water as calcium sulfoaluminate and calcium chloroaluminate, respectively.

$$6Ca^{2+} + 2Al^{3+} + 3(SO_4)^{2-} + 12OH^- \Leftrightarrow Ca_4Al_2Cl_2(OH)_{12} \quad (1)$$

$$4Ca^{2+} + 2Al^{3+} + 2Cl^- + 12OH^- \Leftrightarrow Ca_4Al_2Cl_2(OH)_{12} \quad (2)$$

Solubility products of 10^{-109} and $10^{-94.75}$, are reported for calcium sulfoaluminate and calcium chloroaluminate, respectively (Batchelor, et al., 1991, Abdel-Wahab, 2002). Since RO reject streams typically contain large amounts of chloride and varying amounts of sulfate, the UHLA process may effectively be used to remove these components. However, the UHLA process for sulfate/chloride removal has so far been evaluated through bench scale studies only. Another significant limitation of UHL/UHLA processes is that the large volume of sludge generated by these processes may pose sludge handling/disposal problems.

Minimizing Solids Production by Pellet Softening Process

Some water softening facilities in Europe and United States are using an innovative approach known as "Pellet Softening" process to mitigate the sludge production issues. The pellet softening process uses a fluidized bed of grains (typically sand) on which crystallization of calcium carbonate and, to a lesser extent, magnesium hydroxide precipitates occurs. Unlike the conventional softening process, the pellet softening process produces a much denser sludge that contains significantly higher solids percentage, much smaller in volume and that can be readily dewatered. The resulting pellets can be beneficially used; e.g., as a soil amendment or road fill. Hence, if UHLA process can be successfully carried out in a pellet softening fluidized bed reactor, the sludge production/handling problems can be significantly mitigated.

Although pellet softener process can produce a lower volume of sludge with better dewatering characteristics, it is not widely used by water agencies due to limited information on i) the impact of water quality characteristics on crystallization over the pellets, and ii) impact of lime characteristics on pellet formation. Also, performance data to date indicate higher suspended solids carryover, poor magnesium crystallization and poor crystallization of calcium carbonate under conditions favoring magnesium hydroxide precipitation (i.e. pH ~ 10.8). Furthermore, pellet softening processes have been primarily performed on less saline potable waters requiring hardness removal. No information is available on the use of this process on brackish waters similar to RO reject streams. Finally, it is not currently known if the calcium sulfo/chloro aluminate solids from UHLA process can crystallize effectively on pellet surfaces. Nebgen, et al., (1973) reported that the sulfoaluminate solids were microcrystalline in nature and readily amenable for dewatering. However, the settling properties of these solids were very poor. However, if the UHL process is carried out in a pellet softening fluidized bed, and pellets can be successfully formed, the problems associated with UHLA process can be mitigated.

Objectives

This study proposes to perform a conceptual evaluation of combining these two technologies to remove dissolved salts (chloride and sulfate) from membrane reject streams to facilitate recovery and reuse of the brine streams. In addition, this study proposes to evaluate the economic impact of such technology in the RO treatment process in SCE footprint area.

The specific objectives of this study are:

- Survey of membrane (RO/NF) facilities in SCE foot print area
- Conceptual evaluation of combining UHLA and pellet softening processes
- Evaluation of the impact of such processes to membrane facilities in SCE service area

Methodology

The following paragraphs briefly describe the methodologies used in achieving the goals of this study.

Survey of Membrane Facilities in the project area

This task identified the RO/NF groundwater, wastewater, desalination and reclamation facilities in the SCE footprint area. Available information on the type of membrane process, capacity, raw & treated water quality and equipment specification will be identified. The information was obtained from various sources including surveys, reports, policy documents, meeting minutes, web searches and personal communications with various water and wastewater agencies, water and wastewater agency associations, the Bureau of Reclamation, the USGS, California Department of Health Services, California Energy Commission, vendors of membrane technologies, and Kennedy/Jenks staff.

Conceptual Evaluation of Combining UHLA and Pellet Softener Processes

The approach used in this study involves a “conceptual evaluation” of the proposed process from studies conducted individually to evaluate UHLA and pellet softening processes. In particular, Kennedy/Jenks Consultants recently concluded a pilot study to treat brackish groundwater for the City of Oxnard. The study included evaluation of a large diameter RO process, UHLA treatment to remove chloride and sulfate from the RO reject stream, pellet softener process for hardness removal from the brackish groundwater. The results from these studies were the key for evaluating the conceptual feasibility of the proposed approach. Among the various issues evaluated from the pilot operation included i) characteristics and stability of the pellets during lime precipitation, ii) field verification of laboratory findings of the UHLA process, iii) potential for pellet formation of UHLA sludge, and iv) volume of sludge produced from pellet processing.

Report Outline

Section 1 of this report provides the background and methodology of the study. Section 2 presents the survey results on the number, location and size of membrane units used for water and wastewater treatment in the project area. The background of the pilot study performed at the City of Oxnard facility is presented in Section 3. An evaluation of UHLA pilot process performed (NOT in a pellet softening mode) is provided in Section 4. Section 5 presents the results from the pellet softening pilot process for treating untreated groundwater (NOT RO brine) using caustic, lime and barium (NOT aluminum). Section 6 provides conceptual evaluation of performing UHLA softening process in a pellet softening fluidized bed configuration based on Section 4 and 5 data.

SECTION 2: IDENTIFICATION OF MEMBRANE UNITS IN SCE SERVICE AREA

Scope Of Work

Objective and Data Sources

The overall objective of this task included the following:

- Identify water & wastewater facilities using membrane processes in SCE service area
- Develop profile of available information on equipment, energy, volume and quality of water treated.

The following sources were used to obtain the above information:

Table 1: Sources Used for Data Collection

Source	Type of Information
DHS Water Quality Monitoring (WQM) database	Water Quality Data for Impacted Sources
DHS Permits, Inspection, Compliance, Monitoring and Enforcement (PICME) database	Groundwater Sources Using Membrane Processes
Various Water Utilities	Membrane Treatment Capacity
Others	Number, location and size of membrane facilities

Project Area

The following eleven counties where SCE provides power to customers (per SCE Territory Boundary Map of 02/08/2002) were selected as the SCE foot print area for this study:

- Inyo
- San Bernardino
- Riverside
- Orange
- Los Angeles
- Ventura
- Santa Barbara
- Kern
- Tulare
- Fresno

Membrane Treatment Facilities In The Project Area

Table 2 shows the list of water and wastewater facilities using membrane treatment processes in the project area. As shown in the table there are

- 16 Reclamation facilities
- 8 Desalination facilities
- 26 Brackish water facilities
- 5 Municipal water treatment facilities serving > 500 people, and
- 19 Municipal water treatment facilities serving < 500 people

in the project area.

Table 2: List of Membrane Facilities in SCE Service Area

Facility Name	Owner	County	Feed Water	Design Flow	Membrane Type
<u>Full-Scale Reclamation Facilities</u>					
Alamitos Barrier Recycled Water Project, CA	City of Torrance, Orange County Water District	Los Angeles	Wastewater	"3 -3.2"	MF+RO
Carlsbad, CA	Carlsbad MWD	San Diego	Wastewater (Unfiltered Secondary)	1.000	MF+RO
OCWD MF Demo Project #1, CA	Orange County Water District, CA	Orange	Wastewater (Unfiltered Secondary)	0.792	MF/RO
OCWD MF Demo Project #2, CA	Orange County Water District, CA	Orange	Wastewater (Unfiltered Secondary)	0.720	MF
OCWD, Water Factory 21, Fountain Valley, CA	Orange County Water District, CA	Orange	Wastewater (Unfiltered Secondary)	5.000	RO
OCWD/OCSD GWRS	Orange County Water District/Sanitation District, CA	Orange	Wastewater (Unfiltered Secondary)	70.000	MF+RO
Terminal Island Treatment Plant, CA	City of Los Angeles, Department of Public Works, Bureau of Sanitation	Los Angeles	Wastewater	5.000	MF+RO
West Basin, Carson	West Basin Water District, CA	Los Angeles	Municipal Tertiary WW (Title 22)	5.000	MF+RO
West Basin, El Segundo Phase 1	West Basin Water District, CA	Los Angeles	Wastewater (Unfiltered Secondary)	5.000	RO
West Basin, El Segundo Phase 2	West Basin Water District, CA	Los Angeles	Wastewater (Unfiltered Secondary)	2.500	MF+RO
West Basin, El Segundo Phase 3	West Basin Water District, CA	Los Angeles	Wastewater (Unfiltered Secondary)	"4.3 - 4.6"	MF+RO
West Basin, Mobil Torrance Refinery	West Basin Water District, CA	Los Angeles	Municipal Tertiary WW (Title 22)	3.200	MF+RO
Glenwood Nitrate Water Reclamation Project	Foothill MWD	Los Angeles		1.430	
Terminal Island I		Los Angeles		5.000	
Yucaipa Valley Regional Water Supply Renewal	Yucipa Valley WD	San Bernardino		12.050	

Project					
Groundwater Replenishment System				90.000	
Existing RO Desalination Facilities					
Gaviota Oil and Gas Processing Plant	Chevron	Santa Barbara	Ocean	0.411	RO
Santa Barbara Treatment Plant	Santa Barbara Water District	Santa Barbara	Ocean	2.8	RO
Santa Catalina Island	SCE	Los Angeles	Seawater wells	0.132	RO
San Nicolas Island	U.S. Navy	Los Angeles	Seawater wells/ocean	0.024	na
Port Hueneme	U.S. Navy test facility	Ventura	Seawater wells/ocean	0.013	na
Huntington Beach	SCE	Orange	Seawater wells/ocean	0.215	RO
National Seawater Test Center/ El Segundo	na	Los Angeles	Seawater wells/ocean	0.430	MF + RO
Sepulveda Desalination Facility	West Basin MWD	Los Angeles	Groundwater/sea water wells	2.140	
Brackish Water RO Treatment Plants					
West Basin Desalter	West Basin Water District	Los Angeles	Groundwater	"1.36 - 1.5"	RO
17th Street Desalter (Well #1)	City of Tustin	Orange	Groundwater	2.300	RO
Main Street Desalter (Wells # 3, 4	City of Tustin	Orange	Groundwater	0.5	RO
Chino Basin Desalter Phase I	Western MWD, Inland Empire Utilities Agency	San Bernardino	Groundwater	"7.14 - 8"	RO
Chino Basin Desalter Phase II	Western MWD, Inland Empire Utilities Agency	San Bernardino	Groundwater	10.000	
Port Hueneme Brackish Water Reclamation I, II, III	Port Hueneme Water Agency	Ventura	Groundwater	1+1+1	RO+NF
Tustin Desalter Project, I and II	City of Tustin	Orange	Groundwater	"0.5 - 2.92"	RO
Tustin Desalter Project, III	City of Tustin	Orange	Surface water	0.300	
Arlington Desalter	Santa Ana Watershed	Riverside	Groundwater	"4 - 6"	RO

	Project Authority				
Port Hueneme	Port Hueneme Water Agency	Ventura	Groundwater	0.730	RO+NF
Goldsworthy Desalter	Water Replenishment District	Los Angeles	Groundwater	2.500	RO
Menifee Basin Desalination Facility	East MWD	Riverside	Groundwater	"1.5 - 3"	RO
(Salt Creek Well 75, Mclaughlin Well 76)	East MWD				
Irvine Desalter Project	OCWD	Orange	Groundwater	5.980	RO
Capistrano Beach Desalter	Municipal Water District of Orange County	Orange	Groundwater	1.160	na
Beverly Hills Desalter	City of Beverly Hills	Los Angeles	Groundwater	2.320	NF
San Juan Basin Desalter	Municipal Water District of Orange County	Orange	Groundwater	4.290	RO
Rowland Desalter	Three Valleys MWD	Los Angeles	Groundwater	0.460	na
Brewer Desalter	West Basin WD	Los Angeles	Groundwater	1.3	
Madrona Desalination Facility	City of Torrance	Los Angeles	Groundwater	2.140	
Juan Well Filter Facility	Central Basin MWD	Los Angeles	Groundwater	0.800	
Colored Water Treatment Facility	Municipal Water District of Orange County	Orange	Groundwater	10.090	
Westlake Wells - Tapioa WRF Intertie Project	Las Virgenes MWD	Los Angeles	Groundwater	0.130	
Riverside		Riverside	Groundwater	4.000	
Santa Monica Groundwater Treatment Project	City of Santa Monica	Los Angeles	Groundwater		
Glenwood Nitrate Water Reclamation Plant	Foothill MWD	Los Angeles	Groundwater		
Integrated Chino Arlington Desalination				14.290	
<u>Municipal Treatment Facilities Serving More Than 500 People</u>					

Dominguez	California Water Service Company	Los Angeles	Groundwater	1.4	RO
Santa Barbara Research Center, Wells 1 & 2	Santa Barabara Research Center	Santa Barbara	Groundwater		RO
Santa Catalina	SCE	Los Angeles		0.132	RO
Madrona Well 02	Torrance City	Los Angeles		2	
Municipal Treatment Facilities Serving Less Than 500 People					
WELL 01	THE RIVER COMMUNITY		Groundwater		RO
WELL 02	HATHAWAY CHILDRENS HOME	Lake View, CA	Groundwater		RO
RO PLANT EFF (TDS REDUC)	CALIFORNIA WATER SERVICE CO. - DOMINGUEZ	Long Beach	Groundwater		RO
RO PLANT INF., WELL 232-01 AND 232-02	CALIFORNIA WATER SERVICE CO. - DOMINGUEZ	Long Beach	Groundwater		RO
WELL 01	QUAIL RANCH GOLF CLUB	Moreno Valley, Riverside, CA	Groundwater		RO
WELL 01 SOUTH	WHISPERING SANDS MOBILE HOME PARK	Desert Hot Springs, CA	Groundwater		RO
WELL #1	GOOSE CREEK GOLF CLUB	Mira Loma, Riverside, CA	Groundwater		RO
TREATMENT PLANT	GOOSE CREEK GOLF CLUB	Mira Loma, Riverside, CA	Groundwater		RO
WELL 01	Zzyzx Desert Studies Center - NPS	Barstow, San Bernardino, CA	Groundwater		RO
CV KANE WELL	CAL TRANS - C.V. KANE	San Bernardino	Groundwater		RO
TREATMENT PLANT - TREATED	THE BRIDGEHOUSE	Santa Barbara			RO
WELL 02 - STANDBY	SANTA CLARA SCHOOL	Ventura	Groundwater		RO
WELL 01	BOUQUET MULTIMEDIA	Ventura	Groundwater		RO
Port Hueneme	Port Hueneme Water Agency	Ventura	Groundwater	0.730	RO+NF

San Nicolas Island	U.S. Navy	Los Angeles	Seawater wells/ocean	0.024	na
San Nicolas Island	U.S. Navy	Los Angeles	Seawater wells/ocean	0.024	na
Well # 1	Word of Grace Christian Center	Santa Barbara	Groundwater		RO
Well #2	University Properties	Santa Barbara	Groundwater		RO
Spring #1	Charles Brown Water Company	Inyo	Spring #1		RO

Flow Rates

Available flow rates for the membrane treatment facilities are shown in Table 2. The flow rates for 54 out of the 74 facilities were obtained. Sixteen out of the twenty facilities with unknown flow rates are small facilities serving less than 500 people. The overall treatment capacity of these facilities varied from 0.1 to 90 MGD. The total flow rate for the facilities with known flow rates is about 315 MGD. For the remaining facilities, assuming an average flow rate of 2 MGD for the larger systems and 0.25 MGD for the smaller system, the total water treated by membrane processes in the project area is about 330 MGD.

Water Quality

The average and maximum levels of key water quality parameters for the groundwater sources (as reported in DHS water quality database) using membrane treatment in the project area are shown in Table 3. These results exclude one saline source, with TDS of 42,000 mg/l and hardness of 7,100 mg/l. Nevertheless, significant variations were observed in the water quality characteristics of these remaining waters. For example, the average and maximum TDS values were 1,050 and 3,650 mg/l, respectively, and the average and maximum hardness were 490 to 1,600 mg/l as $CaCO_3$. In most cases, the hardness was primarily due to calcium (i.e., magnesium levels were low), which makes pellet-softening technology more attractive.

Table 3: Summary of Water Quality Characteristics of Groundwater Sources Using Membrane Processes in the Project Area

Constituent	Maximum	Average
Alkalinity (as mg/l $CaCO_3$)	575	250
Calcium	440	132
Chloride	1700	250
Hardness, Total (as mg/l $CaCO_3$)	1,600	470
Magnesium	130	35
Nitrate (as NO_3)	220	72
pH	8.6	7.5
Sodium	700	105
Sp. Conductance	3,700	1,400
Sulfate	560	150
TDS	3600	1,000

Energy Use

The energy use for RO/NF operations depend on various factors including water quality characteristics (e.g. TDS, hardness, silica), type of membrane (low pressure, high rejection) and percentage recovery. However, based on Kennedy/Jenks experience with several membrane operations in California, the following are the typical operational parameters for brackish/saline waters membrane (RO) treatment processes:

Table 4: Typical operational parameters for Membrane Process

TDS (mg/l)	% Recovery	Operating Pressure (Psi)	Power (KW/M. gallon treated water)
500 – 1,000	75	125	1,600
6,000 – 7,000	75	350	4,500
33,000 – 40,000	50	900	12,000

SECTION 3: EVALUATION OF UHLA AND PELLET SOFTENING PROCESSES USING PILOT STUDIES AT CITY OF OXNARD

Background – Current Status of the Proposed Technologies

The UHLA process proposed in this study is still an emerging technology. Most of the field studies performed to date have evaluated silica removal using the UHL (no addition of aluminate) process. The UHLA process that involves precipitation of chloride/sulfate using aluminate addition has been evaluated only in laboratory scale studies (Batchelor et al., 1984, 1991; Abdel-Wahab, 2002). Furthermore, simultaneous removal of chloride and sulfate has not been evaluated in these studies. The solubility products for calcium sulfoaluminate (10^{-109} M) and calcium chloroaluminate ($10^{-94.75}$ M) were developed independent of each other, and other interfering compounds. Hence, a field/pilot scale evaluation of UHLA process is required to evaluate the feasibility of this process under real world conditions, and verify simultaneous precipitation of the two salts.

Pellet softener technology has been successfully employed for softening processes in the United States and Europe. While most European facilities use caustic for hardness removal by this process, the preference in the U.S. appears to be lime. Some pellet softening facilities experienced higher turbidity carryover in the treated water. Ineffective softening due to incomplete dissolution of the lime is suspected as a possible cause. Also, while this technology effectively removed calcium hardness, magnesium did not effectively crystallize over the pellets. Harms and Robinson (1992)., reported that, optimization pH (~10.8) for magnesium precipitation may even reduce the efficiency of calcium carbonate crystallization over the pellets Hence, some water agencies that initially installed pellet softening process for hardness removal (e.g. White Sulfur Springs, W.VA) subsequently converted to conventional softening treatment. Design issues, operational difficulties and target water co-constituents may impact the pellet softener performance. A detailed evaluation of water quality characteristics on the pellet formation has not been performed to date.

City of Oxnard Pilot Study

Kennedy/Jenks Consultants recently performed a pilot study to treat brackish groundwater for the City of Oxnard, California. The pilot study evaluated various technologies to treat raw water and process waste streams. Among them, the two technologies that are relevant to the proposed SCE study are

- Treatment of Reverse Osmosis (RO) reject stream using UHLA process

  - The treatment configuration used in this study was a conventional softening configuration. The UHLA pilot study was not performed in a pellet-softening mode.

- Treatment of source water using pellet softening process

  - Unlike the UHLA process, which was performed using the RO brine, the pellet-softening pilot was performed using the untreated groundwater at the City of Oxnard. In addition, the chemicals used in the pellet softener studies did not include aluminum to precipitate chloride/sulfate.

The Oxnard Groundwater and RO process reject stream characteristics are presented and briefly discussed in this section. The results from the UHLA and pellet softening processes are presented in the next two sections.

The City of Oxnard Groundwater

Table 5 shows the water quality characteristics of Well 21 of the City of Oxnard groundwater (influent to pellet softener) and the RO process reject streams (influent to UHLA process) used in this study. The water quality characteristics had some unique features that are relevant to the proposed application. The groundwater for the pilot study can be characterized as very high in hardness (~ 540 mg/l as CaCO3), total dissolved solids (TDS (~ 1000 mg/l), and sulfate (~ 475 mg/l), making this a challenging water to treat. The RO reject stream contained 1,970 mg/l sulfate that is ideal for evaluating the removal of calcium sulfoaluminates in the UHLA process. In addition, a significant amount of TDS in the water is contributed by calcium and magnesium (hardness) making the source water an ideal candidate for evaluating pellet-softening process.

Table 5: Well No. 21 and RO Reject Stream Water Quality

Parameter	Well 21 (Pellet Softener Influent)	RO Reject (UHLA Influent)
General Physical		
pH	7.4	7.8
Specific Conductance (µmho/cm^2)	1372	4607
Turbidity (NTU)	1.1	
Total Dissolved Solids (mg/l)	1006	4102
Total Hardness (mg/l as $CaCO_3$)	540	2135
General Minerals		
Calcium (mg/l)	135	533
Magnesium (mg/l)	46	190
Sodium (mg/l)	97	373
Potassium (mg/l)	4	18.6
Total Alkalinity (mg/l as $CaCO_3$)	212	817
Sulfate (mg/l)	475	1973
Chloride (mg/l)	46	193
Nitrate (mg/l)	12	51.5
Silica (mg/l)	31	135
Detected Inorganics		
Iron (µg/l)	46	<50
Manganese (µg/l)	7	36.7

SECTION 4: UHLA Performance

The City of Oxnard pilot study evaluated UHLA process to remove calcium and magnesium (hardness), carbonate alkalinity, and sulfate in a clarification unit (equations 1 and 2). No significant removal of total dissolved solids (TDS) was anticipated, but the treated brine would be more amiable to further RO treatment. Calcium, to the carbonate hardness limit, and magnesium removal were facilitated by addition of lime. Sulfate removal was evaluated by addition of lime, aluminate, and caustic.

The objective of the Oxnard pilot study with respect to the goals of the proposed SCE project were:

- To evaluate the performance of UHLA process to remove sulfate from RO brines
- To compare the field data with the speciation model predictions
- To evaluate sludge generation during the UHLA process

Operating Conditions And Objectives

In the pilot study the reject stream from a large diameter RO process treating a groundwater source (Well No. 21) water was used as the influent to the UHLA process (Table 2). Clarification occurred in an upflow solids-contact clarifier (Claricone™), manufactured by CBI Walker, Plainfield, IL. The clarifier consists of a conical steel vessel, with a 2-ft diameter base that expands to 8-ft at the top. Feed water was introduced at the base of the unit. The inlet flow into the conical vessel imparts a helical flow pattern that mixes the precipitated solids and maintains the sludge blanket as the treated water and precipitated solids flow upwards through the unit. Because of the conical design of the vessel, the upflow velocity of the water decreases as it moves upwards through the unit. The decreasing velocity helps prevent the smaller precipitated particles from being carried over. The unit is designed to capture solids in the collection funnel located near the center of the unit and remove them via a timed blowdown valve. The unit also has a grit blowdown line for removing dense solids that collect at the bottom of the unit. The clarified water spills over a weir into a collection box, which then was discharged to the sanitary sewer.

Table 6: Ultra High Lime Aluminate Process Design Criteria

Design Parameter	Units	Value
Solids Contact Clarifier	-	CBI Walker ClariCone™
Nominal flow rate	gpm	30
Operational flow rate	gpm	10
Recirculation rate	gpm	20
Surface Loading Rate	(gallons/ft^2/minute)	0.6
Hydraulic Retention Time	(min)	90
Surface Diameter	ft	8
Base Diameter	ft	2
Unit Height	ft	7.67

Design Parameter	Units	Value
Water Volume	gallons	900

The nominal design capacity of the Claricone™ unit is 30 gpm. Due to the potential for a large solids production in this pilot study, some modifications were incorporated in the flow configuration. The RO brine was fed at a rate of 10 gpm to lower the solids flux rate. However, to maintain the hydraulic mixing and sludge blanket properties of this clarifier, 20 gpm of treated effluent was recirculated to the unit's inlet. The treated effluent was discharged to the sanitary sewer. Table 6 provides a summary of the design criteria for this pilot system.

The chemical feed rates to obtain target water quality goals during the pilot studies were determined using a chemical speciation model, Phreeqc (USGS, 2002) to confirm precipitation assumptions. Throughout the pilot study the Clarifier was operated under two key chemical feed conditions. The chemicals used, dosage, target pH and the objectives of each condition is described below and summarized in Table 7:

- Lime Treatment: During this phase of the study only lime was added to the influent stream. The key objectives of this phase were i) to gain experience with the ClariCone™ unit, the lime feeding systems, ii) evaluate calcium and magnesium (hardness) removal and iii) to verify the chemical feed rates predicted by the Phreeqc model in achieving the target water quality goals. Two lime feed concentrations (600 and 1,200 mg/l) were used. The lower lime concentration was added to primarily remove calcium, and the higher dose was used primarily to remove magnesium. Table 7-2 summarizes this information.
- Lime-Sodium Aluminate Treatment: The goal of this phase was to remove hardness and sulfate by UHLA process. Lime, sodium aluminate and sodium hydroxide were added.

Table 7: Chemical Feed Rates for the UHLA Process

Test	Chemical	Target pH	Feed Rate (mg/l)	Objective
Lime Treatment (600 mg/l)	Lime	8.5	600	Gain operational experience, Calcium and TDS Removal.
Lime Treatment (1,200 mg/l)	Lime	11.5	1,200	Gain operational experience, Magnesium Removal.
Lime – Sodium Aluminate Treatment	Lime	11.8	1,200	Sulfate/ Hardness removal
	Sodium Aluminate		600	
	Caustic		750	

Results From Uhla Process

Lime Treatment, 600 mg/l – Treated Water Characteristics

The following reactions describe hardness and calcium removal by lime addition:

$$Ca(OH)_2 + H_2CO_3 \Leftrightarrow CaCO_3\downarrow + 2\ H_2O. \qquad (3)$$

$$Ca(OH)_2 + Ca^{2+} + 2\ HCO_3^- \Leftrightarrow 2\ CaCO_3\downarrow + 2\ H_2O. \qquad (4)$$

Table 8 shows the water quality characteristics of the influent and effluent streams and the model predicted concentrations for the treatment using 600 mg/l lime. Approximately 40% of calcium and 10% of magnesium were removed at this lime feed rate. Sulfate levels did not decrease significantly. The magnesium and sulfate levels in the effluent were slightly higher than those predicted by the model. In general, the observed median concentrations were within 20% of the model predicted levels.

Table 8: Influent and Effluent Water Quality Characteristics with 600 mg/l Lime Treatment of RO Concentrate

Parameter	No. of Samples	UHLA Influent	UHLA Effluent	% Change	Model Predicted Eff. Conc.
		Median	Median		
Calcium (mg/l)[2]	3	523	**322**	- 38%	**355**
Magnesium (mg/l)[2]	3	206	**190**	- 8%	**156**
Alkalinity (mg/l as CaCO3)[1]	12	820	**285**	- 65%	
EC (umho/cm)[2]	3	4,945	**4,040**	- 11%	
TDS (mg/l)[2]	3	4,320	**3,290**	- 24%	
Sulfate (mg/l)[2]	3	2,050	**2,030**	- 1%	**1,737**
Chloride (mg/l)[2]	3	207	**200**	- 3%	**180**
pH[1]	12	7.8	**8.04**	NA	**8.5**

1 – Field data; 2 – Lab data; 3 – "-" indicates decrease in conc., and "+" indicates an increase in concentration; NA – Not Applicable

Lime Treatment, 1200 mg/l - Treated Water Characteristics

The goal of this operational condition was to remove the carbonate hardness and magnesium hardness from the RO reject stream. Magnesium removal occurs as per the following reaction:

$$Ca(OH)_2 + Mg^{2+} \rightarrow Ca^{2+} + Mg(OH)_2\downarrow \qquad (5)$$

Table 9 shows the results from the study. About 95 percent of the magnesium was removed during this treatment. A small net amount (~10 percent) of calcium was also removed because the amount of lime fed exceeded the available carbonate alkalinity. TDS decreased by about 15 percent. No significant removal of sulfate was observed. In general, the observed data agreed with the Phreeqc model predictions. Effluent calcium, sulfate and chloride levels were within 20 percent of the model predicted values.

Table 9: Influent and effluent water quality characteristics during 1,200 mg/l lime treatment of RO reject stream

Parameter	Samples	UHLA Influent	UHLA Effluent	% % Change[3]	Model Predicted Eff. Conc.
		Median	Median		
Calcium (mg/l)[2]	1	509	**552**	-8%	**686**
Magnesium (mg/l)[2]	1	180	**8**	-96%	**0.2**
Alkalinity (mg/l as CaCO3)[1]	4	875	**390**	-55%	
EC (umho/cm)[2]	1	4,360	**4,310**	3%	
TDS (mg/l)[2]	1	3,880	**3,250**	-16%	
Sulfate (mg/l)[2]	1	1,780	**1,740**	-2%	**1616**
Chloride (mg/l)[2]	1	182	**186**	2%	**180**
pH[1]	4	7.8	**11.6**	NA	**11.5**

1 – Field data; 2 – Lab data; 3 – "-" indicates decrease in conc., and "+" indicates an increase in concentration; NA – Not Applicable

Lime Sludge Characteristics

The sludge characteristics during the lime treatment processes are shown in Table 10. The % solids at 600 mg/l and 1,200 mg/l lime feed conditions are 0.7 and 0.9%, respectively. These values are lower than the > 5 percent solids that would be expected in a full-scale process and are a consequence of the need to remove solids from the pilot clarifier quickly to prevent them from building up in the settling zone (limited storage capacity).

An estimate of dry solids produced was made assuming that all the calcium removed from the water precipitated as calcium carbonate, and all the magnesium removed precipitated as magnesium hydroxide. These estimates indicated that approximately 12 and 18 lb of dry solids were generated at the two feed conditions. These values closely agreed with those (13 and 18 lb/1,000 gallons) predicted by the computer model.

Table 10: Lime Treatment Sludge Characteristics

Treatment	No. of Samples	% Solids	Dry Solids Produced (lb/1000 gallons treated)	
			Estimate from Pilot Data[1]	Model Prediction
600 mg/l Lime	3	0.7	12.07	13.1
1,200 mg/l Lime	2	0.9	18.02	18.1

[1] Median Value

Lime And Sodium Aluminate Testing - Treated Water Characteristics

The objective of this treatment was to remove sulfate as well as hardness from the RO reject stream (equations 1-4). Results from the lime treatment events indicated that the chemical dosing estimates using the Phreeqc model were reasonably effective in confirming target treated water quality. Hence, chemical dosing for this treatment was also selected using this model, along with limited jar testing. Lime (1,200 mg/l), sodium aluminate (600 mg/l) and sodium hydroxide (700 mg/l) were added.

Table 11 shows the results from the 'Lime – Sodium Aluminate' treatment evaluation. More than 95 percent of calcium and magnesium from the influent stream was removed. The measured effluent calcium concentrations were lower than the model predicted concentration. Magnesium concentration was similar to that predicted by the model. However, the sulfate and aluminum removal was significantly lower than that predicted by the model and the actual pH was higher than the model assumption (pH 12.0 vs pH 12.4). The measured sulfate and aluminate levels were 1,690 and 40 mg/l, respectively. The model predicted about 60 and 99.5 percent of sulfate and aluminum removal in the process. Only 9 and 60 percent of the influent sulfate and aluminum (from chemical feed) were removed.

The level of aluminum in the treated effluent is more than an order of magnitude higher than acceptable for RO feed water and would need to be removed in a second precipitation step at lower pH suitable for RO feed. The effluent sulfate level may be higher than desired for RO feed water and more optimization of the chemical additions is necessary. The variation in the observed effluent water quality from the model predictions may be due to:

- Impact of co-constituents in the RO reject stream (e.g., silica)
- Potential complexation of calcium with other constituents, rendering it unavailable for calcium sulfoaluminate precipitation
- pH above the target goal of 11.8. Nebgen (1973) suggests that pH control in this region is important to forming calcium sulfoaluminate precipitates.
- Treatment configuration (upflow with no treated water recirculation) may not have provided an optimum environment for calcium sulfoaluminate formation

Table 11: Influent and Effluent Water Quality Characteristics During Lime-Sodium Aluminate Treatment of RO Concentrate

Parameter	No. of Samples	UHLA Influent	UHLA Effluent	% Change	Model Predicted Eff. Conc.
		Median	Median		
Calcium (mg/l)[2]	3	515	**28**	-95%	**24.5**
Magnesium (mg/l)[2]	3	181	**1**	-99%	**0.006**
Alkalinity (mg/l as CaCO3)[1]	9	830	**820**	-1%	
EC (µmho/cm)[1]	9	4,350	**6,875**	58%	
TDS (mg/l)[2]	3	3,840	**3,570**	-7%	
Sulfate (mg/l)[2]	3	1,855	**1,690**	-9%	**1,107**
Chloride (mg/l)[2]	3	195	**206**	6%	**180**

pH[1]	9	7.8	**12.4**	NA	**12**
Aluminum (mg/l)[2]	2		**40**		**5.5**
Silica	1	117	**17**	-85%	**0.02**

1 – Field data; 2 – Lab data; 3 – "-" indicates decrease in conc., and "+" indicates an increase in concentration: NA – Not Applicable

Lime-Sodium Aluminate Sludge Characteristics

Table 12 shows the sludge characteristics (percent solids, dry sludge) of the 'Lime-Aluminate' treatment. The percent solids varied from 0.5 to 1.5 percent. This low solids concentration in the sludge blowdown was necessary due to the constraints of the pilot scale unit. For a full-scale unit, the sludge would be expected to have more than 5 percent solids.

The model predicted precipitation of calcite, magnesium hydroxide, calcium aluminosulfate, diaspore (AlO(OH)) and crystolite ($Mg_3Si_2O_5(OH)_4$). Since the amount of aluminum and sulfate precipitated in the pilot process differed from the model predictions, the following assumptions were made in the estimation of solids produced in the pilot process:

- All the carbonate precipitated as calcite
- All the magnesium precipitated as magnesium hydroxide
- Amount of calcium sulfoaluminate was determined based on the amount of each of the constituent precipitated and the stoichiometry of the compound
- Finally, the remaining calcium, aluminum, silica, and hydroxide removed in the pilot were included in the estimate of dry sludge produced.

The amount (dry weight) of sludge thus estimated compared well with the model predicted amount. However, the differences in the concentrations of various compounds suggested that additional studies are needs to resolve these differences for the UHLA process.

Table 12: Lime-Sodium Aluminate Treatment Sludge Characteristics

Parameter	Value
No. of Samples	3
Percent Solids	1.2
Dry Solids Produced (lb/1,000 gallons Treated)	
Estimate from pilot data	31.8
Model Prediction	33.8

Pilot Study Results Versus Phreeqc Model Predictions

Table 13 summarizes the results from the three chemical feed regimes. The performance of pilot unit at these two lime dosing rates was consistent with the Phreeqc model predictions. Lime, at a dosing rate of 600 mg/l, removed 10 to 40 percent of calcium, magnesium and TDS from the RO reject stream. Increasing the lime feed to 1,200 mg/l removed more than

90 percent of the magnesium. However, no significant net removal of calcium and TDS occurred at this dosage.

The 'Lime – Aluminate' process effectively removed almost all of the calcium and magnesium from the RO reject stream. This was consistent with the model predictions. However, sulfate and aluminum levels in the treated effluent were significantly higher than those predicted by the model. In particular, aluminum concentration in the treated effluent (40 mg/l) is an order of magnitude higher than that predicted by the model (5 mg/l).

The deviation of pilot 'Lime – Aluminate' process performance from the model predictions may be due to

- The effects of co-constituents in the groundwater on calcium aluminosulfate precipitation are not currently known.
- The clarifier configuration (up-flow with 200 percent recirculation) may not have provided the optimum environment for calcium aluminosulfate precipitation.
- The pH maintained in the clarifier.

Table 13: Summary Of Treated Water Quality Under Different Treatment Conditions

Parameter	Effluent Water Quality		
	600 mg/l Lime Treatment	1,200 mg/l Lime Treatment	Lime + Sodium Aluminate
Calcium	322	552	28
Magnesium	190	8	1
TDS (mg/l)	3,290	3,250	3,570
Conductivity (μmho/m)	4,195	4,545	6,875
Sulfate (mg/l)	2,030	1,740	1,690
Aluminum (mg/l)	-	-	40
pH	8.04	11.6	12
Agreement with Model Predictions	Very Good	Very Good	Fair

Additional studies must be performed to further investigate these factors prior to recommending a full-scale treatment for the Ultra High Lime Aluminate process.

Summary And Recommendations

In summary, the key findings from the UHLA study are the following:

- The treated water quality for the lime testing (600 and 1,200 mg/l lime dose) was consistent with the water chemistry model predicted water quality
- The treated water sulfate and aluminum levels in the "lime and sodium aluminate" feed tests were not consistent (i.e., higher) with the model predictions.
- Less than 10 percent of TDS was removed in the 'lime and sodium aluminate' treatment.
- For treatment of 1 MG of raw water by RO (assuming a 75 percent yield), the UHLA process would generate 3.6 (pilot study data) to 3.8 (model prediction) tons of dry

sludge. Assuming a percent solids of 5 percent, the wet sludge mass will be 70 to 75 tons per MG of raw water treated by RO process.

- The difference between the observed and predicted water quality for the ‘lime and sodium aluminate’ may be due to the complexity of these precipitating reactions with RO concentrates or the pilot clarifier configuration.
- A very large quantity of solids is generated when using RO concentrate as the raw water.
- Further studies are needed before moving forward with this process. The high concentration of aluminum in the treated effluent is a significant issue for this process for brine recovery by RO. The observed concentration was unexpected (as compared with the model) and a better understanding, especially the process’ sensitivity to pH, is needed before additional work can be recommended.

1 SECTION 5: EVALUATION OF PELLET SOFTENENING PILOT PERFORMANCE

The key issues addressed in the pilot pellet softener regarding the technical feasibility of the proposed technology include:

- Pellet build-up/change out frequency
- Solids content in the spent pellets

The pellet growth in the reactor is evaluated by the increase in headloss across the unit. Solids content in the pellet was evaluated by measuring the % solids and the major cations and anions in the pellets. Measurement of these parameters facilitates estimation of sludge production, need for sludge drying, and ability of various precipitates to crystallize on the pellets.

Pellet Softener Operation Conditions

Table 14 provides the operations conditions from the pellet softener study at Oxnard. The design conditions were selected based on field operations by Wheelabrator Water Technologies (1996), and earlier Kennedy/Jenks studies.

Table 14: Pellet Softening System Design Criteria

Design Parameter	Units	Value
Pellet Softener	-	Roberts Filter Group
Feed rate	gpm	16
Column diameter	inches	12
Column Height	ft	22
Fluidization loading rate	gpm/sf	20.4
Sand		
Depth (Initial)	ft	6.5
Effective Size	mm	0.3
Uniformity Coefficient	-	<1.5
Water Stabilization Tank		
Volume	gallons	1,000
Granular Media Filter		Roberts Filter Group
Feed Rate	gpm	1.75
Column Diameter	inches	8
Column Height	ft	11.25
Filtration Rate	gpm/sf	5
Filter Media		
Anthracite		

Depth	inches	24
Effective size	mm	1.0 to 1.1
Uniformity Coefficient	-	< 1.5
Sand		
Depth	inches	12
Effective size	mm	0.5 to 0.55
Uniformity Coefficient	-	<1.5
Support Gravel		
Depth	inches	3
Size	mm x mm	4.75 x 2.00
Backwash Rate	gpm/sf	20
Ultrafilter		Koch Membrane Systems
Feed Rate	gpm	10
Reject Rate	gpm	<0.5
Membrane Element	-	Koch PMPW 2
Size (diameter x length)	inch x inch	5 x 72
Nominal Pore Size	µm	0.01
Active Membrane Area	sf	160
Flux Rate	gpd/sf	90
Transmembrane Pressure	psi	1 - 35

Three different chemical precipitation strategies, i) caustic (sodium hydroxide), ii) lime (calcium hydroxide), and iii) lime-soda ash-barium (calcium hydroxide-sodium carbonate-barium chloride) were used to evaluate pellet softening processes. Table 15 summarizes the test conditions for each chemical precipitation strategy.

Table 15: Pellet Softener Test Run Summary

Run	Run Length (days)	Headloss (Psi)	Chemical Addition Targets	Goal
1	13.7	6.25	Caustic (NaOH): pH = 9.6	Gain experience, $CaCO_3$ Crystallization
2	18.6	6.8	Caustic (NaOH): pH = 9.6	
3	15.2	6.5	Caustic (NaOH): pH = 9.6	
4	11.8	5.9	Caustic (NaOH): pH = 10.8	$CaCO_3$ & $Mg(OH)_2$ Crystallization
5	8.1	5.4	Caustic (NaOH): pH = 10.8	
6	15.0	6.1	Caustic (NaOH): pH = 10.8	
7	-	4.8	Lime ($Ca(OH)_2$): pH = 9.6	Evaluate lime $CaCO_3$ crystallization
8	8.1	5.1	Lime ($Ca(OH)_2$): pH = 9.6	
9	7.0	4.3	Lime ($Ca(OH)_2$): pH = 9.6	
10	7.0	3.6	Lime ($Ca(OH)_2$): pH = 9.6	

11	6.9	3.5	Lime-Soda Ash – Barium: pH = 9.6	New solid ($BaSO_4$) crystallization in addition to $CaCO_3$
12	4.0	4.25	Lime ($Ca(OH)_2$): pH = 9.6	$CaCO_3$ crystallization

The caustic feed strategy was evaluated under two dosing rates, i) at pH 9.6, where only calcium hardness was removed through $CaCO_3$ precipitation, and ii) at pH 10.8, where both calcium (CaCO3 solids) and magnesium ($Mg(OH)_2$ solids) hardness were removed.

The lime feed strategy was evaluated at pH 9.6. The goal of this test was to evaluate the crystallization with lime feed conditions. Finally, the lime-soda-ash-barium strategy was adopted to study crystallization of an additional solid (barium sulfate) along with calcium carbonate on the pellet surface.

Results

In this section, the effluent water quality data from various tests are presented and discussed first. Subsequent sections discuss the headloss buildup across the reactor and solids content in the pellet.

Caustic Softening, pH 9.6

This test was performed to optimize precipitation of calcium carbonate. The following chemical reactions describe the water quality changes anticipated at this pH.

$$2\ NaOH + Ca^{2+} + H_2CO_3 \rightarrow 2\ Na^{+} + CaCO_3\downarrow + 2\ H_2O \qquad (6)$$

$$NaOH + Ca^{2+} + HCO_3^{-} \rightarrow Na^{+} + CaCO_3\downarrow + H_2O \qquad (7)$$

The net result is a decrease in calcium hardness and alkalinity, addition of sodium, and an overall decrease in TDS.

Table 16 shows pellet softener influent and effluent concentrations for key water quality parameters. These results indicate that about 85 percent of the calcium and 12% TDS were removed under the test conditions. The sodium level increased about 74 percent.

Table 16: Summary of Pellet Softer Performance with Caustic Feed, pH 9.6 Target, Laboratory Data

Parameter	No. of Samples	Well W-21	PS Effluent	% Removal
Total Hardness	5	426	241	43 %
pH	4	7.3	9.3	
Alkalinity	5	210	102	51.4%
EC	4	1375	1308	4.9%
TDS	5	1012	888	12.3%
Calcium	5	132.6	19.8	85.1%
Magnesium	5	45.6	46	0.0%
TOC	5	0.8	0.6	24.4%

Sodium	5	102.8	179.5	-74.3%
Turbidity	5	1.1	8	-620%

Caustic Softening, pH 10.8

The goal of this operational condition is to evaluate precipitation and crystallization of magnesium in addition to calcium hardness removal. The additional chemical reactions are described below.

$$2\ NaOH + Mg^{2+} + \rightarrow 2\ Na^{+} + Mg(OH)_2\downarrow \qquad (8)$$

Table 17 presents the pellet softener influent and effluent concentrations for key water quality parameters. These results indicate that about 92 % of the calcium and 12% of TDS were removed. Magnesium reduction was about 5.4 percent. The sodium level increased about 126 percent.

Table 17: Pellet Softer Performance with Caustic Feed, pH 10.8 Target

Parameter	No. of Samples	Well W-21	PS Effluent	% Removal
Total Hardness	4	530	207	61%
pH	4	7.5	10.5	
Alkalinity	4	210	145	31.0%
Conductivity	4	1,380	1,385	-0.7%
Total Dissolved Solids	4	1025	902.5	12.5%
Calcium	4	135.5	10.3	92.5%
Magnesium	4	45.8	43.5	5.2%
Total Organic Carbon	4	0.8	0.7	8.3%
Sodium	4	95.5	215.5	-125.7%
Turbidity	4	1.1	8.2	-635

Lime Softening

The goal of the lime softening trials was to compare $CaCO_3$ precipitation and crystallization under lime feed conditions with that of caustic feed conditions. Removal of carbonate hardness occurs through reactions 3 and 4.

$$Ca(OH)_2 + H_2CO_3 \rightarrow CaCO_3\downarrow + 2\ H_2O \qquad (3)$$

$$Ca(OH)_2 + Ca^{2+} + 2\ HCO_3^{-} \rightarrow 2\ CaCO_3\downarrow + 2\ H_2O \qquad (4)$$

The net result is a decrease in calcium hardness, alkalinity, and TDS. Note that there is no sodium addition, but more solids may be produced. Again, the reactions are limited by the carbonate hardness available. The target lime dosage ranged from 220 mg/l to 360 mg/l.

Table 18 presents the pellet softener influent and effluent characteristics under lime feed conditions. These results indicate that only about 10 percent (net) of the calcium and 12.5 percent TDS were removed. The calcium removal was lower than expected. The higher levels of calcium in the treated effluent may be due leakage and subsequent dissolution of calcium. In any case, the lime was more difficult to control and was not as stable as the caustic softening process.

Table 18: Performance of Lime Pellet Softening

Parameter	No. of Samples	Well W-21	PS Effluent	% Removal
Total Hardness	8	532	492	7.5%
pH	8	7.4	9.5	
Alkalinity	8	210	84	59.9%
Conductivity	8	1368	1183	13.6%
Total Dissolved Solids	8	993	869	12.5%
Calcium	8	136	122	10.1%
Magnesium	8	46	45	1.9%
Total Organic Carbon	8	0.8	0.9	-6.3%
Sodium	8	95	94	0.3%

Lime-Soda-Barium Softening

The goal of lime-soda-barium trial was to evaluate precipitation/crystallization of a sulfate solid (barium sulfate) in addition to calcium carbonate solids evaluated in the previous studies. Because of chemical availability, barium chloride was used instead of barium hydroxide, adding some TDS to the treated water. The softening chemistry would be through the following reactions:

$$Ba(OH)_2 + H_2CO_3 + SO_4^{2-} + Ca^{2+} \rightarrow BaSO_4\downarrow + CaCO_3\downarrow + 2\ H_2O \quad (9)$$

$$Ca(OH)_2 + Ca^{2+} + 2\ HCO_3^{-} \rightarrow 2\ CaCO_3\downarrow + 2\ H_2O \quad (10)$$

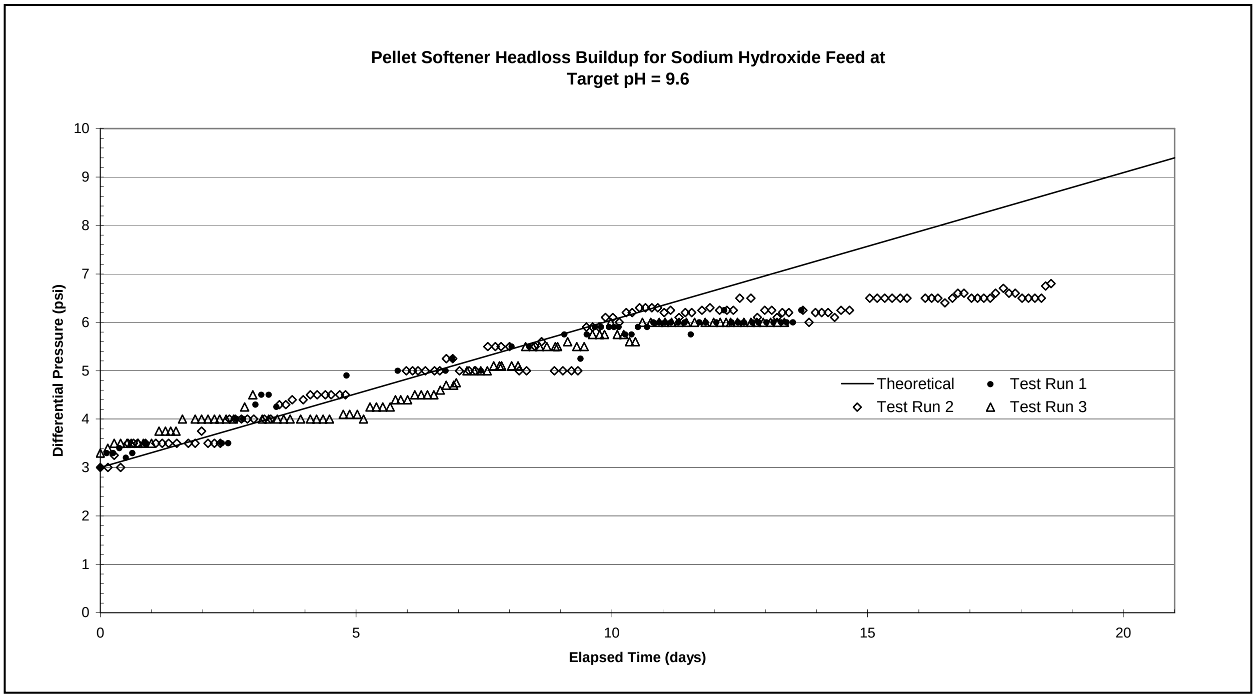
$$Na_2CO_3 + Ca^{2+} \rightarrow CaCO_3\downarrow + 2\ Na^{+} \quad (11)$$

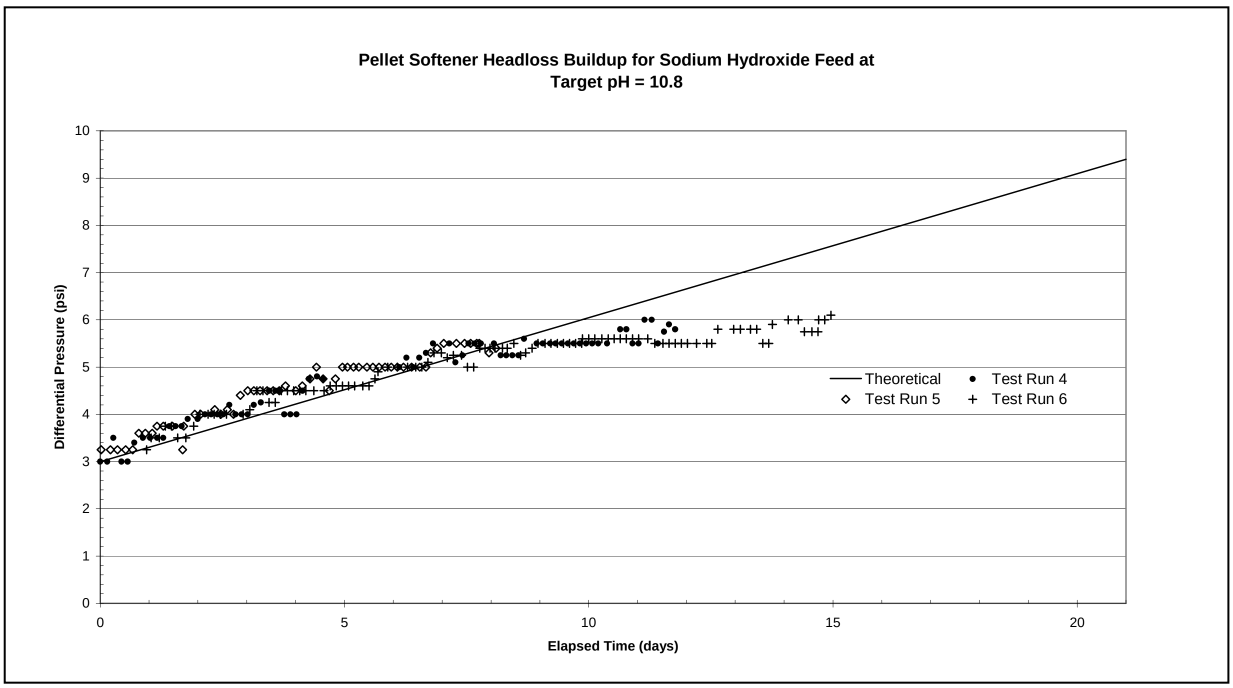
The net result is a decrease in calcium hardness, alkalinity, sulfate, and TDS, and an increase in sodium. However, because barium chloride was used instead of barium hydroxide, there was an expectation that the TDS would increase. The use of the chloride form was to determine the validity of the conceptual model of this approach. The target chemical dosages were about 180 mg/l barium chloride, 220 mg/l lime, and 160 mg/l sodium carbonate.

Field measurements were not taken during the periods when barium was fed and the laboratory analyses for two samples taken during these periods were not reliable. In particular, the sulfate concentrations in Well 21 and the pH of pellet softener effluent were significantly lower than anticipated. The results indicated that no significant amount of sulfate was removed. In addition, some barium carryover was observed (2.2 mg/l and 0.6 mg/l) in the effluent. Thus, test results were inconclusive and further studies are required prior to pursuing this chemical feed strategy for simultaneous hardness and sulfate removal.

Headloss Buildup

The headloss build up was monitored during each pellet softening run to evaluate crystallization of the precipitated on the pellets. The pellet softener was operated in a fluidized mode at a hydraulic loading rate of 20.4 gpm/sf (16 gpm). The buoyant weight of the 500 pounds of sand creates an initial headloss of about 3 psi. As calcium carbonate coats the sand, the pellet weight increases, resulting in headloss build up across the pellet softening column.





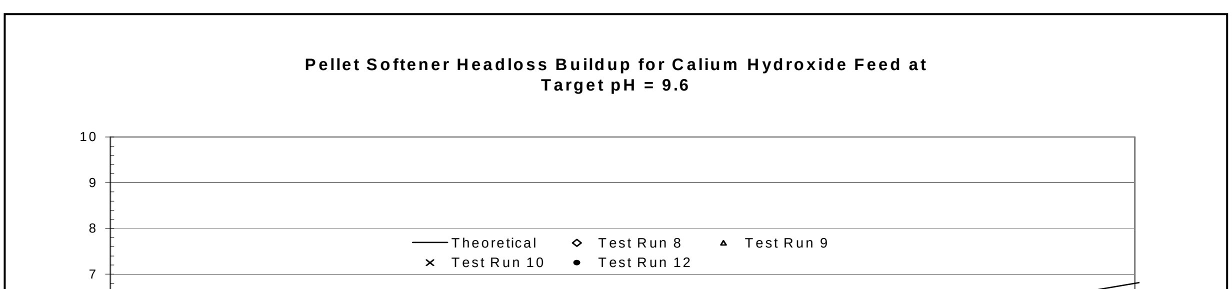


Figure 3. Headloss across pellet softener during lime feed studies at target pH 9.6

Figure 1 shows the headloss build up for caustic softening with target pH of 9.6 (runs 1-3). These curves followed the expected increase until a headloss of 6 – 6.5 psi was reached, and then began to level off. This may be the limit of pellet build up for this pilot softening reactor (straight sided column). Under the test conditions, the pellet saturation occurred after a period of about 10 days. Figure 2 shows similar results for caustic softening with a target pH of 10.8 (runs 4-6); however, the headloss began to level off at 5.5 – 6 psi.

Figure 3 shows the headloss build up for lime softening (runs 7-12). These curve show the headloss leveling off at even lower pressures (~4.5 psig), partially due to lime feeding problems. In some cases when lime feed was lost the headloss decreased, indicating that calcium carbonate was being dissolved from the pellets. The leveling off occurred within 4.5 days under the lime feed conditions, approximately the same time required to reach this headloss level with caustic feed. Thus, the rate of headloss increase for lime feed appeared to be similar to caustic feed.

In summary, results suggested that, as experienced by some water agencies, magnesium solids from the softening processes did not crystallize over the pellets very effectively. In addition, crystallization of calcium carbonate during lime addition was less effective than during caustic addition, although this may have been due to issues related to the lime feed system. Further more, barium sulfate solids during the lime-soda ash-barium study also did not crystallize on the pellets effectively. These results indicated that more studies are required to evaluate crystallization of the calcium sulfo/chloro aluminate salts over the pellets.

Analysis of Pellets

The pellet softener was operated in a batch mode, with all pellets removed after each pellet run. The pellets dewatered readily and may lose more water if put on drying beds. Table 19 provides a summary of the laboratory results on pellet characteristics for the two caustic softening strategies and the lime softening strategy. The average percent solids were about 75 percent for all three strategies. Caustic softening pellets had higher average calcium concentrations (20 percent for pH 9.6 target and 17.5 percent for pH 10.8 target) than the lime strategy (10.7 percent). Note that very little magnesium was removed, with only 0.9 percent magnesium on the pellets with caustic pH target at 10.8. Also, as reported by others (Harms and Robinson, 1992), increasing the pH to 10.8, to facilitate magnesium hydroxide precipitation decreased the efficiency of calcium removal by the pellets. The pellets from the lime-soda-barium run (data not shown) also had about 75 percent solids, but the laboratory did not measure calcium concentrations.

Table 19: Summary for Spent Pellet Analyses

Parameter	Unit	No. Data	Max	Min	Average
NaOH to pH 9.6					
Calcium	mg/kg	6	264,000	90,000	198,833
Magnesium	mg/kg	6	690	520	600
Iron	mg/kg	6	286	164	215
Manganese	mg/kg	6	65.2	5.2	23
% Solids	%	6	98.1	61.8	75.4
pH	Unit	6	9.9	9.0	9.5
NaOH to pH 10.8					
Calcium	mg/kg	6	213,000	139,000	174,667
Magnesium	mg/kg	6	9100	3300	7088
Iron	mg/kg	6	167	77	132.0
Manganese	mg/kg	6	17.3	11.8	15.26
% Solids	%	6	79.9	69.5	75.6
pH	Unit	6	10.4	10.2	10.3
Lime					
Calcium	mg/kg	8	124,000	818,00	106,700
Magnesium	mg/kg	8	1,270	860	1,105
Iron	mg/kg	8	548	227	348
Manganese	mg/kg	8	31.4	10.0	19.1
% Solids	%	8	86.4	73.5	78.6
pH	Unit	8	11.0	8.8	9.4

Comparison Of Sludge Production In Direct Lime Softening And Pellet Softening Processes

The amount of lime produced in direct lime softening process can be estimated by the formula (AWWA, 1999)

$$\Delta S = 86.4\ Q\ (2\ Ca + 2.6\ Mg) \qquad (12)$$

Where

ΔS – Dry weight of the sludge formed (Kg/day)

Q – Flow Rate (m^3/s)

Ca – Calcium Hardness Removed (mg/l as $CaCO_3$)

Mg – Magnesium Hardness Removed (mg/l as $CaCO_3$)

The average initial and final calcium hardness under lime feed conditions are 348 and 247 mg/l as $CaCO_3$, respectively. The average initial and final magnesium hardness are 189 and 167 mg/l as $CaCO_3$, respectively. The average flow rate for the pilot study was 16 gpm. The headloss across the reactor during pellet formation leveled out 4.5 psig. This condition occurred after approximately 4 days of operation under the test conditions. The settled pellet sludge contained about 75 % solids. A 10% solids was assumed for the direct lime softening process in this estimate. The amount of dry solids estimated to be produced by pellet softening process (750 lb/4 days) is about 3 folds higher than that in the direct lime softening process (~ 235 lb/4 days). However, due to significantly lower moisture content, the volume of wet sludge produced by the pellet softener (1000 lb/4 days) is about 40% lower than the direct softening process (2300 lb/4 days). Furthermore, the pellet softening sludge is much denser, with higher calcium content that can be used for construction applications.

Summary And Recommendations Of Pellet Softener Testing

- Caustic softening (110-120 mg/l) at a target pH of 9.6 would produce an effluent with a target total hardness of ~240 mg/l, which is significantly below the Oxnard groundwater level of 540 mg/l and the blended water level of 360 mg/l.
- The filtered, softened water is expected to meet all the primary Title 22 drinking water standards.
- Using 10 days for pellet residence time (caustic feed) it is estimated that 2,200 pounds (1,000 kg) of sand would be needed to treat 1 million gallons of water.
- Using 4.5 days for pellet residence time (lime feed) it is estimated that 5,400 pounds of sand would be needed to treat 1 million gallons of water. This process will generate a dry sludge of about 8,000 lb/MG treated water.
- The pellets dewatered very rapidly.
- The relatively high calcium content suggests that beneficial uses of the pellets can be found.
- High turbidities can be expected when exhausted pellets are not removed from the system at the appropriate time.
- Filtration after the pellet softener and carbon dioxide addition is a requirement for the overall process train.
- A filtration system after the pellet softener and carbon dioxide addition is a requirement for the overall process train.

SECTION 6: CONCEPTUAL EVALUATION OF COMBINING UHLA AND PELLET SOFTENING PROCESSES

Evaluation of the City of Oxnard pilot studies indicated that several issues must be resolved regarding the two technologies prior to conceptual evaluation of combining the two technologies to facilitate recovery of membrane brines. For example, while the UHLA process effectively removed chloride/sulfate in laboratory studies by others, the chloride level in the pilot study was too low to be impacted and only limited amounts of sulfate were removed under the pilot scale testing conditions. This may be due to several reasons including i) the solubility products for the calcium sulfo and chloroaluminates were developed without considering the effect of the other, ii) calcium sulfoaluminate solids do not settle/crystallize readily, iii) presence of co-contaminants in the groundwater impacted precipitation of these salts, and iv) the pilot plant pH was not tightly controlled. Note that the clarifier (Claricone™) unit effectively removed hardness during the caustic/lime feed testing. More studies need to be performed to identify the factors that impacted the precipitation of sulfate solids prior to developing full-scale process for RO brine recovery to estimate the amount of water that can be recovered by this process and determine the overall impact to SCE service area. Another key concern with the pilot result is that the amount of aluminum in the treated water (40 mg/l) must be reduced, perhaps by improving pH control and/or by a second precipitation process so that the treated brine can be recovered by RO.

The pellet softener process, which effectively removed the solids under caustic feed conditions was not very effective in removing calcium carbonate as well as magnesium hydroxide solids under lime feed conditions. The amount of calcium carbonate in the in the pellets during the lime feed conditions was much lower than that during caustic feed conditions, because the runs were shorter and less calcium carbonate was built up on the sand.

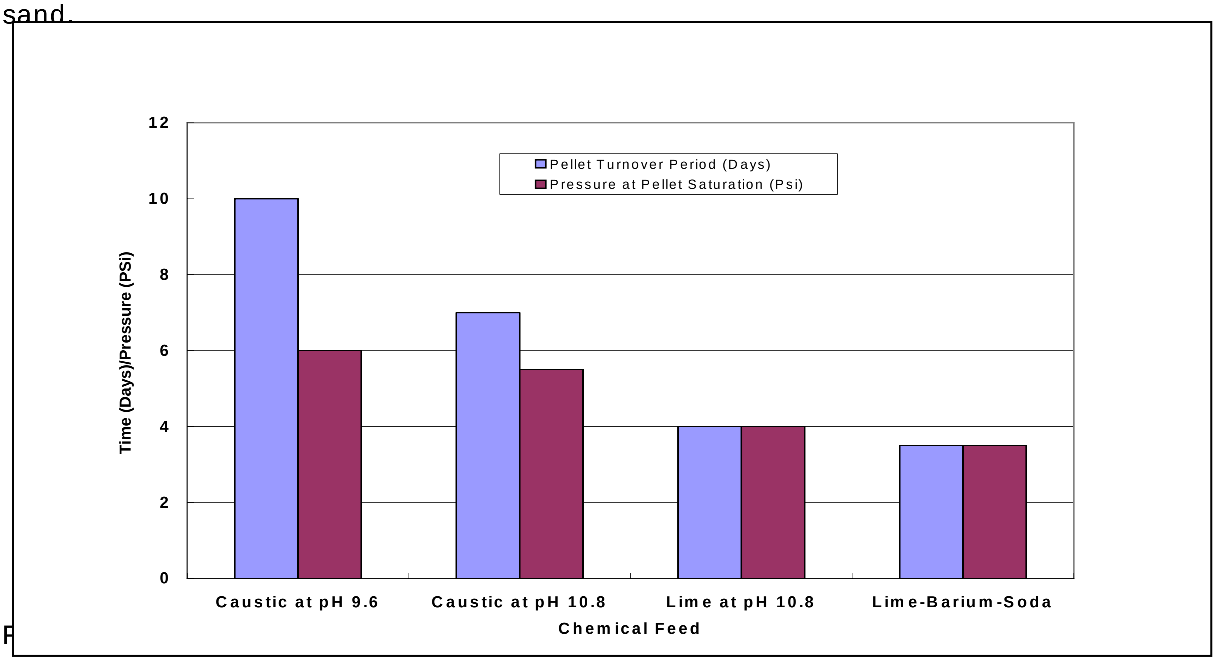


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Figure 4 shows the pellet residence time and headloss across the pellet bed. The pellet turnover period as well as headloss was shorter with lime feed and magnesium precipitation conditions. While the pellet residence time was 10 days during caustic feed, it was only 4.5

days during the lime feed conditions. Furthermore, the process was highly unstable during the lime feed conditions and barium was only intermittently fed to remove sulfate from solution. More studies are required to evaluate crystallization of calcium sulfoaluminate and other sulfate solids such as barium sulfate onto the pellet surface.

The uncertainties involved in the precipitation chemistry, operation requirements and precipitation of the sulfoaluminate solids must be resolved prior to successful conceptual evaluation of combining the UHLA and pellet softening processes. Further studies are required to understand the precipitation/crystallization of these solids, chemical dosing and operational requirements to perform an economical evaluation of this process. Hence, a planning level cost estimate was not developed for the proposed process. However, Table 20 presents various capital and O&M components associated with the conventional RO process and proposed process to recover reject streams by RO.

As shown in the table, it is anticipated that the technology proposed in this study, if successfully implemented, will enhance the water recovery by about 10 to 15% using almost the same amount of energy as the conventional RO process. Also, the proposed technology will reduce the volume of waste stream generated, and hence, will reduce the sewer connection as well as discharge costs. Furthermore, the used pellets can be reused for road construction and other applications. However, the capital cost of the proposed technology will be higher than the conventional RO process due to the addition of pellet softener reactor unit. Also, the process will include additional chemical costs for hardness/sulfate precipitation and labor cost for operating the pellet softener unit.

Table 20: Comparison of Capital and O&M Components for the Conventional RO Process and the Proposed Brine Recovery Process

Component	**Conventional RO Process**	**RO + Brine Recovery Using Proposed Technology**
Anticipated Recovery	70 to 75%	~ 85 to 90%
<u>Capital Cost</u>		
RO Equipment, pumps & installation	Similar for both processes	
Anti-scalent, anti-foulant and clean-in-place and energy recovery systems	Similar for both processes	
Sewer connection fee for waste discharge	Higher than that for the proposed application	Lower than conventional process due to lower wastewater discharge
Pellet Reactor and Chemical (Lime, caustic & aluminate) feed system equipment and installation costs	Not Applicable	Required to treat reject stream.
Indirect Construction Costs		Slightly higher due to installation of additional equipment

O&M Cost		
Antiscalent, antifoulant and RO cleaning solution	Similar for both the processes	
RO Element Replacement	Similar for both the processes	
Lime, Caustic, aluminate	Not Required	Required for UHLA + Pellet Softening
Pellet Replacement	Not Required	Required for UHLA + Pellet Softening
Electricity	Similar for both the options	
Wastewater Discharge	High due to larger wastewater discharge	Lower than the conventional process
Pellet Disposal/Reuse	Not Applicable	Pellets can be reused
Labor	Lower than the proposed application	Slightly higher than the conventional system due to pellet softener operation

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