Upflow Calcite Contactor Study

Final Report

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List of Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AF	acre-feet
Ca	calcium
Ca^{2+}	soluble calcium
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate
$CaSO_4$	calcium sulfate
CCPP	Calcium Carbonate Precipitation Potential
CCSP	Calcium Carbonate Scaling Potential
H_2CO_3	carbonic acid
CO_2	carbon dioxide
CO_3^{2-}	carbonate species
NaOH	caustic soda
CRC	Columbia River Carbonates
°C	degrees Celsius
DIC	dissolved organic carbon
EBCT	empty bed contact time
EPA	Environmental Protection Agency

Fe	ferrous iron
ft/min	feet per minute
gpm/ft^2	gallons per minute per square foot
LSI	Langelier Saturation Index
MCL	maximum contaminant level
m	meter(s)
m/hr	meters per hour
µg/L	micrograms per liter
µm	micrometers
µS/cm	micromhos per centimeter
mg/gal	milligrams per gallon
mg/L	milligrams per liter
MGD	million gallons per day
ML	Mississippi Lime
mm	millimeter
NSF	National Sanitation Foundation
NTU	nephelometric turbidity units
O&M	operations and maintenance
ppm	parts per million
psi	pounds per square inch
RO	reverse osmosis
RSI	Ryznar Stability Index
SiO_2	silicon dioxide
SMCL	Secondary Maximum Contaminant Level
$NaHCO_3$	sodium bicarbonate
SWTR	Surface Water Treatment Rule
TCEQ	Texas Commission on Environmental Quality
TDS	total dissolved solids
TLV	Threshold Level Value

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1 Executive summary

Projected decreases in water supplies in Texas due to sediment accumulation in reservoirs and aquifer depletion have led state and regional water planning agencies to turn to brackish water supplies to address rising water demands.

Reverse osmosis (RO) is a viable treatment technology for removing dissolved solids from such high-saline supplies, making them suitable for potable use. However, the resulting permeate (product water) from the treatment process typically has unacceptably low levels of calcium hardness and alkalinity, which renders the product water corrosive to distribution system components and aesthetically unappealing. To stabilize the corrosive permeate, post-treatment via pH adjustment and the addition of calcium and alkalinity are needed to remineralize the water.

The chemical stability of potable water is typically determined by three parameters:

- pH buffering capacity or alkalinity;
- Tendency of the water to precipitate calcium carbonate or scaling potential; and
- Concentration of soluble calcium ions in the water.

pH is also a relevant parameter in the finished water, but is dependent on the values of the three parameters above. In general, calcite dissolution decreases as temperature increases. However, given the permeate temperature range of 25 to 27 degrees Celsius (°C) at the Kay Bailey Hutchison Desalter, temperature effects on calcite dissolution is insignificant. Several calculated indices are used in the water industry for water stability control to determine the scaling tendency of calcium carbonate. The most commonly accepted indices are Calcium Carbonate Scaling Potential (CCSP), Ryznar Stability Index (RSI), and Langelier Saturation Index (LSI). The typical targeted post-treatment water quality objectives are as follows:

- $60 <$ Alkalinity < 80 milligrams per liter as calcium carbonate (mg/L as $CaCO_3$)
- Langelier Saturation Index > 0
- Ryznar Stability Index < 10
- $4 <$ $CaCO_3$ Precipitation Potential < 10 mg/L as $CaCO_3$
- $50 <$ Calcium (Ca) < 120 mg/L as $CaCO_3$
- $6.5 < \text{pH} < 8.5$

Generally, post-treatment remineralization can be achieved by four treatment processes. These four treatment methods are:

- Chemical addition – materials other than lime or calcite;
- Blending with a water containing high mineral content;

- Carbon dioxide (CO_2) addition followed by calcite or dolomite dissolution; and
- CO_2 addition followed by lime (slurry) dosing.

Chemicals such as sodium bicarbonate, calcium sulfate, or calcium chloride can be used, but there are challenges associated with chemical costs and storage. Addition of chemicals also introduces additional minerals into the finished water. The United States Environmental Protection Agency (EPA) has a secondary maximum contaminant level (MCL) for chloride set at 250 mg/L. Kay Bailey Hutchison Desalter draws from a number of high salinity (high total dissolved solids [TDS]) wells, and the resulting permeate chloride levels are between 110 to 180 mg/L. To avoid exceeding the chloride limit, chemical addition for post-treatment was eliminated from further consideration. Blending with a saline feed water is a cost-effective option; however, undesirable constituents in the blend water, such as color-causing agents, radionuclides, heavy metals, excess organic matter, and/or nutrients can prevent such an approach. With respect to slurry treatment, increased turbidity due to particle carryover is a major operational challenge. CO_2 consumption for lime addition doubles when compared to calcite addition in the post-treatment process to produce the required alkalinity and calcium hardness. In addition, lime is far more challenging to store and feed than calcite. For this reason, calcite has been selected as the preferred remineralization compound of choice.

A literature review of the calcite contactors revealed that acidification of the permeate by addition of CO_2 followed by upflow calcite (limestone) contacting is recognized in Europe and the Caribbean to be an emerging method of post-treatment of RO permeate. The design criteria used to develop these systems are not well established in the United States. Dissolution of calcite is a dynamic process, which may be enhanced or inhibited depending on the contactor design and influent water quality.

Contactor design factors include: superficial velocity (loading rate), calcite particle size and purity, contactor bed height, and bed porosity. Particle size affects the contact surface area and therefore, the contactor performance. As particle size increases, the contact surface area with the water decreases, and longer contact times are required to reach the desired water hardness and alkalinity level. Similarly, increased levels of impurity in the calcite particles, i.e., magnesium, aluminum, and iron, will lower calcite dissolution rate. Influent water quality parameters that affect calcite dissolution include influent calcite saturation level, pH, temperature, ionic strength, and feed water impurities.

In the literature survey, available design correlations and recommendations were derived from upflow contactor studies where calcite particles were in the 2 to 3 millimeter (mm), 12 to 15 mm, and 20 to 25 mm size range. A preliminary survey of NSF[1] 60 approved calcite sources in United States for drinking water applications showed that the available nominal particle size is usually 1 mm and below. Purity of the available commercial calcite particles ranged from 95 to 98 percent. Five major calcite suppliers were identified:

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1 National Sanitation Foundation, Ann Arbor, Michigan.

- Imerys,
- Mississippi Lime (ML),
- Columbia River Carbonates (CRC),
- Specialty Chemicals, Inc., and
- Lhoist.

An alternate source for calcite is also proposed for RO permeate remineralization. Municipalities that own brackish water desalters in California and Arizona are evaluating means to maximize water recovery by sending RO concentrate through an intermediate precipitative softening step to remove calcium and magnesium hardness. The effluent is then sent to a second RO process to recover additional water. One such precipitative softening technology is the "pellet softening" process, where dried pellets that are rich in calcite content are recovered at the end of the softening step. The size of the pellets range from 0.4 to 1.4 mm, and can potentially be reused as a source of calcite particles in contactors instead of purchasing manufactured calcite products commercially. For softening pellets to be considered as a calcite source in post-treatment applications, NSF 60 approval would be required. However, for the purpose of this study, the use of softening pellets was only performed as a proof-of-concept test.

The objectives of a calcite contactor design are to maximize the contact area between calcite particles with the water and minimize the amount of time that water needs to spend in the reactor to achieve the desired hardness and alkalinity levels. Loading rate and contact time will determine the height of the calcite bed. However, no direct correlation between treatment capacity and loading rate was evident in the published literature. The relationship between calcite particle size and effluent turbidity was reported for upflow contactor designs that used 2 to 3 mm particles, and no other references revealed the effect of other calcite particle sizes on finished water turbidity. Calcite consumption is determined by the influent water characteristics, calcite purity, and size; therefore, pilot testing is always recommended for site-specific treatment with actual water samples. Analysis models derived from calcite dissolution theory are helpful in determining theoretical consumption rate, but performance testing is still required to validate model results.

Due to the myriad of parameters that affect calcite contactor performance and the lack of established design criteria for upflow contactors in the United States, a series of experimental matrices to verify design parameters for pilot testing was developed. The experimental plan includes testing upflow calcite contactors for RO permeate stabilization by varying empty bed contact time (EBCT), calcite purity, and calcite particle size.

In this work, four experiments were conducted in four phases to determine design criteria for RO permeate stabilization. The first three phases of experiments involved varying one of three design parameters (calcite particle size, calcite purity, and EBCT) and holding the other two constant. The fourth phase of experiments used combinations of selected values for these parameters to validate the design criteria values developed using the results of the first three experiments.

Monitored parameters included water temperature, conductivity, mineral ion concentrations, dissolved organic species, change in calcite particle size, contactor head loss, and post-contactor calcite particle surface element composition. These results were used to determine the sizing and loading rate of the calcite contactor, select an optimum calcite purity and size, and select a calcite consumption rate to estimate the annual costs of the system.

Phase	Description	Purpose
1	Vary calcite purity while keeping calcite particle size constant.	Determine appropriate calcite purity for permeate stabilization.
2	Vary influent flow rate while keeping calcite particle size and purity constant.	Determine the minimum EBCT for optimum permeate stabilization.
3	Vary calcite particle size while keeping influent flow rate and calcite purity constant.	Determine the optimum calcite particle size for permeate stabilization.
4	Selected three combinations of flow rate, particle size, and purity for testing. The fourth column included testing of particles from a pellet softening process (Carollo Pellet).	Validate performance of three combinations of design criteria and the use of particles from pellet softening process (Carollo Pellet).

1.1 Results and conclusions

In any calcite dissolution reaction, though it is possible to achieve finished water calcium hardness and alkalinity goals, final polishing by caustic soda (NaOH) dosing is required to elevate the LSI and Calcium Carbonate Precipitation Potential (CCPP) indices to above zero and 4 mg/L as $CaCO_3$, respectively, for anti-corrosion purposes. This phenomenon was observed for all four phases of upflow calcite contactor testing. Fluctuations in the influent water quality was monitored constantly with reliable field measurements so operators could adjust CO_2 dosing to meet finished water quality goals. Specific conclusions for each of the phases are summarized below.

1.1.1 Phase 1: Impact of calcite purity on effluent water quality

In Phase 1, calcite particles in the 1-mm (nominal) size range (manufacturer-reported) were tested at a fixed influent loading rate of 3.8 gallons per minute per square foot (gpm/ft^2) (0.51 feet per minute [ft/min]) across a range of calcite purities varying from 95 to 98 percent. The results indicated that within the tested range of calcite purities, there was no discernible impact on effluent water quality in terms of pH, alkalinity, and calcium hardness. Sieve analysis of the media samples revealed a relatively broad particle size distribution compared to the suppliers' nominal size label of 1 mm, particles and comparison of effluent turbidity with particle size distribution suggested that smaller calcite particles (< 0.5 mm) could have contributed to the high turbidities. The initial height of the media in the column was 30 inches, and the loading rate of 3.8 gpm/ft^2 (0.51 ft/min) provided a design EBCT of five minutes. However, the flow significantly expanded some of the media beds because of the significant proportion of small particles in the size distribution, which resulted in initial EBCTs of approximately 5 to 8 minutes in the four columns. As the calcite media dissolved during Phase 1 (four weeks), the EBCT decreased to approximately 3 to 5 minutes in the four columns. Throughout Phase 1, all four-column effluents successfully achieved the target water quality goals of calcium, hardness, and pH. No significant increases in other ion concentrations were observed, except for an increase in concentration of strontium from approximately 0.02 mg/L in the permeate to approximately 0.1 mg/L in the Lhoist media effluent, and approximately 0.2 mg/L in the CRC media effluent. Of the tested calcite products, CRC Puri-Cal C media was selected for subsequent testing in Phase 2 due to its narrow size distribution (approximately 1 mm) and low effluent turbidity.

1.1.2 Phase 2: Impact of influent flow rate on effluent water quality

In Phase 2, the objective was to determine the impact of influent loading rates from 1.9 gpm/ft^2 (0.26 ft/min) to 17 gpm/ft^2 (2.3 ft/min) on effluent water quality. CRC Puri-Cal C was used as the test sample calcite media. The initial media bed height was approximately 30 inches, which resulted in EBCTs of 1.1 to 9.8 minutes. The experimental results indicated that the average rate of decrease of calcite media bed height (from 0.13 inches/day to 0.83 inches per day) was nearly proportional to the loading rate, which was expected. At the highest influent loading rate of 17 gpm/ft^2 (2.3 ft/min), the velocity of the flow fluidized the calcite bed within the contactors and led to high effluent turbidity due to calcite particle blow out. The optimum loading rate that best achieved effluent water quality goals was determined to be 9.5 gpm/ft^2 (1.3 ft/min). The corresponding EBCT was 1.0 to 2.5 minutes in the contactor columns. It was also observed that the column effluent alkalinity and calcium concentrations significantly diminished when the column influent pH was greater than 5.7.

1.1.3 Phase 3: Impact of particle sizes on effluent water quality

In Phase 3, the objective was to determine the impact of calcite particle sizes (0.25 to 2 mm) on effluent water quality. Four calcite products from the same manufacturer were selected, all with the same reported calcite purity of 95 percent and tested at the same loading rate of 3.8 gpm/ft^2 (0.51 ft/min). Smaller calcite particles in the contactor bed resulted in higher surface area, which led to a higher rate of calcite dissolution and hence, more calcium and alkalinity were added to the permeate. Calcite particles that were less than 0.5 mm with a broad size distribution contributed to high effluent turbidities, and 1 mm particles produced marginally better effluent water qualities compared to 2 mm particles.

1.1.4 Phase 4: Optimized treatment conditions

In Phase 4, higher loading rates of 9.5 gpm/ft^2 (1.3 ft/min) and 17 gpm/ft^2 (2.3 ft/min) were tested with the calcite samples selected from Phase 1 to 3. The goal was to demonstrate sufficient calcite dissolution at a loading rate high enough that the economics of implementation were significantly improved. The tested calcite samples were CRC Puri-Cal C and Imerys Z White in the 1 -mm range, the 2 -mm Imerys OZ White, and an additional calcite sample derived from RO concentrate softening (pellets from Carollo pilot testing in Mira Loma, Calif.) as a means for reuse.

Of the four products tested, the smallest calcite sample in Phase 4 was the pilot test pellet softener sample at a purity of less than 90 percent. At a constant loading rate of 9.5 gpm/ft^2 (1.3 ft/min), smaller pellets dissolved faster, followed by CRC Puri-Cal and Imerys Z White, and lastly by OZ White. The Phase 4 test results confirmed that contact times between 1.50 and 2 minutes were optimum for meeting post-treatment water qualities. Operating the reactor at a loading rate of 9.5 gpm/ft^2 (1.3 ft/min) also minimized turbidity spikes as demonstrated in Phase 2. Among the tested calcite samples, CRC Puri-Cal C at 1 mm and 95 percent purity is recommended for calcite post-treatment of the permeate from the Kay Bailey Hutchison Desalination Plant.

The experiment results from each of the four project phases were used to determine the size and loading rate of the calcite contactor, the optimum calcite purity and size, and the expected calcite consumption rate to estimate the annual capital and Operations and Maintenance (O&M) costs of a 1.0-million gallons per day (MGD), 5.0-MGD and 10.0-MGD system; reference Tables 6.1 and 6.2 for a summary of these cost estimates.

2 Introduction

The population in Texas is expected to increase between the years 2010 and 2060, growing from 25.4 million to 46.3 million. As a result, the demand for water is expected to increase by 22 percent, from almost 18 million acre-feet (AF) of water in 2010 to about 22 million AF in 2060. Existing water supplies—the amount of water that can be produced with current permits, current contracts, and existing infrastructure during drought—are projected to decrease about 10 percent, from about 17.0 million AF in 2010 to about 15.3 million AF in 2060. This decrease is primarily due to the depletion to the Ogallala Aquifer and reduced reliance on the Gulf Coast Aquifer. Texas is going to need an additional 8.3 million AF of water by 2060 if new water supplies are not developed (Texas Water Development Board State Water Plan, 2012).

The current model for state and regional water planning involves: (1) forecasting future conditions, including population, water demand, and water supplies; (2) describing and assessing regional conditions, including existing water supplies and water demand; (3) identifying and comparing alternative water management strategies to address future deficits; and (4) recommending water management strategies for implementation. The fourth item listed typically includes RO as a treatment option for treating brackish feed waters as a strategy for identifying additional water supplies.

The RO process removes dissolved solids from feed water, including calcium and bicarbonate/carbonate ions. The resulting RO permeate will typically have unacceptably low levels of calcium hardness and alkalinity. Without additional treatment, the RO permeate would be unappealing aesthetically, poorly buffered against changes in pH, and aggressive to infrastructure components (especially metal pipes). Typically, pH adjustment and the addition of calcium and alkalinity to remineralize the permeate are required prior to distribution.

A corrosive RO permeate is "stabilized" to protect distribution pipelines, pump stations and storage tanks. Blending the RO permeate with the feed water is currently the most common approach used in the United States, for example, Chino Desalter in California, Kay Bailey

Hutchison Desalter in Texas, and The City of Sarasota Water Treatment Facility in Florida. However, this approach may be limited in many regions, including Texas, by feed waters that have high concentrations of nitrates, arsenic, radionuclides, or other regulated contaminants. It is the engineer's experience in each case to obtain feed water quality analysis and determine through mass balance if the bypass blending of feed waters and desalter permeate will exceed federal or state regulations when it comes to drinking water regulations. In situations where feed water bypass is not an option, dosing the permeate with multiple chemicals (for example, calcium chloride, lime, sodium bicarbonate) is possible, but may be complicated exceeding EPA Secondary MCL for chloride (250 mg/L) and sulfate (250 mg/L) concentrations when adding excess minerals into the permeate to achieve the desired water quality. Other challenges such as chemical overdosing/underdosing and storage could arise. An upflow calcite[2] contactor utilizes simple chemistry, avoids overdosing, and provides straightforward operation to maintain a stable permeate.

The use of upflow contactors is recognized in Europe and the Caribbean as an established method of post-treatment of RO permeate to provide a stable non-blended, non-corrosive, finished water. However, the rate of calcite dissolution depends on many parameters, including calcite characteristics and feed water quality. To date, a majority of the work on upflow calcite contactors has been performed outside of the United States using permeate from seawater desalination plants. Permeate from seawater desalination plants tend to have higher concentrations of dissolved solids in them that may affect the design of an upflow calcite contactor. Also, calcite characteristics (that is, impurities and available particle sizes) will vary from one region to another, and it is important to understand the available supply in and near Texas as those are the supplies that will be used there. This report will provide a summary of the state of the technology, a preliminary assessment of calcite sources in the United States, an evaluation of gaps in the available information, an analysis of results from pilot testing, and present cost estimates for conceptual full-scale upflow calcite contactor designs.

The following reference facilities currently provide remineralization of RO permeate using calcite contactors:

1.	Blue Hills Desalination Facility, Bahamas	7.2 MGD
2.	St. Martin (French) Desalination Facility	2.5 MGD
3.	Telde I Desalination Facility Canary Islands, Spain	3.5 MGD
4.	Telde II Desalination Facility Canary Islands, Spain	4.2 MGD
5.	Lldoregat Desalination Plant Barcelona, Spain	53 MGD
6.	Alicante II Desalination Plant , Spain	17 MGD

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[2] There are three polymorphs of calcium carbonate ($CaCO_3$) that exist in nature, including calcite, aragonite, and vaterite. Calcite is the dominant form of the mineral available on the Earth's surface. In this report calcium carbonate will be referred to as calcite.

2.1 Post-treatment water quality objectives

As mentioned previously, finished waters need to be stabilized so that they will not increase metal corrosion and concrete dissolution in water distribution pipelines (Birnhack et al., 2008, Lahav et al., 2007). Three parameters are considered to control the chemical stability of drinking water:

1. The buffering capacity of the water;
2. The tendency of the water to precipitate $CaCO_3$; and
3. The concentration of soluble calcium (Ca^{2+}) ions in the water.

A fourth parameter relevant to water quality stability is pH, which controls the previous three parameters. The apparent $CaCO_3$ equilibrium constant becomes lower as temperature increases and the ionic strength decreases. However, given the permeate temperature range of 25 to 27 degrees Celsius at the Kay Bailey Hutchison desalter, temperature effects on calcite dissolution is insignificant.

Several calculated indices are used in the water industry to determine acceptable ranges of alkalinity, Ca^{2+} concentration, and other water quality parameters to maintain acceptable water stability. Lahav et al. (2009) and Duranceau (2009) generally agree that alkalinity, Ca^{2+}, and calcium carbonate precipitation potential (at times replaced by the qualitative parameter Langelier Saturation Index) should be used for water stability control. These and other water stability indices are presented in more detail below.

2.1.1 Alkalinity

Alkalinity depends on the concentration of bicarbonate, carbonate, and hydroxide ions in the water. It provides a measure of the water's general acid buffering capacity. In other words, alkalinity is the ability of the water to withstand substantial changes in pH when an acid is added to it. The higher the alkalinity, the higher the ability of the water to withstand a change in pH. The Texas Commission on Environmental Quality (TCEQ) does not have a primary or secondary MCL for alkalinity. Rather, the need for it to be present in water is implied by other primary and secondary MCLs, including corrosivity, pH, lead, and copper restrictions.

The impact of alkalinity on other aspects of distributed water is more complex. Increasing the alkalinity generally leads to lower corrosion rates, but may also cause scale deposition in excess concentrations where calcium is present. Corrosion of metals, such as copper and lead, are dependent on the pH and dissolved inorganic carbon (DIC) of the distributed water. A higher alkalinity at a given pH results in a higher DIC, concentration of the carbonate species (CO_3^{2-}). However, excessively high alkalinity with high pH may accelerate copper metal release. It is desirable to maintain the alkalinity concentration in distributed water between 60 and 80 mg/L as calcium carbonate (mg/L as $CaCO_3$; D'Antonio et al., 2008). To control lead release, it has been found that maintaining an alkaline condition (*i.e.*, pH > 7) in the water is desirable.

2.1.2 Water hardness & calcium ion concentration

Hardness in water is an indicator of the overall concentration of divalent ions (calcium, magnesium, iron, etc.). Practically, it is typically calculated as the sum of the calcium and magnesium ionic concentrations in the water. While magnesium can be added to increase the hardness level in the water, calcium-based products are more commonly used and also conveniently represented in the water stability indices. The desired dissolved calcium ion concentration in distributed water typically ranges from 50 to 120 mg/L as $CaCO_3$ (Ramond, 1999). The lower limit is based on published guidelines by the World Health Organization for recommended calcium levels in drinking water to induce $CaCO_3$ precipitation and supplement the human diet (World Health Organization, 2004 and Birnhack et al, 2008). The upper limit is based on undesirable effects of calcium at high concentrations, including scale formation, “soap scum,” and taste effects. Similar to alkalinity, TCEQ does not have a primary or secondary MCL for hardness. Rather, the need for it to be present in water is implied by other secondary MCLs, such as corrosivity. The magnesium level in drinking water is not currently regulated by EPA. However, high concentrations (above 850 mg/L) of magnesium sulfate have been reported to have offensive tastes. The 2004 World Health Organization’s drinking water guideline (citation) published a recommendation for the addition of 90 mg/L of magnesium sulfate to distilled water for optimal taste.

2.1.3 Water stability indices

Although a number of corrosion indices have been developed, none has demonstrated the ability to accurately quantify and predict the corrosivity or aggressiveness of water. They can only give a probable indication of the potential corrosivity of water. For this reason, multiple indices may be used to evaluate the stability of finished water. The three most commonly used indices in the water industry, Langelier Saturation Index, Ryznar Stability Index, and Calcium Carbonate Precipitation Potential, are summarized in Table 2-1 and discussed in more detail below (Lahav and Birnhack, 2007).

The LSI provides a measure of the stability of water with respect to its degree of $CaCO_3$ saturation. The LSI is based on the difference between ambient water pH and pH that would exist when the water is saturated with calcium carbonate (pH_s):

$$LSI = pH - pH_s \qquad \text{(Equation 2-1)}$$

where

$$pH_s = (9.3 + A + B) - (C + D) \qquad \text{(Equation 2-2)}$$

$$A = (\text{Log}_{10}\,[TDS] - 1)/10 \qquad \text{(Equation 2-3)}$$

$$B = -13.12 \times \text{Log}_{10}\,({}^{o}C + 273) \qquad \text{(Equation 2-4)}$$

$$C = \text{Log}_{10}\,[Ca^{2+} \text{ as } CaCO_3] - 0.4 \qquad \text{(Equation 2-5)}$$

$$D = \text{Log}_{10}\,[\text{Alkalinity as } CaCO_3] \qquad \text{(Equation 2-6)}$$

If water has a negative LSI value, it is under-saturated with respect to calcium carbonate and is potentially corrosive. Conversely, for waters with a positive LSI value, a protective layer of calcium carbonate may form on the interior surface of pipes and other water distribution fixtures as the water is over-saturated with $CaCO_3$. Saturated water has a LSI of zero.

In practice, water is considered to be potentially aggressive if it has a LSI of less than zero. A primary disadvantage of relying on the Langelier Saturation Index is that it gives a thermodynamic prediction of the likelihood of calcium carbonate precipitation, but not the amount the amount of calcium carbonate that may precipitate.

Table 2-1. Comparison of various corrosion indices.

Index and Goal	Considered parameters	Features
Langelier Saturation Index (LSI > 0)	pH, temperature, calcium hardness, TDS, alkalinity	Does not account for chlorides, sulfates, or dissolved oxygen. Only accounts for $CaCO_3$ solubility. A qualitative parameter that indicates tendency to scale.
Ryznar Stability Index (RSI < 10)	Calcium and pH	An alternative to LSI. Also not suitable for estimating other calcium deposits such as calcium phosphates, calcium sulfates, magnesium silicates, or silica.
Calcium Carbonate Precipitation Potential (4 < CCPP < 10 mg/L as $CaCO_3$)	Alkalinity, calcium, pH, TDS, temperature	Indicates tendency and quantity of $CaCO_3$ scale, but ignores chloride and sulfates. More direct relation to the reaction kinetics of $CaCO_3$ precipitation than LSI.

Another related parameter is the RSI. Like the LSI, the RSI is also a qualitative assessment based upon the difference between ambient and saturation pH values.

$$RI = 2pH_s - pH \qquad \text{(Equation 2-7)}$$

Due to the difference in calculating the RI when compared to the LSI, different values are used to express the scale forming potential of water. With the RSI, values between 6.5 and seven (7) are considered to be near saturation equilibrium with calcium carbonate. The RSI value of water should be less than 10, in order for the water to be considered stable and non-corrosive.

The CCPP is a more reliable water stability index to use since it provides a quantitative measure of the calcium carbonate deficit or excess in the water, giving a more accurate guide as to the likely extent of $CaCO_3$ precipitation. Previously, CCPP has been less frequently applied because it is a lengthy iterative calculation. CCPP is a function of the ions in the water, the pH, and temperature. The American Water Works Association (AWWA 1996) released a PC-based spreadsheet program, the Rothberg, Tamburini and Winsor Model, which allows a quick calculation of a number of corrosivity indices, including CCPP, based on feed water quality inputs (for example pH, calcium, alkalinity, total dissolved solids). The program also allows calculation of the effects of various chemical additions, including $CaCO_3$, to water (Tetra Tech, 2008). However, despite the time saving abilities of the spreadsheet calculation, it does not provide an accurate simulation of a calcite contactor for design and operation purposes.

A simplified equation used to calculate the CCPP (Faust, 1998) is:

$$CCPP = 50{,}000\ (TALK_i - TALK_{eq}) \qquad \text{(Equation 2-8)}$$

Where: $TALK_i$ = initial total carbonate alkalinity
$TALK_{eq}$ = total carbonate alkalinity at equilibrium

Although a higher CCPP value indicates increased potential for formation of a denser, more effective passivation layer, too high of a CCPP will result in excessive buildup of $CaCO_3$ scale on pipes and pumping stations. The recommended finished water CCPP is 4 to 10 mg/L as $CaCO_3$, where a protective film of calcium carbonate on the pipe wall is formed, thereby preventing corrosion.

2.1.4 pH

pH is used to express the acid-base intensity of a solution. It is dependent on both temperature and ionic strength and, as presented above, has an important relationship with alkalinity and corrosivity in water chemistry. In general, lower pH values (acidic conditions) promote lead and copper corrosion, while higher values reduce the potential for metal corrosion/decomposition. Conversely, a pH in the range of 8 to 8.5 may promote iron corrosion and “red water” events. Based on the *Revised Guidance for Selecting Lead and Copper Control Strategies*, the United States Environmental Protection Agency (2003) recommends that utilities maintain pH greater than seven in their distribution systems. Concurrently, TCEQ has established a secondary MCL for pH at a value greater than seven. In addition, it is also important to note that sufficient alkalinity (acid buffer capacity) is necessary to maintain a stable pH and minimize changes in the corrosivity of a water throughout a distribution system. For the purpose of this report, a pH range of 7 to 8.5 will be considered acceptable.

2.2 Options for water remineralization

To increase the alkalinity capacity, minimize infrastructure due to corrosion, and improve aesthetics of the finished water, the RO permeate will require post-treatment remineralization. Water remineralization can be achieved by various methods. Generally, it is achieved by the following four treatment processes (Withers, 2005):

- Chemical addition – excluding lime or calcite;
- Blending with a water containing high mineral content;
- Carbon dioxide addition followed by lime (slurry) dosing; or
- Carbon dioxide addition followed by calcite contactor.

Table 2-2 provides a summary of each of the methods and its corresponding advantages and disadvantages. Further details for each post-treatment remineralization method are included in the subsequent sections.

Table 2-2. Summary of post-treatment water remineralization methods.

Option	Method	Advantage	Disadvantage
Chemical addition	Uses sodium bicarbonate, calcium chloride and calcium sulfate to add calcium hardness and alkalinity.	Straightforward chemical addition, based on simple dissolution of chemicals where handling of slurries or gases is not required. Low capital cost and required space.	$CaSO_4$ and $NaHCO_3$ have low solubilities and require large tanks to dissolve the chemicals. Both chemicals have a tendency to cake. $CaCl_2$ increases chloride concentration and can potentially exceed the chloride MCL.
Blending with water containing high mineral content	Blend permeate with feed water proportionately to achieve sufficient calcium and alkalinity concentrations.	Most economical approach.	Undesirable constituents in the water such as high color levels, radionuclides, heavy metals and excess organic matter may prevent blending . Further chemical addition may still be needed for pH adjustment. Additional treatment may be required depending on blend source.
CO_2 addition followed by lime dosing	Lower permeate pH by adding CO_2 and dissolving lime slurry to introduce calcium and alkalinity.	Lime is relatively economical and readily available.	Potential deposition of lime in the piping and injection equipment. Lime is corrosive and injection of slurry may increase finished water turbidity significantly. Also requires more O&M. Difficulties in maintaining consistent product water pH.
CO_2 addition followed by calcite contactor	Lower permeate pH by adding CO_2 and dissolving calcite to introduce calcium and alkalinity.	Calcite is not corrosive and more operator-friendly compared to lime. Calcite dissolution is more efficient than lime.	Calcite dissolution typically requires sodium hydroxide (NaOH) addition for final pH adjustment. Calcite contactors require additional plant footprint.

2.2.1 Chemical addition – excluding lime or calcite

Two chemical addition methods can theoretically introduce calcium hardness and alkalinity to permeate water. Each is presented in more detail below.

Sodium bicarbonate ($NaHCO_3$) and calcium sulfate ($CaSO_4$) addition is one possible chemical addition method, as shown in Equation 2-9.

$CaSO_4 + 2\ NaHCO_3 \rightarrow Ca(HCO_3)_2 + Na_2SO_4$ (Equation 2-9)

This method is not generally practiced since calcium sulfate (gypsum) has low water solubility. Large tanks would be required to dissolve the chemicals. Furthermore, sodium bicarbonate is very costly and has a low solubility. The storage of both chemicals is challenging because they have a tendency to cake in the presence of moisture. Using this method for remineralization is not adequate for pH adjustment, so other chemicals such as hydroxide addition would be required, adding unnecessary total dissolved solids to the finished water.

Calcium chloride ($CaCl_2$) and $NaHCO_3$ addition can also be used to introduce hardness and alkalinity to the water, as shown in Equation 2-10.

$CaCl_2 + 2\ NaHCO_3 \rightarrow Ca(HCO_3)_2 + NaCl$ (Equation 2-10)

Similar to the previous method, pH correction using acids and bases will be required. This method will increase the chloride concentration in the water, and could potentially elevate the chloride concentration above the limit for drinking water (250 mg/L secondary standard).

2.2.2 Blending with a saline feed water

A cost-effective option for post-treatment stabilization of RO permeate is to blend it with the feed water at a proportion that achieves a sufficient level of calcium hardness and alkalinity in the finished water. However, undesirable constituents in the feed water, such as elevated color levels, radionuclides, heavy metals, excess organic matter, or nutrients may prevent such an approach. In feed waters containing high levels of these constituents, only partial remineralization may be achieved by blending feed water with the desalinated permeate. Additional chemicals may still be necessary to stabilize the water for distribution.

2.2.3 Carbon dioxide followed by lime slurry treatment

In this method, the pH of the treated water is lowered via CO_2 addition. Lime ($Ca(OH)_2$) slurry is pumped into the water to introduce the required hardness and alkalinity, as shown in Equation 2-11.

$2CO_2 + Ca(OH)_2 \rightarrow Ca^{2+} + 2HCO_3^-$ (Equation 2-11)

Users of conventional lime slurry or lime powder systems face the difficulty of handling the powder or the formation of scale and deposition of calcium in the injection equipment. Piping systems to convey the lime should be kept as short as possible to prevent settling and scaling of the lime in the pipe. Lime is a corrosive chemical and therefore less operator-friendly than calcite

(Shih, 2006). In addition, the use of this method may increase the turbidity of the finished water to as high as five nephelometric turbidity units (NTU) due to increased particle carryover.

2.2.4 Carbon dioxide addition followed by calcite contacting

In the absence of suitable and sufficient feed water for blending, chemical dosing or lime/calcite dissolution by CO_2 will be needed. However, chemical dosing systems may suffer from residual turbidity, maintenance problems, high operational costs, and introduction of unwanted chlorides to the finished water. A calcite contactor pretreated with CO_2 may provide simpler and more cost-effective alternative to remineralize desalination permeate stream. Figure 2-1 shows a typical schematic of the calcite contactor for post-treatment in a RO desalination plant.

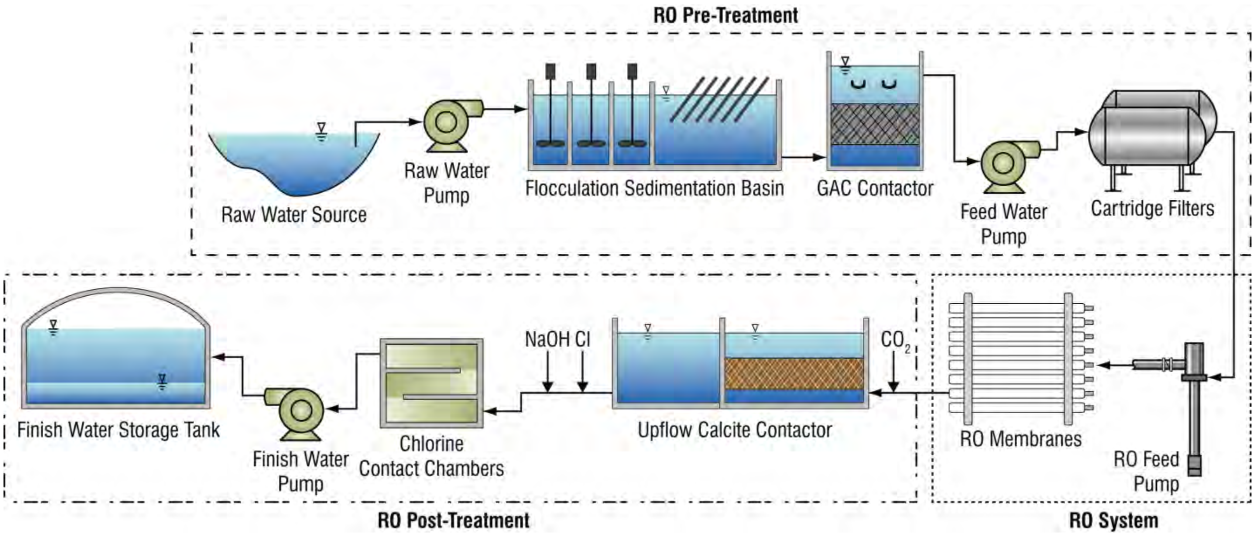

Figure 2-1. Schematic of calcite contactors as RO post-treatment in a desalter.

Under normal conditions, $CaCO_3$ is only slightly soluble in water. However, its dissolution in water can be enhanced in acidic conditions. The use of CO_2 for this purpose is advantageous because it will both lower the pH and convert to alkalinity as the calcite raises the pH of the water. When CO_2 is added to water, the acid equivalent of CO_2 in water, carbonic acid (H_2CO_3) is formed, which is regularly used in soft drinks. Figure 2-2 illustrates the proportion of available H_2CO_3 as a function of pH in the water.

In calcite dissolution by CO_2, the first step is the carbonic acidification of the water, shown in Equation 2-12.

$$CO_2 + H_2O \rightarrow H_2CO_3\ (aq) \qquad \text{(Equation 2-12)}$$

Calcite will then react with the carbonic acid as indicated in Equation 2-13.

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Equation 2-13)}$$

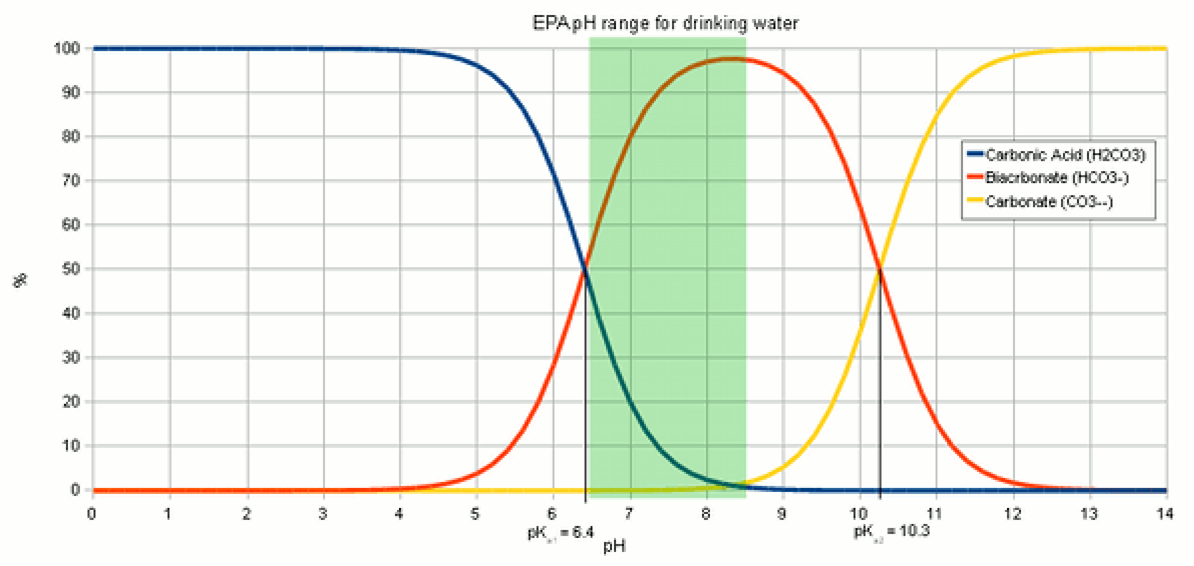

Figure 2-2. Proportion of H_2CO_3 available as a function of pH in the water.

Compared to lime dissolution, calcite is generally more efficient because it requires half the CO_2 to achieve a certain alkalinity or calcium concentration, as demonstrated in Equations 2-11 and 2-12. For this reason, calcite was selected as the remineralization method for further testing.

In addition to a calcite contactor, OMYA (a global producer of industrial minerals, including calcium carbonate and dolomite) has introduced a calcite slurry injection system for water remineralization. The OMYA remineralization process is performed by adding a slurry of micronized (0.2- to 25 -µm) calcium carbonate into desalinated water previously acidified with CO_2. This method is more cost-effective due to using calcite instead of lime. However, turbidity carryover from slurry pumping is still a risk.

3 Literature review

3.1 Calcite contactor process

In a calcite contactor, water flows through a bed of crushed, sieved calcite. The water flowing through the calcite contactor tank dissolves carbonate minerals from the calcite packed bed until the pH nears equilibrium with the calcium carbonate (Robinson et al., 2005). Dissolution of calcite (calcium carbonate) increases the pH, alkalinity, and dissolved inorganic carbon concentrations in the water. The components of a contactor include a contact tank, calcite bed, inlet/outlet line, overflow line, access lid (for a closed system contactor) and a flush outlet line. Figure 3-1 shows a schematic of a typical calcite contactor. Equilibrium conditions depend on the flow velocity and initial water characteristics (pH, CO_2 content, calcium, alkalinity, total dissolved solids, and temperature.)

As calcite dissolves, particle size, bed depth, bed porosity, flow velocity and pressure drop in the contactor change with time. During the dissolution process, as the calcite bed height diminishes the driving force for dissolution decreases, and the rate of the dissolution reaction decreases proportionally. Thus, the calcium concentration in the contactor feed water can approach the equilibrium concentration, but never exceed or equal it. Calcite will be added to the contactors periodically to replenish dissolved media, and in doing so, steady state conditions cannot be achieved because the calcite particle size distribution continues to widen. In doing so, the resulting effluent will usually be slightly less than the saturation point (i.e., slightly negative LSI), and to bring about a slightly positive LSI and a CCPP of 4-10 mg/L as $CaCO_3$, some caustic soda dosing is required to raise the final effluent pH.

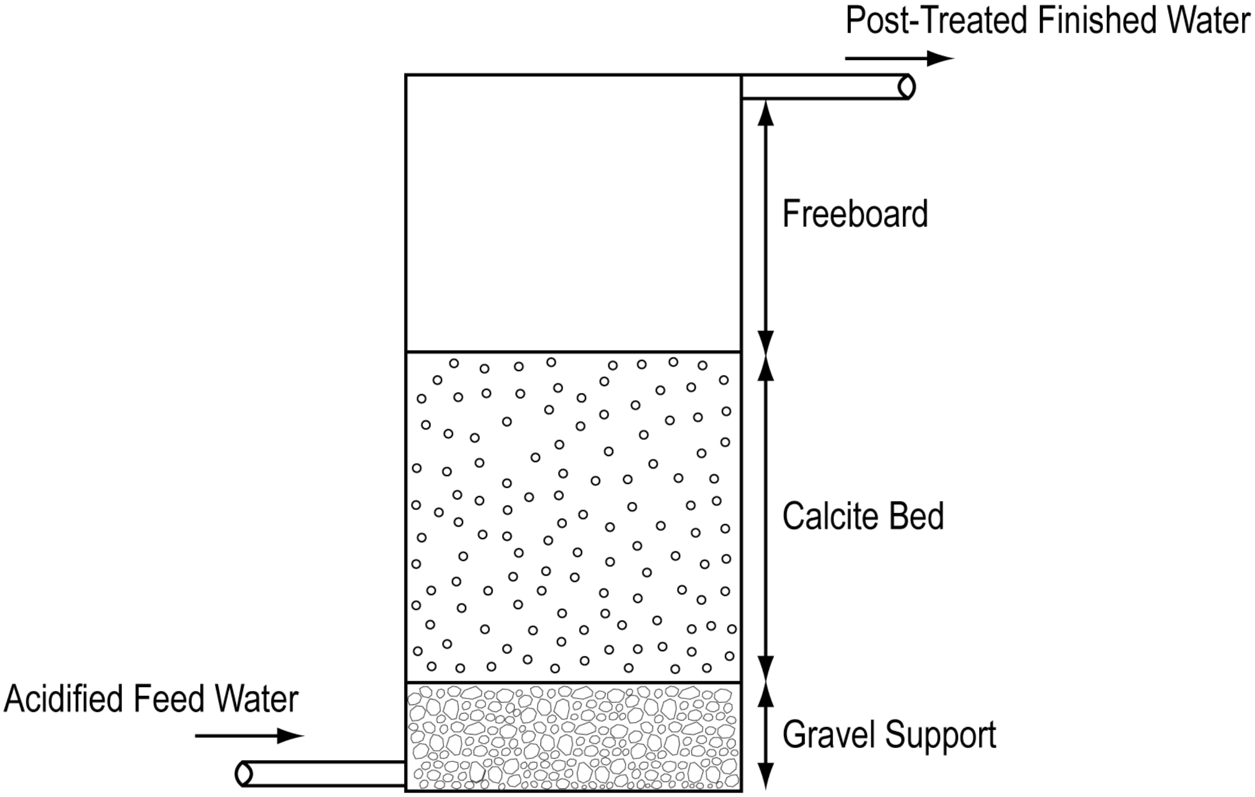

Figure 3-1. Schematic of a calcite contactor.

Traditionally, sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) has been used in water treatment facilities to control pH, and therefore, affects the water alkalinity. The chemical reaction for sulfuric acid and calcite is as follows (Hernandez-Suarez, 2005):

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad \text{(Equation 3-1a)}$$

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \qquad \text{(Equation 3-1b)}$$

As seen in Equation 3-1a, the products of reacting calcite and sulfuric acid are gypsum, carbon dioxide, and water. When hydrochloric acid is used (Equation 3-1b), the products are calcium chloride, carbon dioxide, and water. The produced carbon dioxide will then react with more calcite to form dissolved calcium and bicarbonate to introduce hardness and alkalinity to the water, as shown in Equation 3-2.

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Equation 3-2)}$$

By combining both reactions, the overall chemical reaction is represented by:

$$2CaCO_3 + H_2SO_4 \leftrightarrow CaSO_4 + Ca(HCO_3)_2 \qquad \text{(Equation 3-3a)}$$

$$2CaCO_3 + 2HCl \leftrightarrow CaCl_2 + Ca(HCO_3)_2 \qquad \text{(Equation 3-3b)}$$

From Equation 3-3, it is evident that $CaSO_4$ and $CaCl_2$ are formed as a byproduct of these reactions. In Equation 3-3a, the calcium ions that could be otherwise freed into solution to add hardness are now in the form of an insoluble precipitate that can potentially increase the turbidity of the finished water and settle at the bottom of the finished water tanks. In Equation 3-3b, excess chloride ions are added into the finished water which can potentially exceed drinking water regulations. Instead of a one-step process where the CO_2 reacts with the calcite (Equation 3-2) to produce the needed dissolved calcium and bicarbonates, using sulfuric acid will lead to an additional step to produce CO_2, followed by the CO_2 reacting with the $CaCO_3$. Moreover, sulfuric acid is extremely hazardous and requires special materials for equipment and piping. Hydrochloric acid is also extremely hazardous and very corrosive, also requiring special handling. Maintenance of the system can require frequent component repairs and replacement if not properly designed. CO_2, on the other hand, is comparatively safe to handle, easy to apply, and efficient. CO_2 has an ACGIH (American Conference of Governmental Industrial Hygienists) Threshold Level Value (TLV) time-weighted average of 5,000 parts per million (ppm by volume) and a TLV-Short Time Exposure Limit of 30,000 ppm (by volume). However, CO_2 gas from storage tanks is introduced directly to the water to form carbonic acid; safety measures, such as CO_2 gas leak detectors, pressure relief valves and piped lines to the atmosphere, are built in the design. Typically, solution feed panels are situated outdoors, which minimizes unaccountably high gas leakage into the atmosphere for CO2 to be harmful to operators. For this study, CO_2 is used to acidify the permeate.

3.2 Parameters in calcite contactor design

Dissolution of calcite is a dynamic process, which may be enhanced or inhibited depending on the contactor design and influent water quality. These two groups of factors are presented in more detail below. This section will discuss the parameters relevant for calcite contactor design, cite design examples of existing upflow calcite contactor facilities worldwide, and present the relevant findings from literature. The summary and discussion of the design parameters and how they relate to this project's pilot design are presented in Section 4.0.

3.2.1 Contactor design factors

As $CaCO_3$ dissolves, the superficial velocity, particle size, calcite contactor bed height, bed porosity and pressure drop in the contactor change. In a poorly designed contactor, dissolution takes less time for the calcite to reach the recharge level and it needs to be refilled more frequently. This affects the contactor performance and the operating cost. These contactor design factors are discussed in detail below.

3.2.1.1 Superficial velocity or loading rate

The fluid flow rate through the contactor divided by the cross sectional area is defined as the superficial (or empty tube) velocity. It is also known as the *loading rate* of the contactor. Typical units for superficial velocity are gpm/ft^2 or ft/min. Researchers at the Canary Islands Water Center published guidelines for upflow calcite contactor design for large seawater desalination plants (Hernandez, 2005) using 1-3 mm calcite particles and established that optimum superficial velocities ranged from 1.05 to 1.20 ft/min for a 28 MGD plant. At the 18 MGD Alicante II plant and the 53 MGD Barcelona plant in Spain, the design superficial velocities were 0.48 and 0.67 ft/min, respectively.

South African researchers, who developed the upflow SprayStab II reactor at Stellenbosch, used calcite particle sizes that ranged from 11-14 millimeters; they also recommended that the superficial velocity be kept below 0.55 ft/min (Carmical et al., 2002). In Mars Hill, Maine, the 0.3-MGD upflow calcite contactor uses 25 mm calcite particles and has a design superficial velocity of 0.13 ft/min. For the Blue Hills plant in the Bahamas, 1-mm calcite particles were used, and the design superficial velocity was 0.56 ft/min. Table 3-1 summarizes the calcite particles and the design superficial velocities used for the cited examples.

Table 3-1. Design superficial velocities for calcite contactors from referenced studies.

Reference site	Plant size (MGD)	Superficial velocity (ft/min)	Calcite particle size (mm)
Alicante II, Spain	18	0.48	1-3
Barcelona, Spain	53	0.67	1-3
Blue Hills, Bahamas	3.6 (50 percent of plant flow treated)	0.56	1
Stellenbosch, South Africa	38	0.55	11-14
Mars Hill, Maine	0.3	0.13	25

According to pilot studies conducted in Spain and Canary Islands (Hernandez et al., 2009), fine particles from calcite beds, which are dragged upstream, can affect the turbidity of the effluent. According to Environmental Protection Agency's Surface Water Treatment Rule (SWTR), at no time can turbidity exceed above 5 NTU. Water treatment via filtration systems must ensure that the turbidity go no higher than 1 NTU (0.5 NTU for conventional or direct filtration) in at least 95 percent of the daily samples for any two consecutive months. Even though brackish groundwater treatment systems are not subject to the (SWTR) as long as they are not under the direct influence of surface water, this is a useful guideline when adding chemicals that may increase the turbidity of a distributed water. The relationship between superficial velocity and turbidity depends on the quality of the calcite. If too many fines (< 80 micrometer) are present in the calcite, turbidity is a source of concern. Figure 3-2 illustrates the typical relationship that exists between turbidity and superficial velocities in DrinTec™ contactors for calcite with less than 1 percent fines and with 2-3 percent fines.

For well-washed calcite (less than one percent of fines), turbidity started to increase slowly at 14 - 15 meters per hour (m/hr) or 0.76 - 0.82 ft/min. If the fines were within three percent, turbidity started to increase at around 11-12 m/hr (0.60 - 0.66 ft/min).

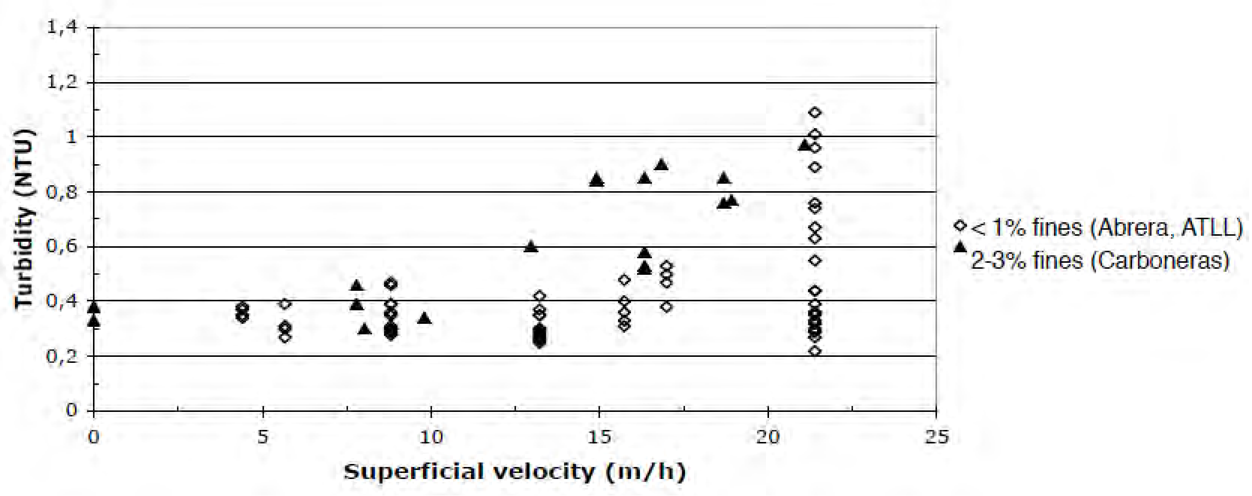

Figure 3-2. **Relationship between superficial velocity (meters per hour) and turbidity (Hernandez et al., 2009).**

3.2.1.2 Empty bed contact time

EBCT is defined as the measurement of the duration of contact between water and the media through which it is flowing and is calculated using Equation 3-4.

$$EBCT = \frac{V_B}{Q} \qquad \text{(Equation 3-4)}$$

Where *EBCT* is the empty bed contact time, V_B is the volume of calcite in the contactor, and *Q* is the flowrate. For a calcite contactor, it is important to allow adequate contact time in a calcite bed to achieve calcium carbonate saturation. However, the rate at which this saturation occurs will depend on several parameters, including temperature, calcite particle size, calcite purity, and alkalinity of the feed water. The impact that each of these parameters has on calcite dissolution rate and EBCT is presented in Section 3.2.2. In general, developing an EBCT is a first step in designing an upflow calcite contactor. As part of this process, the parameters that influence the EBCT need to be understood for each situation.

A compilation of the reported EBCTs from case studies where target water quality was achieved is summarized in Table 3-2.

Table 3-2. Design empty bed contact time for calcite contactors from referenced studies.

Reference site	Initial alkalinity (mg/L as $CaCO_3$)	Empty bed contact time (minutes)	Calcite particle size (mm)	Temperature (°C)
Alicante II, Spain	4.2	11.0	1-3	19
Barcelona, Spain	3.07	12.2	1-3	13-27
Blue Hills, Bahamas	1	3.6	1	25
Stellenbosch, South Africa	18 – 22.5	≥ 20	11-14	25
Mars Hill, Maine	45-83	30	25	Not reported

3.2.1.3 Calcite contactor bed height

The selection of a superficial velocity (cross-sectional area of the contactor) and an EBCT (see above) will determine the volume of the calcite bed. An assumption for the cross sectional area of the contactor will need to be made based on available equipment. From these criteria, the height of the bed depth will be determined. A height for the water distribution zone above the bed depth is considered in the design of the contactor. A minimum clearance height of 10 inches is recommended by South African researchers Mackintosh et al. (2002). For the Barcelona calcite contactor pilot testing, a distribution height of approximately 12 inches was accounted for in the calcite contactor (Hernandez et al., 2009).

During operation, headloss through the contactor will depend on the superficial velocity and particle size. In general, the headloss will increase as the particle size decreases and/or the superficial velocity increases. The relationship between superficial velocity and size of calcite particles ranging between 2 and 2.5 millimeters is presented in Figure 3-3 for an upflow calcite contactor treating permeate from a seawater desalination plant (Hernandez et al., 2009).

As an example, the estimated head loss extrapolated from the above correlation is 43 centimeters per meter of bed for an average superficial velocity of 34.7 centimeter per minute. For a bed height of 1.55 meters (m), the estimated head loss would be $1.55 \times 0.43 = 0.66$ m. The total height of the contactor designed is the sum of the height of the calcite bed, water distribution clearance and the headloss.

3.2.1.4 Calcite particle size and purity

Particle size affects the contact surface area and therefore the contactor performance. As particle size increases, the contact surface area with the water decreases, and hence a longer EBCT is required to reach equilibrium. Only one published study reported the effect of particle size on the height of the calcite bed (Hernandez, 2005). The relationship was obtained by the calcite dissolution model developed by Letterman and Kothari (Letterman, 1995) and is specific to the water quality of the influent feed water.

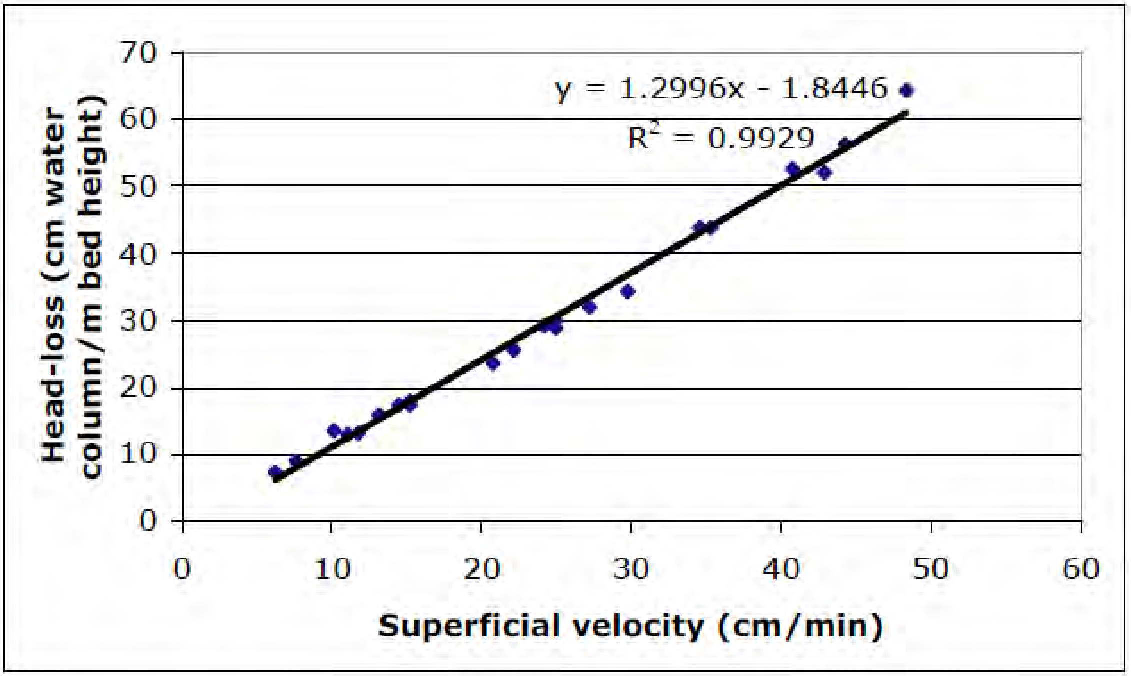

Figure 3-3. **Head loss of the upflow calcite bed for particle sizes between 2.0 and 2.5 mm (Hernandez-Suarez, 2005).**

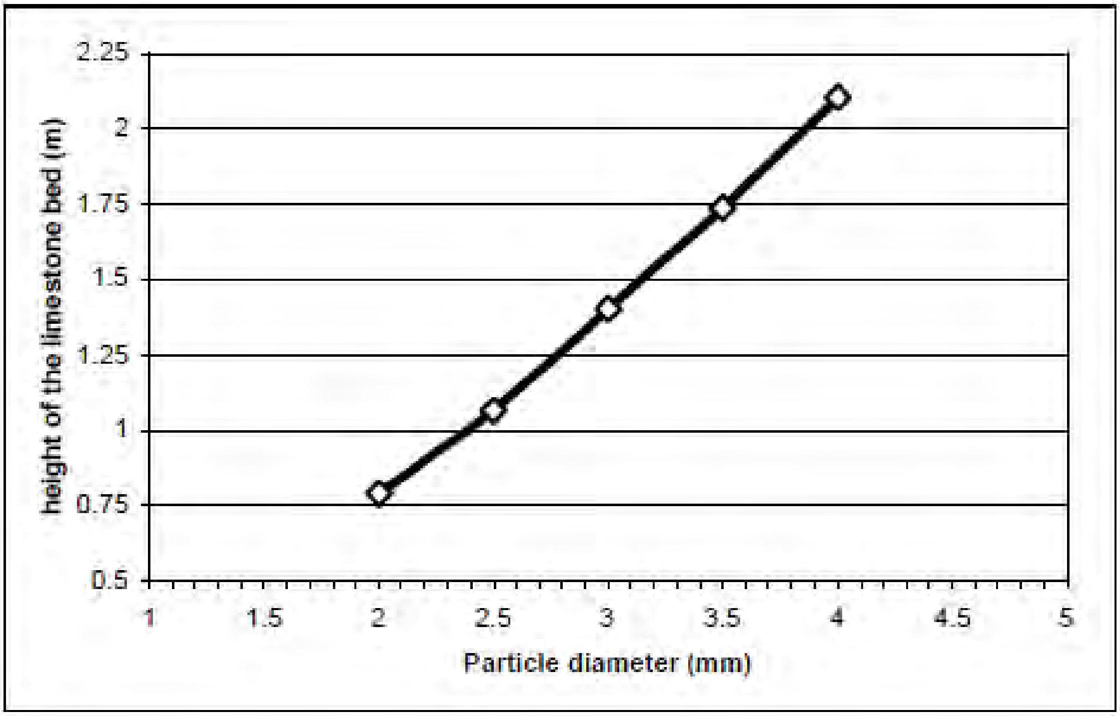

Figure 3-4. **Example of relationship between particle diameter and calcite bed height (Hernandez, 2005).**

The rate of calcite dissolution in the contactor is determined by the physical and chemical characteristics of the calcite, including the type and the amount of impurities in the mineral composition. A limestone selection criteria study for electrodialysis reversal (EDR) water remineralization used five different calcite samples with purities ranging from 92.8 to 99.6 percent (Ruggieri et al., 2008). Table 3-3 summarizes the properties of the calcite samples used.

Table 3-3. Properties of calcite samples used in the Ruggieri et al. (2008) study.

Sample identification	% $CaCO_3$ purity	Particle size (µm)	% MgO	% Al_2O_3	% Fe_2O_3
L1	98.3	< 5	0.20	0.04	0.03
L2	97.9	< 20	0.35	0.25	0.12
L3	99.6	< 5	0.36	0.02	0.01
L4	92.8	> 100	3.26	0.15	0.25
L5	97.5	> 100 with < 5 fines	0.55	0.43	0.26

The authors used effluent water conductivity as a surrogate for dissolution of the five calcite samples as presented in Figure 3-5. Compared to smaller calcite particles with low dolomite content (L1), the larger calcite particles with higher dolomite content (L4) had lower surface areas for water-calcite contact. This, combined with their higher impurity content, decreased the calcite dissolution. However, conclusive results cannot be made whether the calcite particle size or the impurity content had more impact on the slower rate of calcite dissolution. Between L1 and L3, where both calcite samples had high percentages of calcite purities, the higher magnesium content in the L3 sample appeared to have a pronounced decrease in calcite dissolution, and hence, the conductance of the finished water. This suggests that additional contact time may be needed for calcites containing high concentrations of impurities.

3.2.2 Influent water quality factors

Aside from the calcite itself, the characteristics of the water will also affect the rate at which the dissolution occurs. Dissolution of calcite will increase the pH, alkalinity, and concentration of dissolved inorganic carbon in the feed water and deplete the calcite in a bed. The effects of influent water characteristics, such as calcite saturation level, pH, temperature and ionic strength, and feed water impurities, are discussed in the subsequent sections.

3.2.2.1 Calcite saturation level

Dissolution will occur only if the water is under saturated with $CaCO_3$. Initial water quality analysis (e.g., calculation of the LSI) will provide an indication of the initial level of saturation. If the LSI is greater than or equal to zero, the water will not accept more $CaCO_3$. Recommended calcium levels in the influent should be less than 60 mg/L, and the alkalinity should be less than 100 mg/L as $CaCO_3$ (Carmical et al., 2002). This recommendation is not expected to be an issue with permeate from brackish desalination, but may need to be accounted for when bypass blending is used to partially remineralize the permeate.

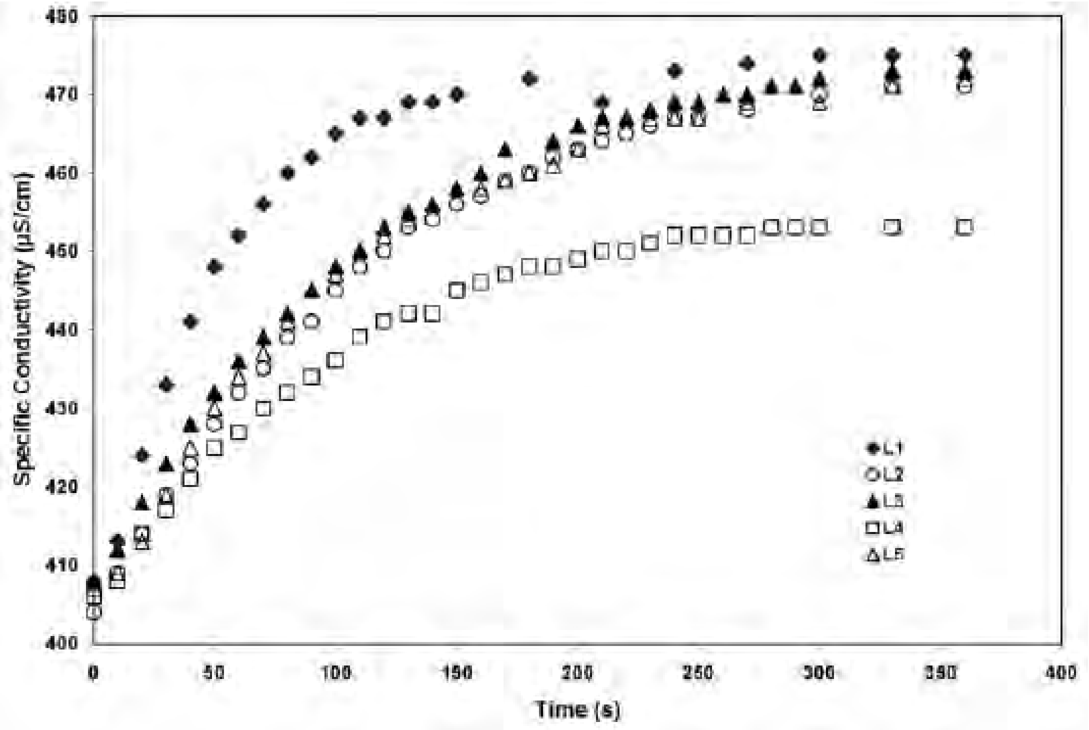

Figure 3-5. **Variation of specific conductivity with contact time with calcite samples L1 to L5 (Ruggieri et al., 2008).**

3.2.2.2 pH level

For the case studies referenced in this report, the influent pH of the water is usually slightly acidic and ranges from five to slightly less than seven. Between a pH of five and six, the water contains mostly carbonic acid, which is what is needed to react with calcite to produce bicarbonates and calcium for added alkalinity and hardness. Practically, when the influent pH is near neutral (pH 7.2), acidifying with CO_2 is desired to shift the pH of the influent to a value of six. This is corroborated by Yu et al. (2008), in which he found that low pH favors calcite dissolution.

3.2.2.3 Temperature and ionic strength

As the temperature and ionic strength of the water increases, the dissolution rate generally increases as well (Rickard et al., 1983). Yu et al. (2008) performed calcite dissolution studies by varying pH and temperature and determined that low pH and high temperature favor calcite dissolution (Yu et al., 2008).

Hernandez et al. (2009) developed an empirical relationship between EBCT and temperature to reach pH 8.2 in the contactor effluent for a feed water with 50-200 mg/L total dissolved solids and 23 milligrams per liter (µg/L) added CO_2 (Figure 3-6). The relationship was based on data from seawater desalination plants in the Canary Islands and Spain. The authors did not explain the origins of the equation, but it appears to be a best-fit regression line using a power function.

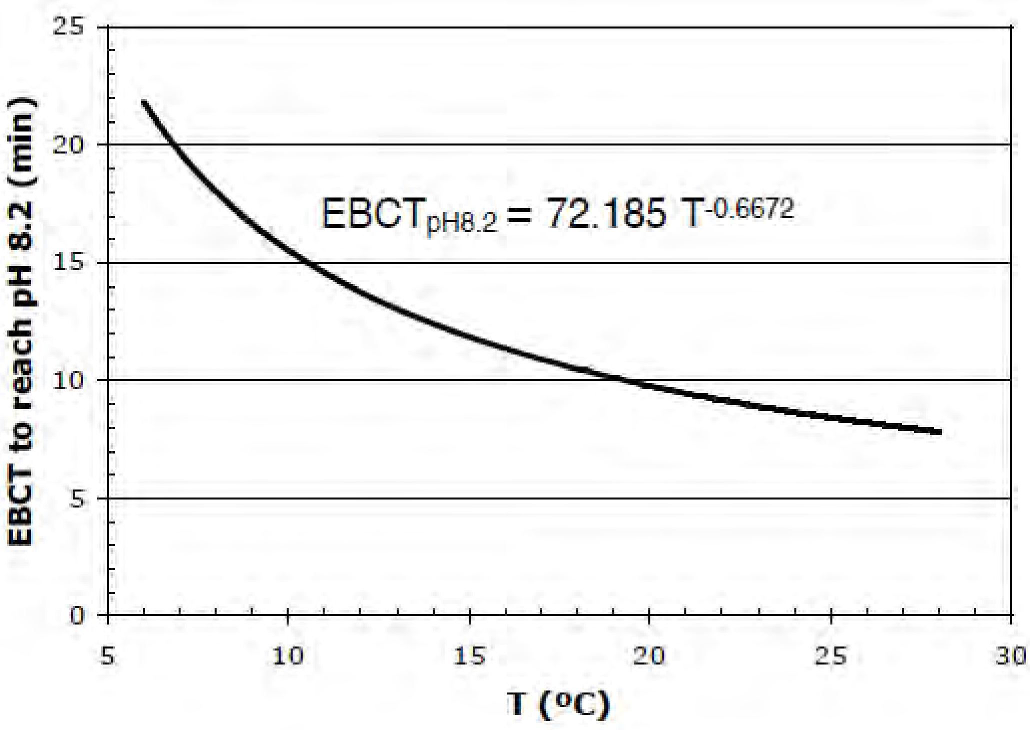

Figure 3-6. Empirical relationship between empty bed contact time required to reach pH 8.2 and temperature for permeate water with a dose of 23 mg/L CO_2 (Hernandez, et al., 2009).

3.2.2.4 Metals in Feed water

Permeate from brackish desalination is expected to have very low metals concentration, in which case they will be of no concern for using a calcite contactor. However, if the permeate is partially remineralized using bypass blending, this may introduce metals that may have a negative effect on calcite dissolution. For example, in the presence of ferrous iron, Fe(II), dissolution of calcite is inhibited due to precipitation of iron oxides on the calcite surface under alkaline pH conditions (Maree et al., 2000).Carmical et al. (2002) developed a list of recommended levels of metals and turbidity for feed water entering a calcite contactor:

- Iron levels in the feed water must be < 0.2 mg/L.
- Manganese levels should be < 0.05 mg/L.
- Aluminum levels should be < 0.05 mg/L.
- Influent turbidity should be < 1.0 NTU.

3.3 Types of calcite contactors

Calcite contactors are typically located at the end of a treatment train–after filtration, primary disinfection, and the clearwell. By placing a contactor at the end of the treatment process, the pH is maintained at a low level for effective chlorination. However, there are some systems where contactors are located after filtration and before chlorine addition. These are mostly located in Germany (Carmical et al., 2002). The reason for placing contactors before chlorine addition is because disinfection is not required in most calcite contactors in Germany, especially if the plants are treating high quality spring water that contains very low turbidity (less than 0.1 NTU) and coliform counts.

There are two types of calcite contactors available: upflow and downflow. Both types of contactors are based on the same operation principle, i.e., allowing water and media into contact for calcite dissolution to add calcium hardness and alkalinity to the water. Variations in the process configurations have their own advantages and disadvantages, which are summarized in Table 3-4. Downflow calcite contactors are typically used in small installations, and are mostly pressurized systems. Operation of downflow contactors require frequent calcite replenishment in order to maintain a constant bed height, as well as frequent backwashing to eliminate the fine particles from each calcite loading event. When a newly replenished contactor is brought online, backwashing is required to eliminate carryover of fine particles. The backwash waste stream generated will require an additional particle removal process prior to disposal into the sanitary sewer. Upflow calcite contactors minimize turbidity problems by not requiring the intermittent turbidity surges during the backwash process, and are favored in large installations. In upflow contactors, since no backwashing is required, dealing with a waste stream is a not an issue. Thus, the focus of this report is on upflow contactors, after reviewing the advantages and disadvantages for both upflow and downflow contactors as listed in Table 3-4.

3.3.1 Council for Scientific and Industrial Research type upflow contactors

The sidestream stabilization process is a process developed by researchers at the Council for Scientific and Industrial Research in South Africa to enable stabilization of water using calcite contactors in large water treatment plants (Tsotsi, 2001; Daniels et al., 2002). The process consists of taking a sidestream of unstabilized water, dosing it with carbon dioxide to lower the pH, and then contacting it with calcite (De Souza et al., 2002). The remaining CO_2 is recovered by air stripping and reused in the process. The stabilized sidestream is blended with the remaining product flow. A simplified sidestream stabilization process may also be used. This process is similar to the sidestream stabilization process with the exclusion of CO_2 recovery.

The Spraystab technology, another process developed at the Council for Scientific and Industrial Research, combines aeration, calcite stabilization and filtration in one tank (Mackintosh et al., 2001). This process is suited for water that may contain iron and manganese. In groundwater where iron and manganese exceed 0.2 mg/L and 0.05 mg/L respectively, the water is aerated to strip excess CO_2 and dissolved oxygen before entering the calcite contactor. After the water is remineralized, it then flows through a dual media filter to remove insoluble matter such as iron and manganese flocs. For groundwater that does not require iron and manganese removal, the multi-media filtration step is excluded and the water enters the bottom of the calcite bed. As seen in Figure 3-7, raw water passes through a false bottom (or a slotted pipe distribution manifold) and percolates in an upward flow direction through a fixed calcite bed. The undersaturated feed water will dissolve the calcium and carbonate upon exposure to the calcite particles in the contactor bed.

Table 3-4. Advantages and disadvantages of upflow and downflow contactors.

Contactor Type	Advantages	Disadvantages
Downflow	In addition to calcite dissolution, media also acts a sediment filter - therefore suitable for water containing sediments. Backwash cycle cleans calcite media and prevents rust particles and other sediment from fouling or coating the media. Calcite is prevented from leaving the filter tank due to the bottom internal distributor screen.	Requires automatic or manual backwash cycles to clean calcite media and interrupt operation. Higher capital and O&M costs. Potentially higher headloss due to calcite media compaction. Longer downtime during media replenishment. Startup waste streams contain high turbidity effluents.
Upflow	No backwash required because media is not compacted. Suitable for flow that is constant and low in iron and sediment content. Less expensive on a capital cost basis. Lower headloss experienced. Effluent turbidity is typically lower.	Requires internal top screen to prevent calcite from blowing out of contactor. Calcite particles that escape into the plumbing system can damage valves and fixtures. If water contains high levels of iron, manganese, or sulfides, internal top screens can become fouled. Flow rates have to be properly controlled to avoid water channels from developing and to reduce effluent turbidity, which minimizes contact with calcite media.

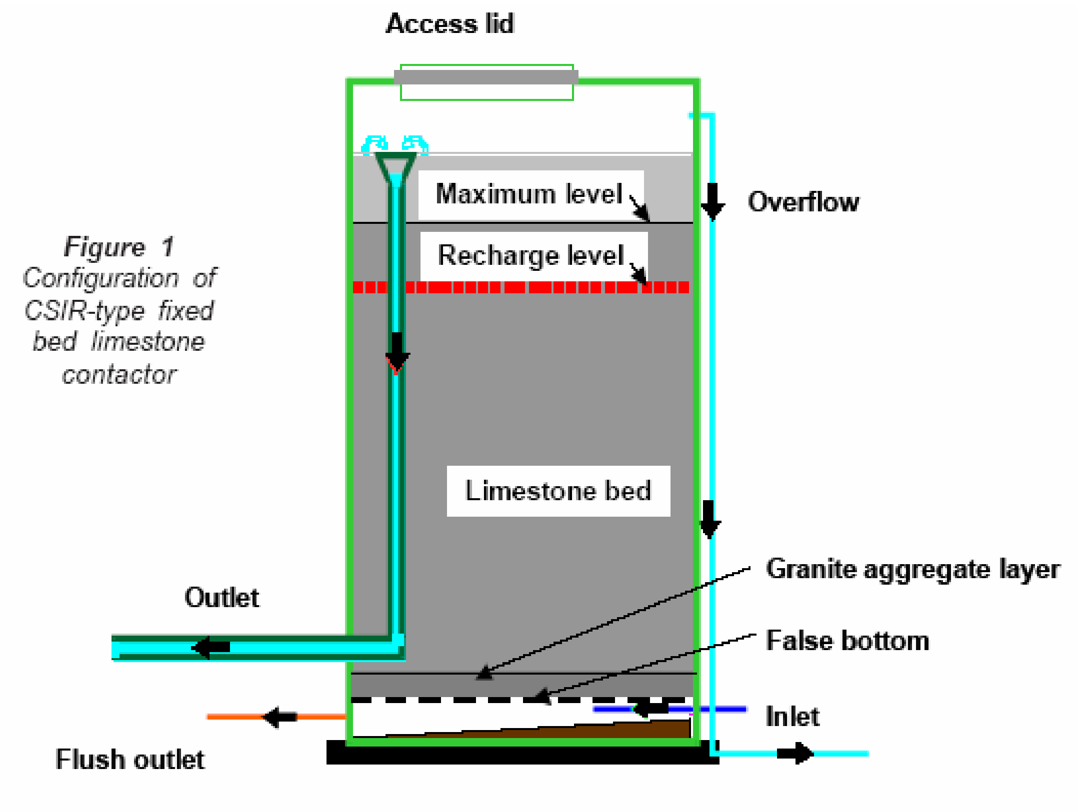

Figure 3-7. **Simplified configuration of a Center for Science and Industrial Research -type fixed bed limestone contactor (Mackintosh et al., 2001).**

3.3.2 Fluidized fixed bed limestone contactor

The fluidized fixed bed limestone contactor, also known as teeter bed reactor or hindered bed reactor, is still in the pilot testing stage (Batson, 2008 and Sibrell et al., 2006). A teeter bed is a type of packed bed reactor in which the upflow velocity is just high enough to fluidize the bed. This state occurs when the upward force exerted by the fluid on the particles is just sufficient to balance the net weight of the bed, and the calcite particles begin to separate from each other and float in the fluid. The idea behind a fluidized calcite contactor design is to jostle the particles constantly so that adhering impurities in the calcite would be dislodged to facilitate optimal calcite dissolution. The fluidized calcite contactor is generally built in three sections: a reservoir section at the bottom, which is normally cylindrical in shape and holds the coarsest and heaviest particles, a conical middle bed, and a cylindrical elutriation section, as shown in Figure 3-8.

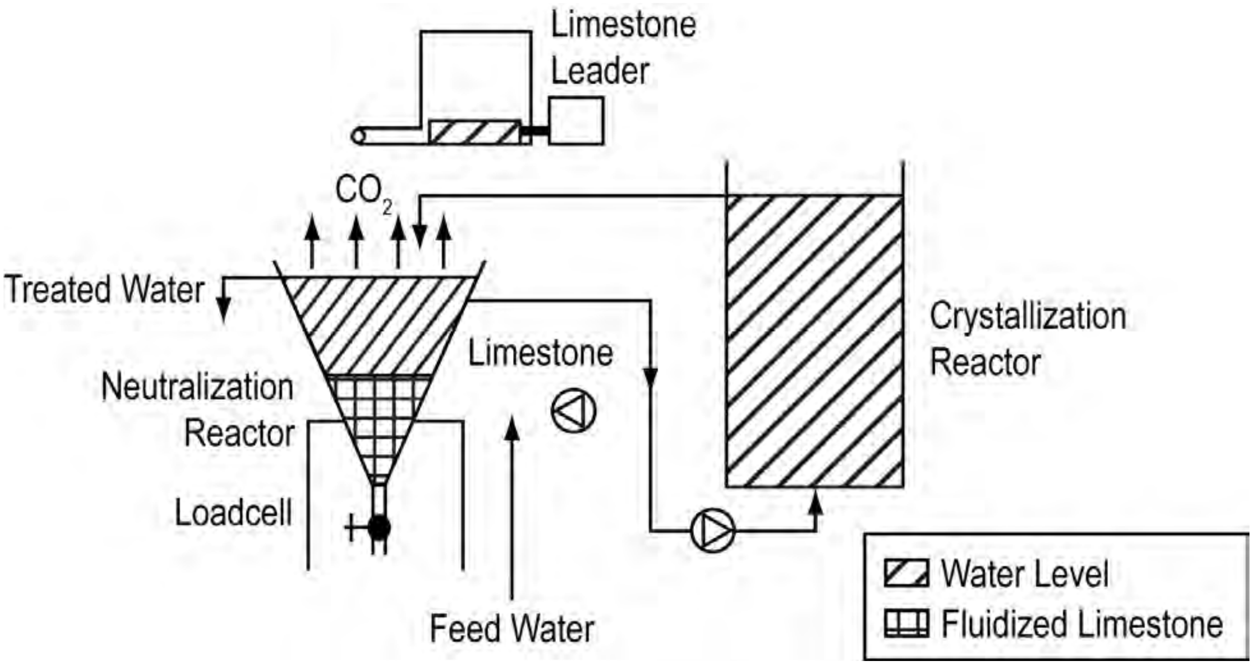

Figure 3-8. Schematic of a fluidized calcite contactor (Batson, 2008).

3.3.3 Constant height DrinTec^{TM} upflow contactors

Conventional upflow calcite contactors have been in use for many years for recarbonating soft waters, but a number of challenges from operating the traditional designs include:

1. Turbidity problems in the effluent during reloading operations.
2. Decreasing performance due to the continually diminishing height of calcite bed between loadings.
3. Turbidity problems during backwashing (Hernandez et al., 2009 and Batson, 2008).

Researchers at the Canary Islands Water Center in Spain have developed an upflow contactor design (DrinTec^{TM}) to overcome the aforementioned difficulties by:

1. Maintaining a constant calcite bed height via a continuous feeding system.
2. Eliminating turbidity events during reloading by separating the filter bed surface from the built-in silo.
3. Using a modular design that allows sparging of a single module during normal operations instead of the entire contactor whereby only a fraction of the total effluent volume is treated, hence minimizing the turbidity caused by fine calcite particle carryovers.

Figure 3-9 shows a cross-section schematic of the patented DrinTec™ calcite contactors. These contactors are installed in the 2.6 MGD Roque Pricto seawater desalination plant, 3.2 MGD Bocabarranco seawater desalination plant, 18.5-32 MGD Alicante II seawater desalination plant, 53 MGD Barcelona seawater desalination plant, and the 3 to 3.7 MGD Telde I and II seawater desalination plants across Spain and the Canary Islands.

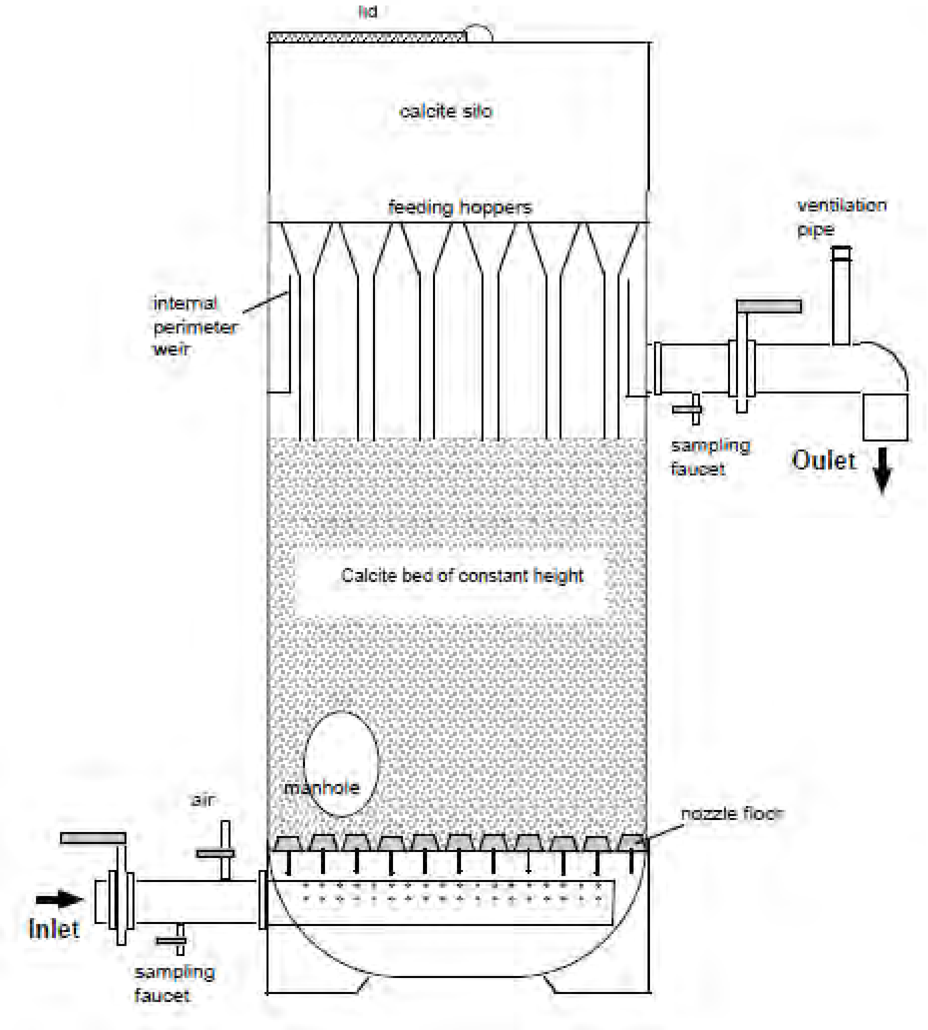

Figure 3-9. Cross-section of DrinTec™ calcite contactor (Hernández, 2009).

In the DrinTec™ system, water enters the lower portion of the tank and is distributed through the underdrain, consisting of perforated pipes and a nozzle floor above the pipes. Water flows upwards through the crushed calcite bed. The calcite bed consists of particle sizes in the range of 1 – 3 mm, which is all that is available locally. Once the water flows through the bed, the now re-carbonated water enters a no-flow area and leaves the contactor via an internal sluice gate at the perimeter. The DrinTec™ contactor has a built-in reserve silo on top with a series of feeding funnels that gravity feed fresh calcite from the silo to the submerged bed. As a result, the dosing occurs gradually and no turbulence is created to promote turbidity. This self-feeding mechanism allows the contactors to operate autonomously with minimum supervision. The finished water is discharged at atmospheric pressure.

3.4 Examples of facilities with upflow contactors

The following are examples of full-scale upflow calcite contactor installations. They were selected based on availability of information at the time this report was prepared.

3.4.1 Recarbonation facilities in the Canary Islands

The DrinTec^{TM} system is used to treat permeate water from the RO plants in the Canary Islands. The salinity and CO_2 content of the desalinated water vary from one RO plant to another but the typical characteristics are pH = 5.6 to 6, CO_2 = 30 - 45 mg/L and conductivity = 600 to 1500 micromhos per centimeter (µS/cm) (Robinson et al., 2005). The calcite contactors use 98 percent pure calcium carbonate with a nominal media size of two mm (Hernandez-Suarez, 2005). Due to variation in desalinated water quality from plant-to-plant, the authors recommended conducting pilot tests to define accurate design parameters. The contactor may be easily added to an existing plant and custom-built for each installation and type of water.

Table 3-5 shows the water quality data before and after recarbonation at the Alicante II calcite contactor plant that was completed in December 2008. The plant capacity is 17.75 MGD, where the flow is distributed through 32 contactor cells (each 6.5 feet by 16.4 feet) at a flow rate of 0.55 MGD per cell. The upflow velocity is 0.48 ft/min, with a bed height of 5.25 feet. pH adjustment is achieved by addition of 19 mg/L CO_2, followed by 11 minutes of EBCT. As seen in Table 3-5, the RO permeate from the plant is low in hardness and alkalinity with an acidic pH level, and is therefore corrosive and not suitable for distribution. In order to add the required hardness and alkalinity for potable water aesthetics, chemical stability, and infrastructure protection against corrosive water, CO_2 is added to increase the permeate water's capacity to dissolve calcite in the contactor to achieve an effluent calcium concentration of 19 mg/L, final alkalinity of 68 mg/L, and a pH of 8.25.

Table 3-5. Water quality of the Alicante II calcite contactor plant (Hernandez et al., 2009).

Parameter	**Permeate**	**Post-CO_2**	**Post-contactor**
Total dissolved solids (mg/L)	102	102	169
Temperature (° C)	19	19	19
Calcium (mg/L)	1.9	1.9	19
Alkalinity (mg/L as $CaCO_3$)	4.2	4.2	68.1
pH	6.20	5.55	8.25
CO_2 (mg/LCO_2)	5.44	26.0	0.76
LSI	-4.27	-6.4	-0.01
CCPP	-16.18	-55.09	-0.01

3.4.2 Blue Hills Bahamas Seawater RO Plant

At Blue Hills Bahamas Seawater Reverse Osmosis Plant, 50 percent (maximum 2,500 gpm) of the flow enters the calcite contactors and the rest is bypassed. Each contactor is 10 feet in diameter and 10 feet tall. Carbon dioxide is diffused into a 50 gpm carrier water flow, which is then added to the main calcite inlet feed line. Six calcite contactors were designed to accommodate the 2,500 gpm flow, where the flow rate per unit is 417 gpm. There are 200 cubic feet of calcite per unit at a bed height of 2 feet with a retention time of 3.58 minutes. The calcite was provided by Imerys (XO White^{TM} NSF), with a nominal grain size of 1 mm.

3.5 Calcite selection criteria

There are several types of minerals that can be considered as suitable media in a calcite contactor. These include calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). Calcite is used widely in the industries other than potable water treatment for applications such as polymer manufacturing, paint and coatings, and fillers. For the design of calcite contactors in drinking water applications, only NSF 60-certified calcite products can be used. NSF-60 certification is a nationally recognized standard to ensure that chemicals used in drinking water treatment do not contribute contaminants that cause adverse health effects to distributed water. For water treatment additives, in this case – calcite, the NSF 60 certification requires that the impurities in the additive cannot exceed more than 10 percent of the MCL. The two key criteria to consider for selection of calcite are purity and particle size. These criteria are presented in more detail below.

3.5.1 Purity

Recommended types of calcite to be used in a contactor should contain minimal impurities. Major impurities in calcite may include magnesium, iron, aluminum, and silica. Ruggieri et al. (2008) identified trace amounts of lithium, bromide, rubidium, and strontium in the calcites they studied. The effect of these impurities is threefold on the performance of a calcite contactor:

1. Decreased dissolution rate – The impurities may reduce the dissolution rate of the calcite by forming residue layers of dolomite, alumino-silicates and iron oxides on the calcite particle surface. As this layer thickens, the rate of transport of calcium ion from $CaCO_3$ surface to the bulk solution decreases, possibly requiring additional contact time with water to reach equilibrium.

2. Increased particulate matter – The impurities that have not dissolved, such as iron oxide and alumino-silicates, may contribute to an increase in particulate matter in the water. Depending on the superficial velocity of the water, these may be carried out of the contactor resulting in elevated turbidity in the distributed water.

3. Increased concentration of impurities in water – As the concentration of an impurity increases in the calcite, the likelihood that it will dissolve into the water will also increase. Ruggieri et al. (2008) observed increases in magnesium and strontium in their contactor effluents when testing their calcites with the highest dolomite (3.3 wt% as MgO) and strontium (247 mg/kg) content. The effluent waters from these contactors

contained 7.5 mg/L magnesium and 324 micrograms per liter (µg/L) strontium, respectively. In general, these constituents are neither regulated nor pose a health hazard at these concentrations. However, this example does highlight the connection between the chemical composition of the calcite and its impact on water quality.

The recommendations for calcite purity are as varied as the studies that report them. This may be, in part, due to the According to Carmical et al. (2002) and Ruggieri et al. (2008), the media with the highest calcite purity and lowest dolomite content has the highest initial rates of dissolution. Other studies (Letterman, 1995) corroborate this finding with a recommendation that the calcite contain no more than five percent magnesium carbonate, and the weighted sum of aluminum and iron should not exceed 10 milligrams per gallon (mg/gal). For calcite contactor facilities tested in South Africa, the calcite media used consisted of 95 percent calcium. In the Canary Islands, the recommended purity of calcite to be used is 99 percent.

3.5.2 Size

The particle size of calcite has three major influences on the design of an upflow contactor. First, the rate of calcite dissolution decreases as the particle size increases, requiring higher EBCTs for beds with smaller particles. Second, headloss through the calcite bed will increase as particle size decreases. Third, as particle size decreases, the superficial velocity will need to be decreased to prevent fluidization and/or "wash-out" of the calcite bed. Therefore, design of an upflow contactor will need to take two factors into consideration when selecting a calcite product:

1. <u>Size distribution</u> – Calcite products are typically not homogeneous in size. They may be described by their standard sieve (or "mesh") size, effective (or nominal) particle size, particle size range, and/or uniformity coefficient. The effective size of a particle is typically the standard sieve size, which passes only 10 percent of the total sample, d_{10}. The particle size range is the minimum and maximum particle sizes for the sample. The uniformity coefficient is the ratio of d_{60} to d_{10}, where d_{60} is the diameter corresponding to 60 percent or finer particles in the size range. A decrease in the uniformity coefficient means that the particle sizes fall within a more narrow range. Conceptually, a smaller uniformity coefficient for calcite particle sizes is advantageous for contactor design to more accurately predict calcite usage (dissolution), control headloss, and minimize bed fluidization and wash-out. However, recommended values for a uniformity coefficient have not been identified in the literature.

2. <u>Availability</u> **-** In different regions where calcite has been used, the particle sizes tested were dependent on local availability. In South Africa, calcite sizes previously tested ranged from 12 to 15 mm (De Souza et al., 2002), and the size of the calcite that produced optimal results was 12 mm. Calcite sizes ranging from 1.0 to 2.0 mm appeared to be common in Germany (Carmical et al., 2002) based on commercial availability. For older plants where backwashing is not possible, larger calcite particles have been used. In the Canary Islands (Hernandez, 2005 and Hernández, 2009), the recommended calcite sizes were between 1 and 3 mm. In general, the particle sizes available in a region are driven by local industrial needs rather than water treatment.

3.6 Calcite manufacturers in United States

3.6.1 Imerys

Imerys produces NSF 60-certified calcium carbonates and has United States production sites in Alabama, Arizona, Maryland, and Georgia. The local distributor for Imerys in Texas is located in Dallas (*Lintech International LLC)*. Imerys carries five calcium carbonate products for water treatment, all of which have 95 percent purity across various size ranges from 75 to 3,360 micrometers (µm). The product summary is provided in Table 3-6. Figure 3-10 provides a visual comparison for the Imerys calcite product samples.

Table 3-6. Imerys calcite product properties.

Grade	**40-200 ™ NSF**	**30-50™ NSF**	**XO White™ NSF**	**Z White™ NSF**	**OZ White™ NSF**
Mesh Size	1% Plus 40 (400 µm 14% Minus 200 (75 µm)	1% Plus 30 (590 µm) 15% Minus 50 (297 µm)	1% Plus 16 (1190 µm) 10% Minus 40 (400 µm)	1% Plus 40 (400 µm) 7% Minus 20 (840 µm)	3% Plus 6 (3360 µm) 3% Minus 14 (1410 µm)
% $CaCO_3$	95	95	95	95	95
% Acid Insolubles	2	2	2	2	2
% SiO_2	0.3	0.3	0.3	0.3	0.3
% Moisture	0.15	0.15	0.15	0.15	0.15

Note: SiO_2 is silicon dioxide.

3.6.2 Mississippi lime

Mississippi Lime is a diversified producer of lime and calcium-based products in North America with production facilities in Ste. Genevieve, Missouri, and Vicksburg, Mississippi. Its calcium carbonate products are distributed via Brenntag in Longview, Texas and via Univar in Beaumont, Borger, Dallas, San Antonio, and Houston, Texas. Mississippi Lime produces two ground calcium carbonate products for water treatment, as shown in Table 3-7. Both products are NSF 60-certified. Figure 3-11 provides a visual comparison between the two samples.

Table 3-7. Mississippi lime calcite product properties.

Grade	**CalCarb®R1**	**CalCarb®R2**
Mesh size	16 (1190 (µm)	200 (75 µm)
% $CaCO_3$	98.4	98.5
% $MgCO_3$	0.8	0.6
% SiO_2	0.7	0.6
% Fe_2O_3	0.04	0.04
% H_2O	0.07	0.03
% Al_2O_3	0.05	0.05
Sulfur (mg/L)	160	160
MnO (mg/L)	4	6

Figure 3-10. **Imerys calcium carbonate samples.**

Figure 3-11. Mississippi Lime CalCarb® R1 and R2 samples.

3.6.3 Columbia River Carbonates

Columbia River Carbonates, located in Woodland, Washington, is a supplier of high-grade ultra-fine ground calcium carbonate products and technical service for the paper, paint, plastic and other industries throughout the Northwestern United States and Western Canada. The company is a joint venture between OMYA and Bleeck Management, Inc. Columbia River Carbonates currently has three NSF 60-certified calcium carbonate products for water treatment, shown in Table 3-8. Figure 3-12 provides a visual comparison between Puri-Cal C^{TM} and Puri-Cal^{TM}. The smallest particle type, Puri-Cal^{TM} 40, is not shown because the particle size is too fine for consideration in the present study.

Table 3-8. Columbia River calcium carbonate properties.

Grade	Puri-Cal ^{TM} 40	Puri-Cal C^{TM}	Puri-Cal^{TM}
Mean particle size	270 µm	1,000 µm	600 µm
% $CaCO_3$	95	95	95
% acid insolubles	1	2	1
% $MgCO_3$	5	3	5
% Moisture	0.2	0.2	0.2

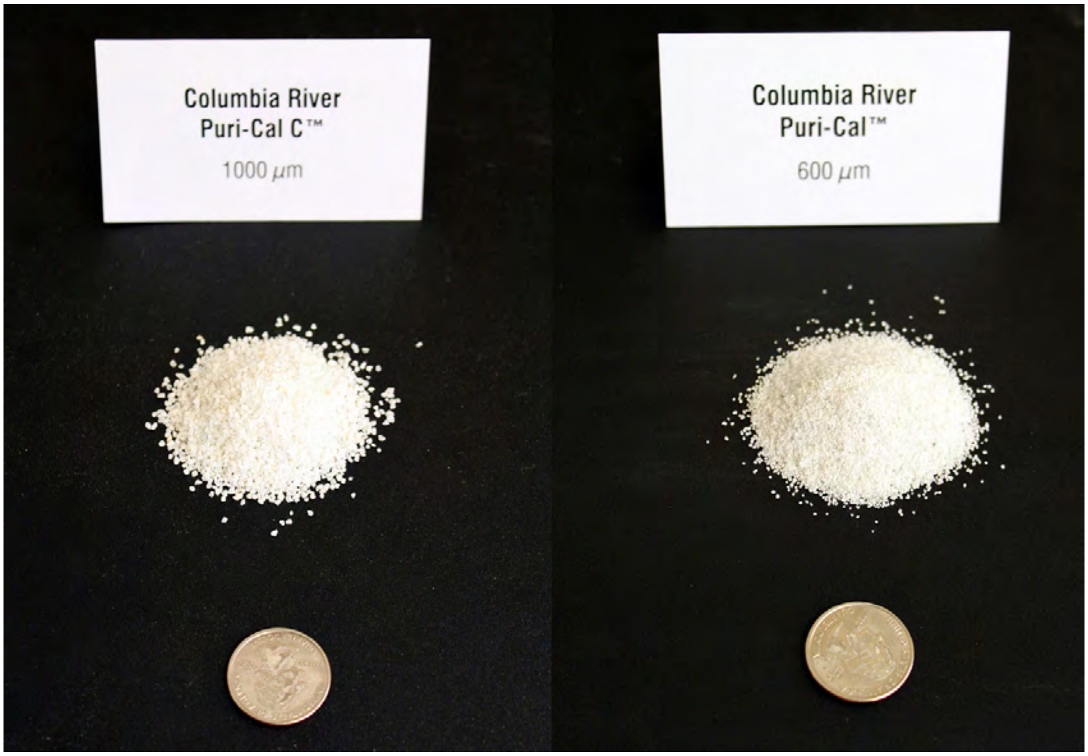

Figure 3-12. Columbia River Carbonates Puri-Cal™ C and Puri-Cal™ samples.

3.6.4 Specialty Chemicals, Inc

Specialty Chemicals, Inc. manufactures crushed and ground calcite products at two of its Performance Minerals plants. At Adams, Massachusetts and Lucerne Valley, California, high brightness calcite from adjacent Specialty Chemicals Inc. mines are ground into products which range in size from 0.5-inch (1.7 centimeter [cm]) white decorative landscaping stones to fine powders, (2 µm),. The VICAL® product line is produced at the Lucerne Valley plant and is NSF 60-certified for drinking water treatment. Table 3-9 illustrates the properties of the VICAL calcites.

Table 3-9. Specialty Chemicals Inc Calcium Carbonate properties.

Grade	Vical 1130	Vical 1600	Vical 3005	Vical 4005	Vical 5030	Vical 5075
Mesh Size	16 (1000 micrometer)	30 (595 micrometer)	40 (400 micrometer)	50 (297 micrometer)	70 (210 micrometer)	100 (149 micrometer)
% $CaCO_3$	97	97	97	97	97	97
% $MgCO_3$	1.4	1.4	1.4	1.4	1.4	1.4
% Fe_2O_3	0.1	0.1	0.1	0.1	0.1	0.1

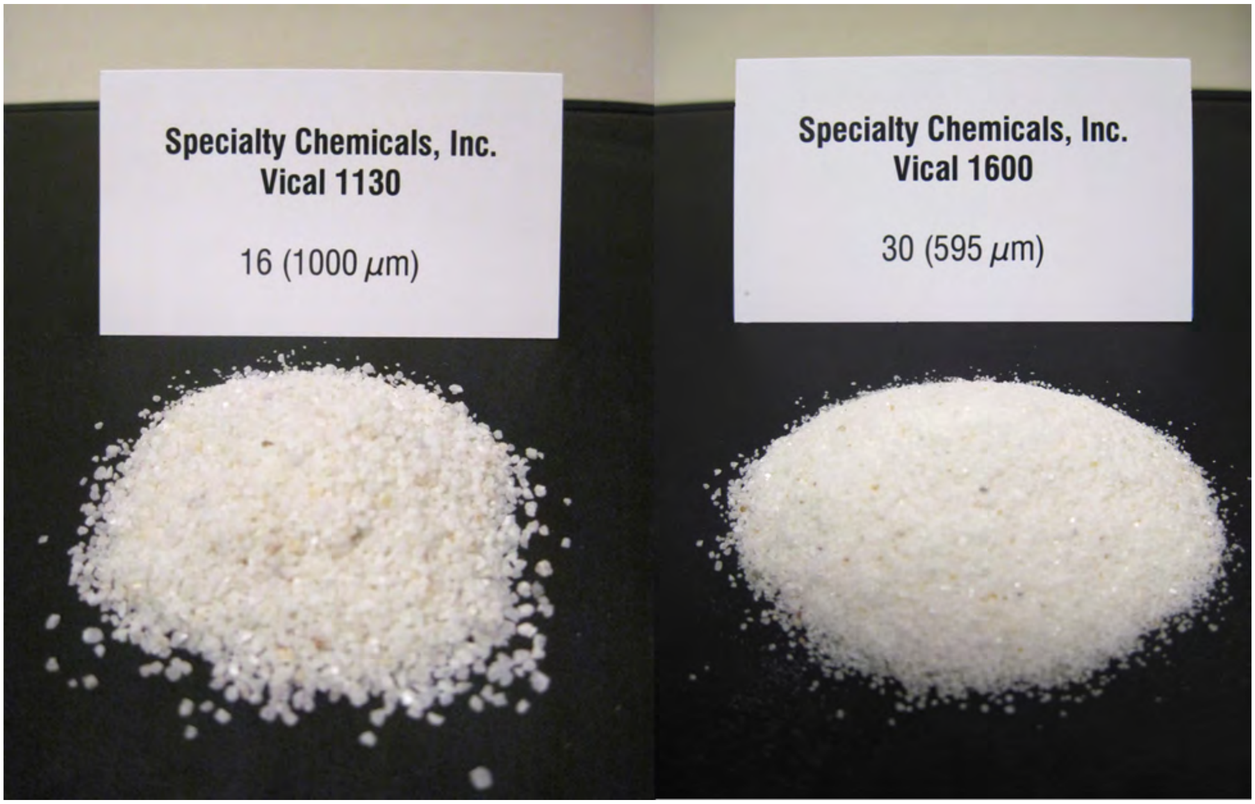

Figure 3-13. Specialty Chemicals, Inc. VICAL samples.

3.6.5 Franklin Industrial Minerals, Lhoist North America

Franklin Industrial Minerals is a Lhoist Group Company headquartered in Nashville, Tennessee. The company operates eight mining and processing facilities, located in Texas (3), Tennessee (2), Georgia, Alabama, and Florida. Crushed and ground limestone is produced in these locations from underground, underwater, and open pit mines. Finished products range from ultra-fine 2-micron calcium carbonate fillers to screened road aggregates. The limestone products are currently not NSF 60 certified, but Lhoist is willing to undergo the certification process if needed.

Table 3-10. Lhoist calcite product properties.

Grade	**W16X120**	**W16X**
Mesh size	-16 by +120 (149 to 1190 µm)	16 (1190 µm)
% $CaCO_3$	96.63	96.59
% $MgCO_3$	0.68	0.67
% SiO_2	1.10	1.07
% Fe_2O_3	0.26	0.20
% H_2O	0.03	0.02
% Al_2O_3	0.29	0.27

Figure 3-14. Lhoist W16X120 and W16X calcium carbonate samples.

3.6.6 Alternative calcite source

Faced with increasing water demands, costs of treating/distributing surface water and waste brine disposal in RO treatment plants, many municipalities in California and Arizona are evaluating means to maximize the efficiency of expanding their treatment system while reducing brine disposal and operational costs. RO process efficiency is typically limited by the concentration factors that can be applied before specific minerals begin to precipitate on the surface of the membranes. Given the typical mineral content of groundwater sources, the water recovery is generally limited to 75 to 85 percent. The remaining 15 to 25 percent of the water is disposed of as RO concentrate waste. Typically, the concentrate is considered a waste stream and is disposed of via sanitary sewers, or brine lines to an ocean outfall, or deep-well injection. The method of disposal is largely dependent on the location of the RO treatment facility and its access to available disposal means.

By sending the RO concentrate through a second RO process, it is now a feed water from which additional potable water can be recovered. In order to maximize the water recovery from the concentrate stream, mineral ions present in the concentrate that can precipitate as salts on the RO membrane will undergo an intermediate softening step to remove as much calcium and magnesium as possible. The approach being considered for improving the RO recovery uses precipitative softening to reduce the mineral content of the RO concentrate, and then uses a second set of RO membranes to recover some of the water in the supernatant of the softening process. This approach could increase the total water recovery from 80 percent to as high as 97 percent, thereby reducing the volume of concentrate for disposal.

One such precipitative softening technology being considered for RO concentrate treatment is the "pellet softening" process. The pellet softening process consists of an upflow vessel with fluidized particles introduced at the bottom of the vessel to act as the seeding nuclei onto which calcite, silica and other minerals will precipitate. Calcium carbonate seed material is used as the seeding nuclei for the pellet softening process. At the end of softening process, hard and durable pellets that are relatively dry and easy to handle and transport are generated. These pellets, shown in Figure 3-15, consist of mostly calcite (up to 91 percent). A potential reuse application for the pellets generated after the softening process could be as media for calcite contactors. The sizes of the pellets range from 0.4 to 1.42 mm (Water Quality & Treatment Solutions, Inc., 2010). Industries that purchase calcite particles as additives for building materials, paper production, paint formulations, and food could use calcite pellets generated from the softener process due to the similarity in the chemical makeup. Calcite contactors could potentially benefit by obtaining the softener-generated pellets for less cost with the added advantage of reusing products that are produced at the RO plant. NSF certification would be needed for these pellets to be used in drinking water applications, but for the purpose of this study, it is simply a proof-of-concept investigation at this stage.

Figure 3-15. Calcite pellets from the intermediate pellet softening process.

3.7 General calcite contactor design guidelines

In addition to specifying the range of parameter values in Section 3.7 for calcite contactor design, additional general guidelines are provided below (Carmical et al., 2002; Mackintosh et al., 2002 and Hernández, 2009):

- Minimize calcite bed contact time.
- Maximize contact efficiency (preventing dead zones in the contactor).
- The contactor should be closed to the atmosphere. This protects the calcite bed and the treated water from air-borne contamination, light penetration and algal growth.
- Design for redundancy (at least two contactors so one unit can be decommissioned for maintenance while the other is still operational).
- Measure headloss across the calcite bed.
- Use only NSF-60 approved calcite particles for drinking water applications.

3.8 Summary of data gaps

The purpose of this section is to summarize the data gaps identified from the information reviewed in the preceding sections. Based on these gaps, recommendations for the piloting testing have been developed and are provided below.

3.8.1 Influent water quality

The evaluations of upflow calcite contactors to date have typically been done on RO permeate generated from seawater sources. RO permeate derived from seawater generally contains higher concentrations of dissolved solids that may affect the dissolution rate of the calcite. The rate of dissolution depends on the influent water quality; therefore, performance of calcite contactors in different locations will vary according to site-specific water quality.

<u>Recommendation</u>

- Develop an experimental matrix to test upflow calcite contactors using permeate from a brackish groundwater RO system.

3.8.2 Empty bed contact time

EBCTs from various case studies ranged from 3.6 to 30 minutes. Based on these installations, there appeared to be no direct correlation between treatment capacity and EBCT as a function of superficial velocity. Selected superficial velocities range from 0.13 to 0.67 ft/min. In addition, published correlations between superficial velocity and turbidity were conducted only for calcite particle sizes that average 2 mm, and the purity of the calcite used was not reported. In the survey for NSF 60-approved calcite products in the United States, the largest calcite particle diameter in common for all manufacturers was 1 mm. Only Imerys has a product in the 3-mm size range. In correlating the superficial velocity with effluent turbidity, it not known whether the results from previous studies are representative of particles smaller or larger than 2 mm.

Recommendation

- Evaluate up to four EBCTs as a function of superficial velocity while other parameters are held constant (influent water quality, calcite purity, and particle size). Record the turbidity profile from each column.

3.8.3 Calcite purity and size

The particle sizes and purity may affect the contactor design and the effluent water quality. In the literature reviewed, the recommended particle size appeared to depend on the calcite supply locally available. For example, recommended calcite particles in the Canary Islands ranged from 1 to 3 mm, while South African researchers claimed that 12-mm calcite particles produced the best results for their waters. Approved NSF 60 calcite sizes in the United States for drinking water treatment range from sub-micron to 3 mm, and thus limits the product sizes that are available for potable water post-treatment. In addition, calcite products are typically not homogeneous in size. Conceptually, a smaller uniformity coefficient for calcite particle sizes is advantageous for contactor design to more accurately predict calcite usage (dissolution), control headloss, and minimize bed fluidization and wash-out. However, recommended values for a uniformity coefficient have not been identified in the literature.

Due to variations in calcite purity in different regions of the world, calcite mined from the United States may perform differently from calcite mined from Spain and South Africa. This may affect the rate of calcite dissolution, concentration of particulate matter in the contactor effluent, and the concentration of impurities from the calcite in the effluent water.

Recommendations

- Evaluate up to four calcite particle sizes from a single supplier.
- Analyze the size distribution of the calcite particles used for testing to determine the uniformity coefficient in addition to nominal size.
- Evaluate up to four calcite products with various percentage purities in the United States to begin developing alternative products that may be used for post-treatment of permeate from brackish groundwater RO.

3.8.4 Calcite consumption

Calcite consumption is determined by taking the difference of final calcium concentration and initial calcium concentration in the influent water. Analysis models (Schott, 2002) are helpful in determining theoretical predictions of the amount of calcite that will be consumed in the contactor process, but such models do not account for the interactions between all components in the water and the distribution of particle sizes for an average sample. Modeling will provide an indication of how the contactor will operate, but site-specific performance testing will still be required to validate model results. By recording the change in height over time, ($\Delta h/\Delta t$), and the dimensions of the contactor bed, the mass of calcite dissolved over time ($\Delta m/\Delta t$) can be approximated by the following equation:

$$\frac{\Delta m}{\Delta t} = \frac{\pi r^2 \Delta h}{\Delta t \cdot \gamma \cdot \rho} \qquad \text{(Equation 3-5)}$$

where

γ is the specific gravity of calcite at 2.7, ρ is the media packing density at 0.7, r is the radius of the calcite bed, Δm is the change in mass, Δt is time interval, and Δh is the change in calcite bed height during the dissolution process. From the piloting results, the consumption rate can be determined by the above equation to derive annual calcite costs.

Recommendation

- Record the change in calcite bed height on a daily basis (inches per day)
- Compare the calcium consumption results achieved through pilot testing.

4 Project implementation

4.1 Influent water quality and finished water quality goals

The influent water quality, which is the RO permeate for the Kay Bailey Hutchison Desalter and the targeted post-treatment goal following calcite dissolution in the upflow contactor is summarized in Table 4-1.

Table 4-1. Influent water quality and finished water quality goals.

Parameter	**Unit**	**Influent water quality**	**TCEQ SMCL[1]**	**Finished water quality goal**	**Basis for goal**
pH	---	6.7-6.8	> 7	7.5 – 8.5	National Secondary Drinking Water Regulations
Alkalinity	mg/L as $CaCO_3$	6.7- 11.6	---	60 - 80	D'Antonio et al. 2008
Calcium	mg/L as $CaCO_3$	6.8 – 15.1	---	50 - 120	World Health Organization, 2004 and Birnhack et al. 2008
LSI	---	-3	Non-corrosive	> -1.5	Lahav and Birnhack, 2007
RI	---	13	Non-corrosive	< 10	Lahav and Birnhack, 2007
CCPP	mg/L as $CaCO_3$	-11	---	4 - 10	Lahav and Birnhack, 2007

Note:

1. Secondary Maximum Contaminant Level

Permeate from the Kay Bailey Hutchison Desalination Plant in El Paso, Texas was analyzed for Radium-226, Radium-228 and both gross alpha and gross beta presence to determine if these radionuclides in the water exceeded the U.S. EPA drinking water regulations. Presence of radionuclides in treated water could be problematic from a treatment, distribution, and disposal standpoint. The results showed that the concentrations in the desalter permeate were below 5 picocuries per liter (pCi/L) for the combined radium, below 15 pCi/L for the gross alpha, and below 50 pCi/L for the gross beta.

4.2 Pilot plant system and design criteria

4.2.1 Process flow diagram

An overall process flow diagram for the testing is presented in Figure 4-1. Permeate from the Kay Bailey Hutchison Desalination Plant was supplied to the pilot via a 4,700-gallon tank, which is used only to store permeate for clean-in-place events at the plant. The permeate was pumped from this tank to the upflow calcite contactor pilot plant using a centrifugal pump. A side-stream of permeate injected with compressed CO_2 was used to generate a carbonic acid solution. This solution was injected into the permeate to lower its pH. The pH of the acidified permeate was controlled by a pH probe with a feedback loop to the Carbonic Acid Solution Feed Panel. The acidified permeate was split between four upflow calcite contactors operating in parallel for each experiment. The effluents from each upflow contactor was combined and sent to the concentrate wet well at the Kay Bailey Hutchison Desalination Plant. Caustic soda was not added to the contactor effluent to elevate the pH further, but the required chemical dose was calculated using RTW model after each phase to achieve final CCPP and LSI targets. At the end of each phase, the remainder of the calcite samples was emptied out from each contactor and fresh calcite samples were loaded to the 30-inch mark on each contactor.

Design criteria used for the various major testing equipment and an experimental plan are presented in the following sections.

4.2.2 Process testing equipment

The following section describes the calcite selection process and provides technical specifications for the following major process testing equipment:

- Upflow contactors.
- CO_2 injection system.

<u>Design criteria for upflow contactors</u>

Design criteria for the pilot-scale upflow contactor columns are presented in Table 4-2. A total of four contactors were operated in parallel for each set of experiments presented below.

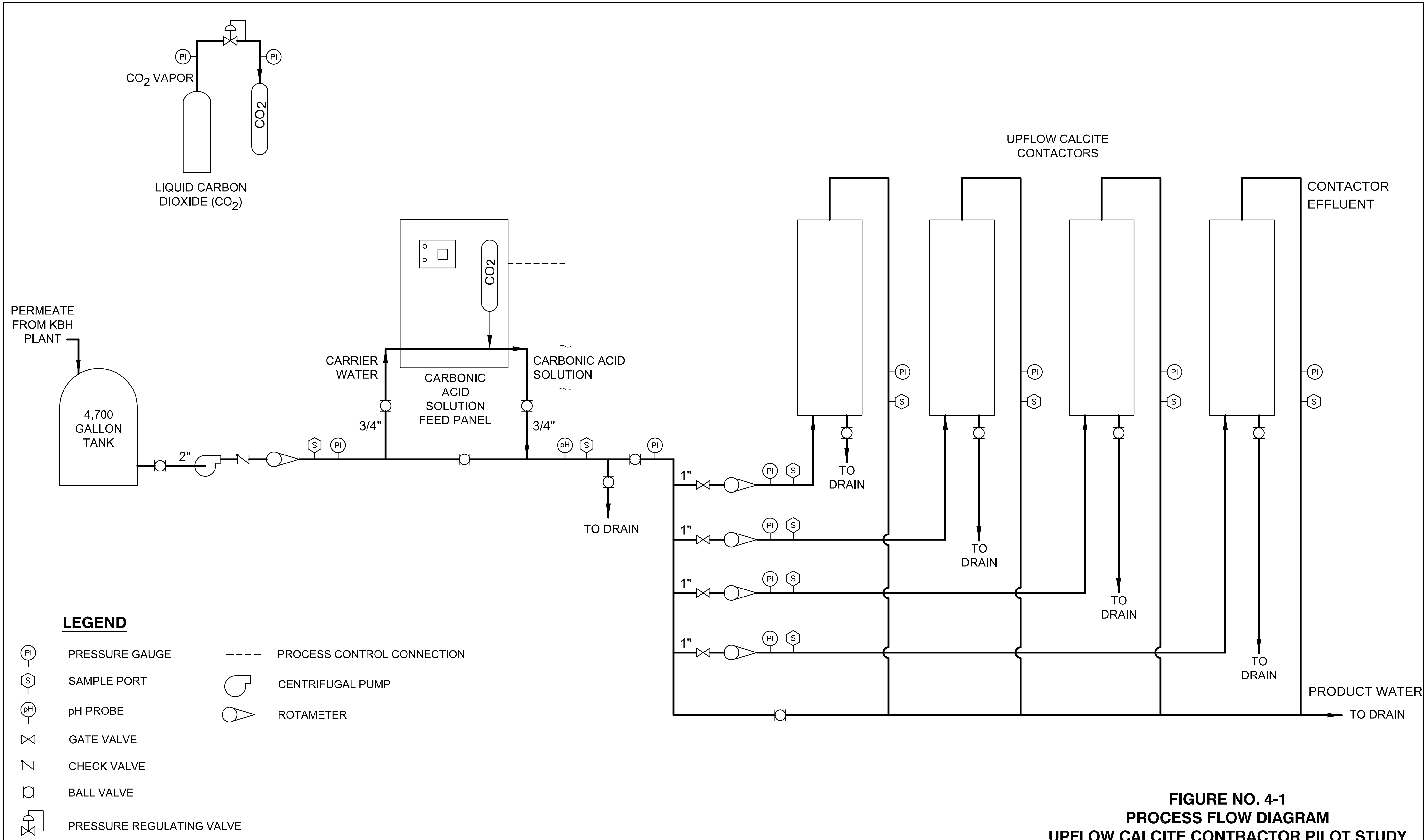

FIGURE NO. 4-1
PROCESS FLOW DIAGRAM
UPFLOW CALCITE CONTRACTOR PILOT STUDY
TEXAS WATER DEVELOPMENT BOARD

Table 4-2. Upflow contactor design criteria.

Parameter	Unit	Value
Columns	---	4
Column diameter : particle diameter	---	> 100:1
Calcite height : column diameter	---	> 1:1
Column dimensions (D × H)	inches × inches	4 × 72
Cross-sectional area	square feet	0.087
Calcite height	inch(es)	30
Hydraulic loading rate	gpm/ft^2	1.9 – 17.2
Empty bed contact time	minutes	1.1 – 9.8
Sample ports	---	Common and individual influents and individual effluents

4.2.3 Design criteria for the CO_2 injection system

One injection system was used to lower the pH of the permeate before it was split into the four upflow calcite contactors. Design criteria for the CO_2 injection are presented in Table 4-3.

Calcite selected for upflow contactor tests

Seven calcite products from four manufacturers were selected for testing. The properties of each of these calcite products are presented in Table 4-4. Samples of each media were analyzed by XRF, XRD, and SEM to confirm elemental composition and mineralogy. All media samples were determined to be predominantly calcite.

Table 4-3. CO_2 injection system design criteria.

Parameter	Unit	Value
pH control	---	Automatic
CO_2 injection rate, maximum	pounds per hour	5
CO_2 inlet pressure	pounds per square inch	55 - 60
Carrier water flowrate, minimum	gpm	5
Panel dimensions (L x H)	inches × inches	42 × 46
Panel mount	---	Free standing
Carrier water connection	inch(es)	3/4 FPT, 304 S.S.
Solution outlet connection	inch(es)	3/4 FPT, 304 S.S.
CO_2 vapor inlet connection	inch(es)	1/4 FPT, 304 S.S.
CO_2 storage container	---	Liquefied gas cylinders
CO_2 per container	inch(es)	400

Table 4-4. Properties of calcite selected for testing.

		Calcite manufacturers			
Description	**Unit**	**Imerys**	**Columbia River Carbonates**	**Specialty Chemicals, Inc.**	**Mississippi Lime**
Product Name	---	40-200™ NSF 30-50™ NSF Z White™ NSF OZ White™ NSF	Puri-Cal C™	Vical 1130	CalCarb®R1
Nominal Particle Size	mm	0.075, 0.3, 0.84, 1.4	1.0	1.0	1.19
NSF Certified	---	Yes	Yes	Yes	Yes
$CaCO_3$ Content	%	95	95	97	98.4
$MgCO_3$ Content	%	Not reported	3	1.4	0.8
Other Reported Impurities	---	SiO_2	Not Reported	Fe_2O_3	SiO_2, Fe_2O_3, Al_2O_3, S

Note:
[1] Based on manufacturer's information.

4.3 Experimental approach

The experimental plan included testing upflow calcite contactors for RO permeate stabilization by varying EBCT, calcite purity, and calcite particle size. An overview of the experimental plan is presented below.

4.3.1 Experimental matrix for upflow calcite contactor testing

Four experiments were conducted to determine design criteria for RO permeate stabilization (reference Table 4-5). The first three sets of experiments involved varying one of three design parameters: calcite particle size, calcite purity, and EBCT. The fourth set of experiments used combinations of selected values for these parameters to validate the design criteria selected. Operating conditions for each experiment are presented in Table 4-6.

4.4 Corrosivity modeling

Based on the effluent water quality produced from each upflow calcite contactor, the corrosivity of each was evaluated using the RTW model (Tetra Tech, 2008) to calculate the LSI, RSI, and CCPP. As mentioned in Section 3.1, to increase the pH and achieve desired slightly positive LSI and CCPP in the final effluent, final adjustments by caustic soda addition is needed. The chemical dosing is also calculated using the RTW model.

Table 4-5. Experimental plan for upflow calcite contactor testing.

Experiment	Description	Purpose
1	Vary calcite purity while keeping EBCT and calcite particle size constant.	Determine appropriate calcite purity for permeate stabilization.
2[a]	Vary EBCT while keeping calcite particle size and purity constant.	Determine the minimum EBCT for optimum permeate stabilization.
3	Vary calcite particle size while keeping EBCT and calcite purity constant.	Determine the optimum calcite particle size for permeate stabilization.
4	Selected three combinations of EBCT, particle size, and purity for testing. The fourth column included testing of particles from a pellet softening process.	Validated performance of three combinations of design criteria and the use of particles form pellet softening process.

[a] It was operationally difficult to maintain a constant empty bed contact because calcite could not be continuously loaded to refresh the calcite bed. In the pilot testing, Phase 2 was modified to vary loading rates, which could be used to deduce the contact time in the column.

Table 4-6. Operating conditions for upflow calcite contactor pilot study.

		Experiment			
Parameter	**Units**	**1**	**2**	**3**	**4**
Upflow contactors	---	4	4	4	4
Calcite depth/contactor	in.	30	30	30	30
Calcite volume/contactor	ft^3	0.87	0.87	0.87	0.87
Calcite particle size	mm	1	1	0.5 – 2	0.125 - 2
Calcite purity	% $CaCO_3$	95.0 – 98.4	95.0	95.0	77 – 98.4
Initial empty bed contact time	min.	4.5 – 7.5	1.2 – 9.9	4.8 - 5	1.1 – 2.0
Flowrate	gpm	0.33	0.17 – 1.5	0.33	0.83, 1.5(1)
Hydraulic loading rate	gpm/ft^2	3.8	1.9 – 17	3.8	9.5, 17
Superficial velocity	Ft/min	0.51	0.26 - 2.3	0.51	1.3, 2.3
Target contactor influent pH	---	5.5	5.5	5.5	5.5

Note:

[1] Three columns were operated at 9.5 gpm/ft^2 (1.3 ft/min) and the fourth was operated 17 gpm/ft^2 (2.3 ft/min).

5 Results and discussion

Average water quality data for the influent permeate from the Kay Bailey Hutchison Desalination Plant, post-CO_2 addition, and post-calcite treated effluents are presented in tabular format for each phase. Alkalinity, hardness, pH and turbidity for individual test dates are summarized in figures. Changes in particle sizes following calcite dissolution were determined by a sieve analysis for samples tested in all four phases. A 100-g sample of dried media was separated through a small stack of successively smaller sieves, where each sieve has a specific mesh size. Larger particles were separated at the top, and smaller particles passed through the upper sieves until they were captured on a smaller screen below. The mass of captured particles on each sieve was subsequently measured and tallied. Field measurements for alkalinity, hardness, and conductivity for the desalter permeate and contactor effluents were measured with a handheld Myron L Ultrameter III 9P with in-cell titrations onsite and later compared to laboratory titration results. Less than 5 percent deviation between the field measurements and lab analysis enabled operators to quickly determine effluent water quality and make operational changes onsite without extended waiting period for lab analysis.

5.1 Phase 1 – Impact of calcite purity

In Phase 1, four calcite samples in the 1-mm size range from different manufacturers with different levels of purity were selected for testing. The selected samples were Columbia River Carbonate (CRC) Puri-Cal C, Lhoist W16X, Specialty Minerals (SM) Vical 1130, and Mississippi Lime (ML) CalCarb R1. Each of these samples ranged in calcite purity from 95 to 98.4 percent. Each of the four calcite contactors was tested at a constant flow rate of 3.8 gpm/ft^2 (0.51 ft/min). The listed impurities contained in the calcite samples are summarized in Table 5.1.

Table 5.1. Listed calcite content.

Constituent	**Columbia River Carbonates (CRC)** (%)	**Lhoist** (%)	**Specialty Minerals (SM)** (%)	**Mississippi Lime (ML)** (%)	**Imerys** (%)
$CaCO_3$	95	96.59	97	98.4	95
$MgCO_3$	3	0.67	1.4	0.8	
Acid Insolubles	2	1.54	0.1	0.79	2
-Al_2O_3		0.27		0.05	
-Fe_2O_3		0.20	0.1	0.04	
-SiO_2		1.07		0.7	0.3
MgO		0.32			
Moisture	0.2	0.02		0.07	0.15

Sieve analysis for the calcite samples were performed prior to and after the dissolution experiments. Figure 5.1 shows the box-whisker plot of the calcite particle sizes in Phase 1. The bottom of each box is the 10th percentile size (d_{10}), and the top of the box is the 60th percentile size (d_{60}). The ratio of d_{60}/d_{10} is the uniformity coefficient of the calcite sample. The lower whisker shows the 5th percentile size, and the upper whisker shows the 95th percentile size. This allows the visualization for 90 percent of the size range of the particles.

In an upflow calcite contactor, the driving force for dissolution is always greater at the bottom of the bed than at the top. The particles at the bottom of an upflow bed are expected to dissolve more rapidly and shrink more rapidly than those at the top of the bed. Depending on the pore structure of the bed, these may be carried out of the bed or may be trapped until they dissolve completely. Consequently, in a bed that is periodically renewed with new particles, the distribution of particle sizes will broaden. As seen in Figure 5.1, most of the Lhoist W16x and ML CalCarb R1 samples displayed a broad size distribution (0.063 to 1 mm), with the majority of the particles retained in the 0.50 mm sieve. SM Vical 1130 samples ranged mostly from 0.25 to 1 mm, and CRC Puri-Cal C samples had the narrowest distribution (0.5 to 1 mm). After the dissolution experiments, 75 percent of Lhoist W16x samples were 0.125 mm and the rest were below 0.063 mm, ML CalCarb R1 retained its broad distribution but its peak was shifted down to 0.125 mm. The corresponding increase in CRC Puri-Cal C and SM Vical 1130 samples retained in the 0.5-mm mesh were the result of the larger 1-mm samples dissolving.

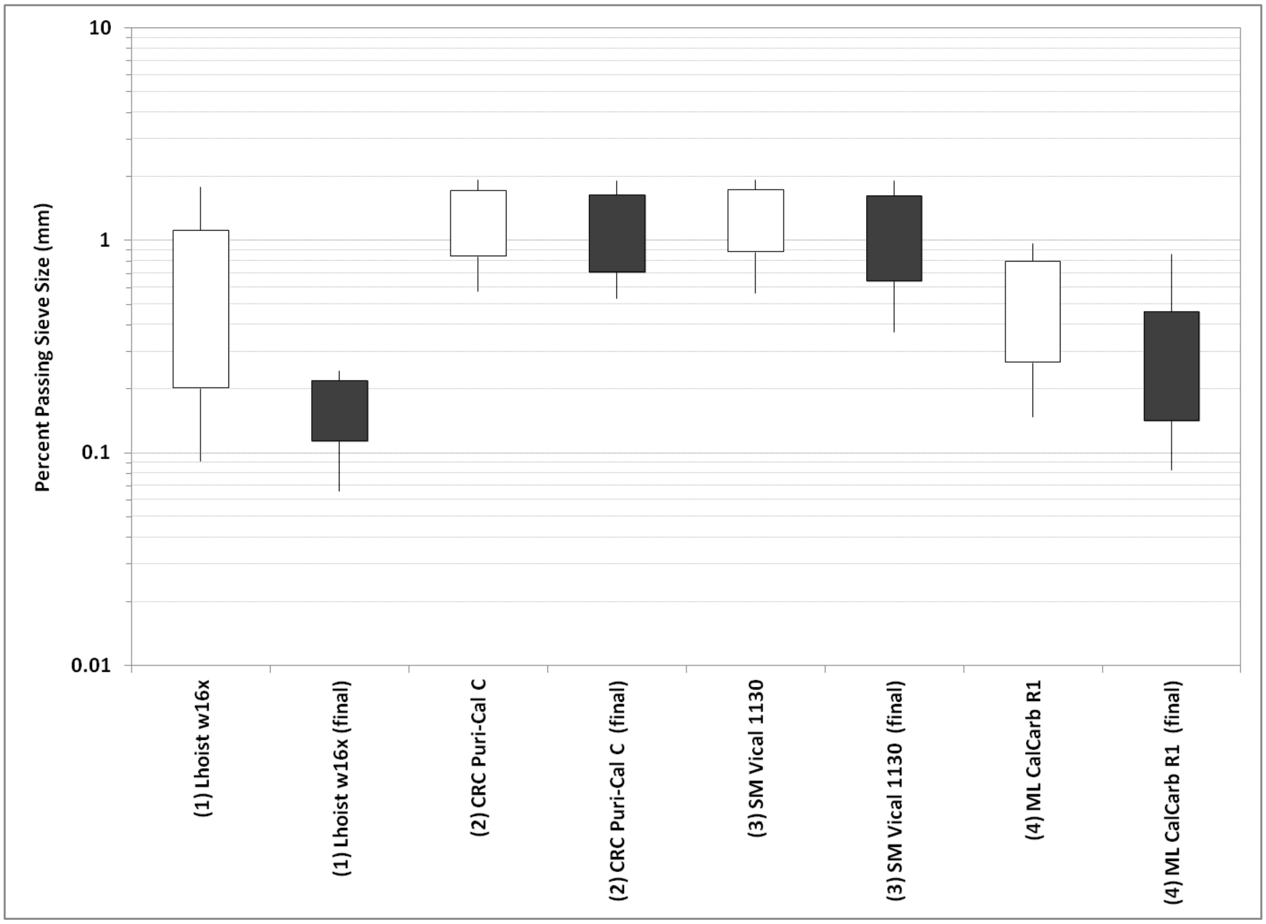

Figure 5.1. Box-whisker plot of calcite particle size changes in Phase 1.

Phase 1 testing began on June 22, 2011 and lasted for 30 days. The results of the average influent and effluent water quality are summarized in Table 5.2. As seen in the table, finished water LSI values were slightly negative, and the CCPP was less than 4 mg/L as $CaCO_3$. This is not atypical, since thermodynamic equilibrium is seldom reached in practice due to kinetic limitations (Birnhack et al., 2011). Typically, in drinking water facilities, caustic soda (NaOH) is added to post-treated water as a final polishing step to increase the pH (7.5 to 8.5), elevate the LSI to slightly above zero and maintain a CCPP value between 4 and 10 mg/L as $CaCO_3$ for anti-corrosion purposes. For the calcite contactor effluent samples tested in Phase 1, less than 3 mg/L of caustic soda dosing would be needed to achieve slightly positive (+0.5) LSI and >4 mg/L as $CaCO_3$ of CCPP.

Table 5.2. Phase 1 Influent and Effluent Water Quality

				Effluent WQ							
				CRC Puri-Cal C		Lhoist w16x		SM Vical 1130		ML CalCarb R1	
PHASE 1	Unit	Influent WQ	Post CO_2 WQ	95.0%	Post NaOH	96.6%	Post NaOH	97.0%	Post NaOH	98.4%	Post NaOH
Alkalinity	mg/L as $CaCO_3$	11.60	12.40	73.60	76.85	80.07	81.95	71.92	75.30	77.00	75.30
Hardness	mg/L as $CaCO_3$	15.13	12.60	77.38	77.38	77.07	77.07	74.60	74.60	81.33	81.33
pH	pH unit	6.76	5.60	7.81	8.53	8.11	8.52	7.81	8.57	8.02	8.52
Turbidity	NTU	0.17	0.18	0.69		69.21		1.74		28.66	
Temperature	^{o}C	26.17	26.36	26.00	26.00	26.01	26.01	26.00	26.00	25.91	25.91
Conductivity	µS/cm	590.01	590.78	700.55		702.39		698.97		702.35	
Total Ions + SiO_2	mg/L	336.31	336.74	404.39	407.91	410.54	412.22	400.62	404.19	407.54	409.66
TDS (SUM)	mg/L			359.03	362.38	361.66	363.60	356.30	359.78	360.36	362.66
LSI		-3.05	-4.18	-0.20	0.54	0.11	0.53	-0.25	0.53	0.00	0.51
CCPP		-13.18	-113.47	-1.82	4.14	0.80	4.21	-2.17	4.02	-0.07	4.04
RI		12.86	13.95	8.22	7.46	7.90	7.47	8.32	7.52	8.02	7.50
Cations											
Calcium	mg/L	< 3	< 3	26.58	26.58	24.94	24.94	24.16	24.16	24.97	24.97
Potassium	mg/L	2.24	2.28	2.08	2.08	2.16	2.16	2.17	2.17	2.12	2.12
Magnesium	mg/L	< 1.5	< 1.5	< 1.5	1.50	< 1.5	1.50	< 1.5	1.50	< 1.5	1.50
Sodium	mg/L	105.96	107.23	107.53	109.03	107.63	108.49	107.67	109.22	107.65	108.69
Aluminum	mg/L	0.01	0.12	< 0.01	< 0.01	0.21	< 0.01	< 0.01	< 0.01	0.04	< 0.01
Iron	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	0.41	< 0.01	< 0.01	< 0.01	0.25	< 0.01
Strontium	mg/L	0.03	0.05	0.27	0.27	0.09	0.09	0.04	0.04	0.05	0.05
Anions											
Silica	mg/L	1.78	1.84	1.85	1.85	2.35	2.35	1.86	1.86	1.92	1.92
Chloride	mg/L	168.23	170.91	171.95	171.95	171.46	171.46	172.63	172.63	172.61	172.61
Fluoride	mg/L	0.10	0.10	0.09	0.09	0.10	0.10	0.09	0.09	0.10	0.10
Nitrate	mg/L	< 0.2	< 0.2	< 0.2	0.20	< 0.2	0.20	< 0.2	0.20	< 0.2	0.20
Sulfate	mg/L	< 3	< 3	< 3	3.00	< 3	3.00	< 3	3.00	< 3	3.00

Effluent alkalinity, calcium concentration, pH and turbidity measurements for individual runs are displayed in Figures 5.2 to 5.5. Finished water quality goals are represented in the figures by the area captured between the two horizontal lines. The targeted alkalinity, calcium, and pH goals were achieved by maintaining a post-CO_2 pH of 5.6 in the calcite contactor influent streams. Lhoist w16x and ML CalCarb R1 calcite samples, which were mostly smaller than 1 mm in particle size, had high turbidity effluents. During experimentation, the smaller particles from these two samples appeared to be fluidized over the full length of the contactor columns and contributed to particle "wash out", which resulted in high turbidity measured in the effluent sample taps. CRC Puri-Cal C and SM Vical 1130, which contained a higher percentage of particles in the 1 mm range, had average effluent turbidities of 0.69 and 1.74 NTU, respectively. Continuous calcite loading to maintain a constant bed height was not possible during these runs; therefore, the EBCT for the contactors decreased as calcite dissolved. The change in EBCT, i.e., the rate of calcite dissolution, is presented in Figure 5.6. In Section 3.5.1, calcite media with the highest purity reportedly had the highest initial rate of dissolution. In the same section, South African researchers used 95 percent calcite samples for testing and the Canary Island researchers recommended 99 percent calcite purity. In Phase 1 of the current study, there was no apparent correlation between calcite purity and dissolution rate. In terms of purity ranking, ML CalCarb 1 > SM Vical 1130 > Lhoist w16x > CRC Puri-Cal C. Dissolution rate ranking showed Lhoist w16x > ML CalCarb R1 > SM Vical 1130 > CRC Puri-Cal C. The amount of acid insoluble impurities, namely the iron, aluminum, and silica content of the calcite samples, also did not illustrate any correlation. There was no decreasing trend in the targeted finished water quality parameters as the EBCT decreased from 8 to 3 minutes. This, indicates that the tested loading rate of 3.8 gpm/ft^2 (0.5 ft/min) provided more than enough residence time in the contactors for calcite dissolution to reach equilibrium. From the Phase 1 results shown in Figure 5.2 to 5.6, effluent water quality and calcite dissolution appeared to be affected more by the presence of smaller particles during startup rather than the range of tested calcite purities (95 to 98 percent).

Ideally, the CO_2 side stream flow rate and pressure for the pilot system would have been maintained at 1 gpm and 40-45 pounds per square inch (psi) above the line pressure to approach 99 percent CO_2 transfer efficiency to the permeate. Carbon dioxide transfer efficiency decreases as the pressure differential decreases, which could result in insufficient CO_2 dissolution into the permeate stream. The pH was monitored in the post-CO_2 effluent streams prior to entering each calcite contactor. In the pilot unit, precise flow control using a 1-inch PVC ball valve was difficult to achieve, and combined with the narrow pump curve for the CO_2 boost pump, it was operationally challenging to maintain the high-pressure differential between the side stream and the influent permeate stream. Only a maximum of 10-psi differential pressure could be achieved. To overcome this operational challenge, the pH of the post-CO_2 stream was set at pH 5.6 before entering the calcite contactors to ensure a constant starting point for calcite dissolution testing. Between July 18 and July 22, 2011, the CO_2-boost pump failed and CO_2 dissolution to form carbonic acid was uncontrollable and erratic. As a result, the alkalinity and hardness measurements for the last three data sets in Phase 1 were not be considered for design purposes.

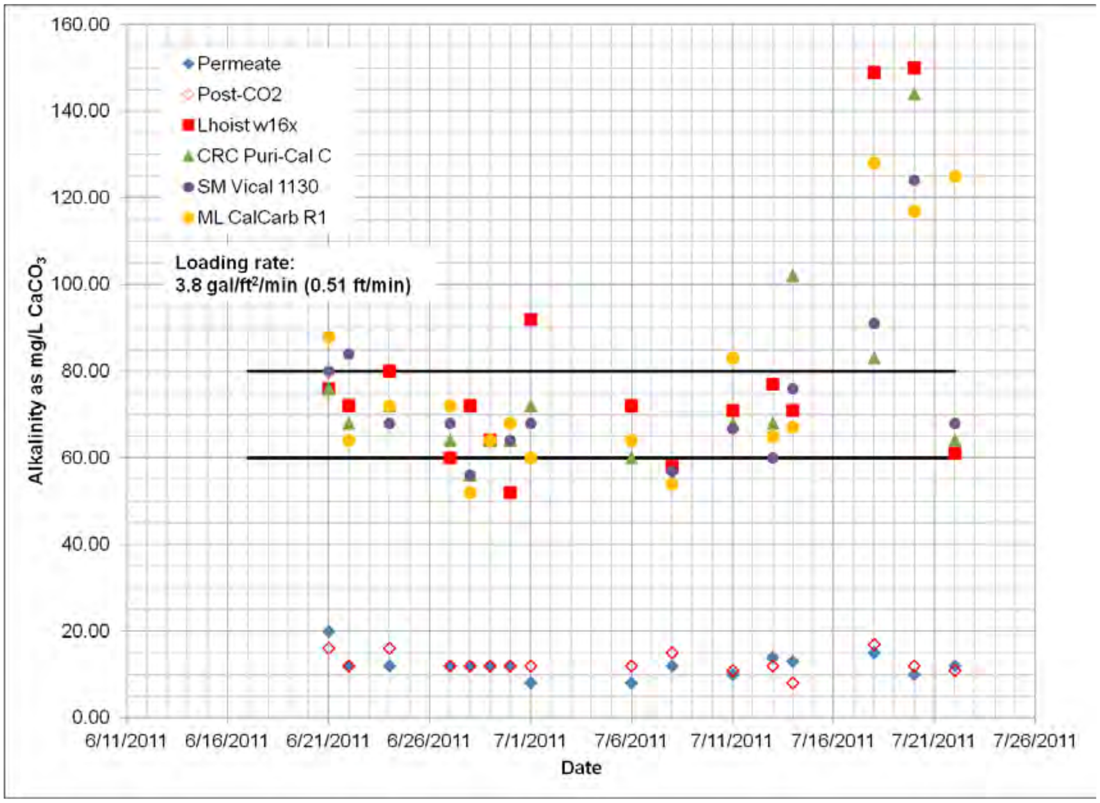

Figure 5.2. **Phase 1: Alkalinity for 3.8 gpm/ft^2 calcite dissolution at various calcite purities. Finished water quality goals are represented by the area between the two horizontal lines.**

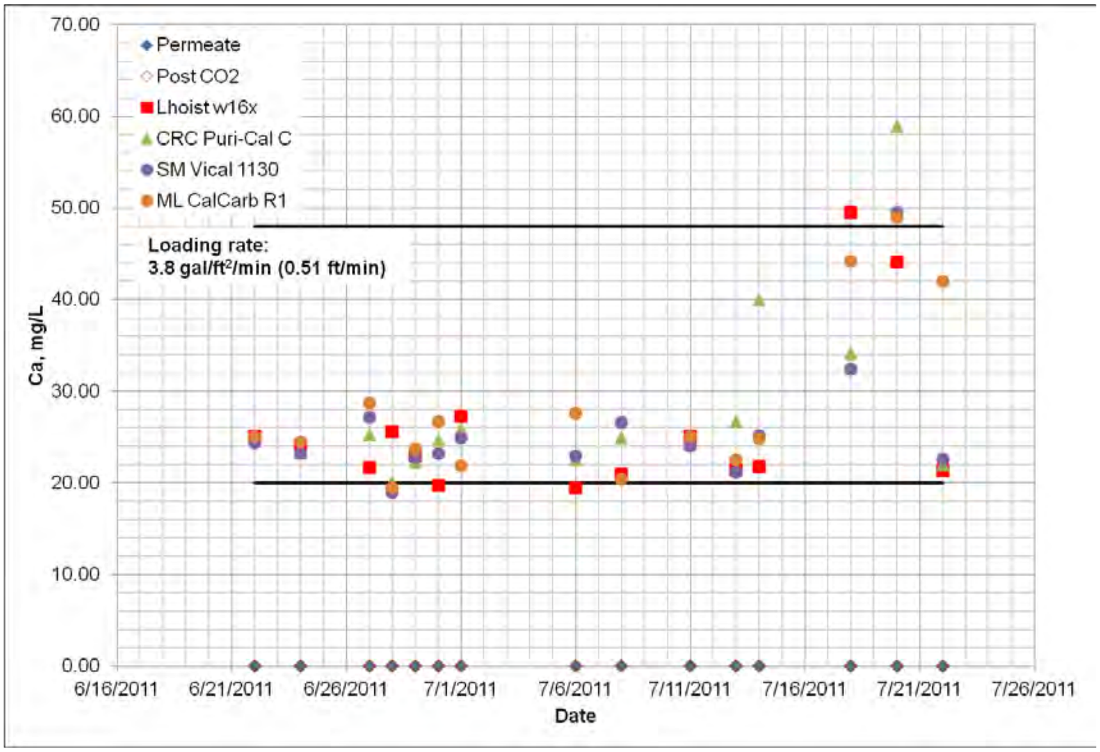

Figure 5.3. **Phase 1: Calcium concentration for 3.8 gpm/ft^2 calcite dissolution at various calcite purities. Finished water quality goals are represented by the area between the two horizontal lines.**

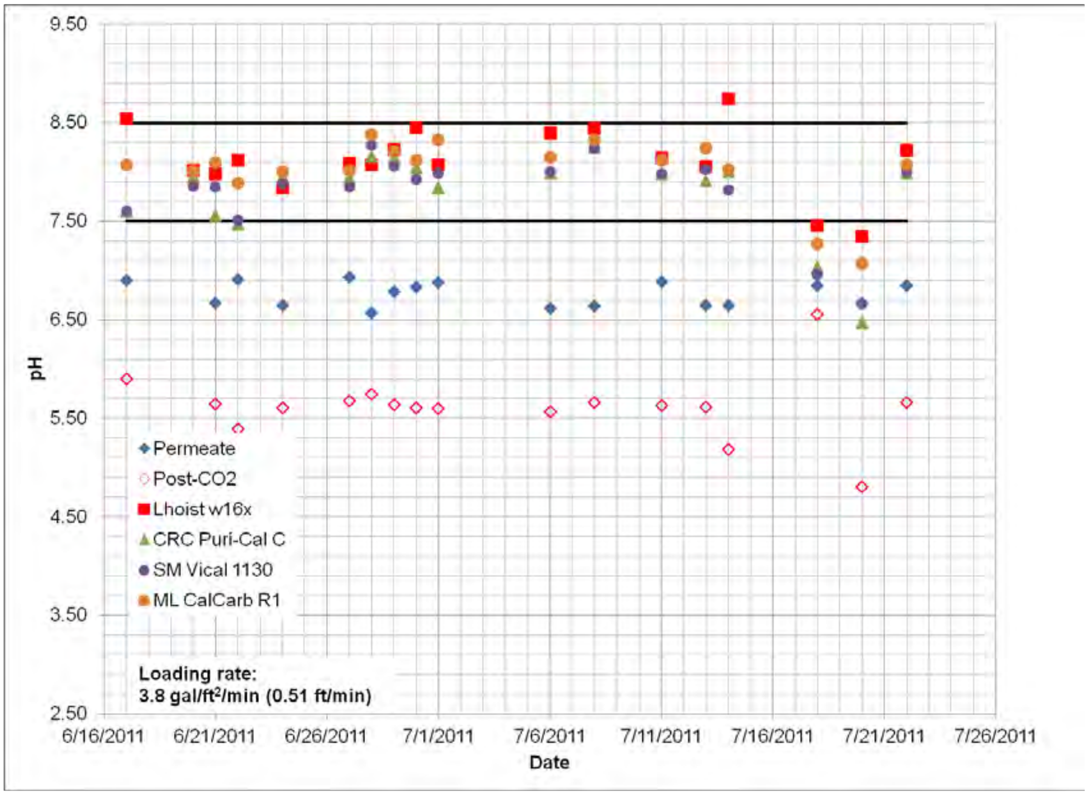

Figure 5.4. **Phase 1: pH for 3.8 gpm/ft^2 calcite dissolution at various calcite purities. Finished water quality goals are represented by the area between the two horizontal lines.**

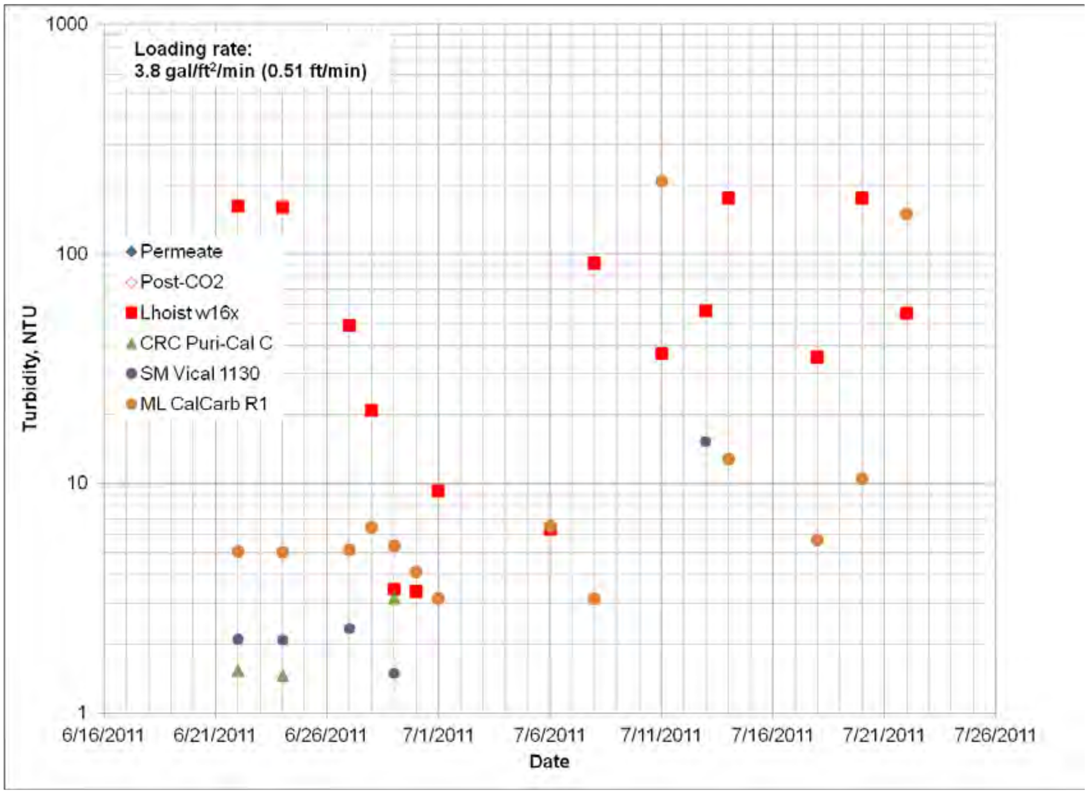

Figure 5.5. **Phase 1: Turbidity for 3.8 gpm/ft^2 calcite dissolution at various calcite purities.**

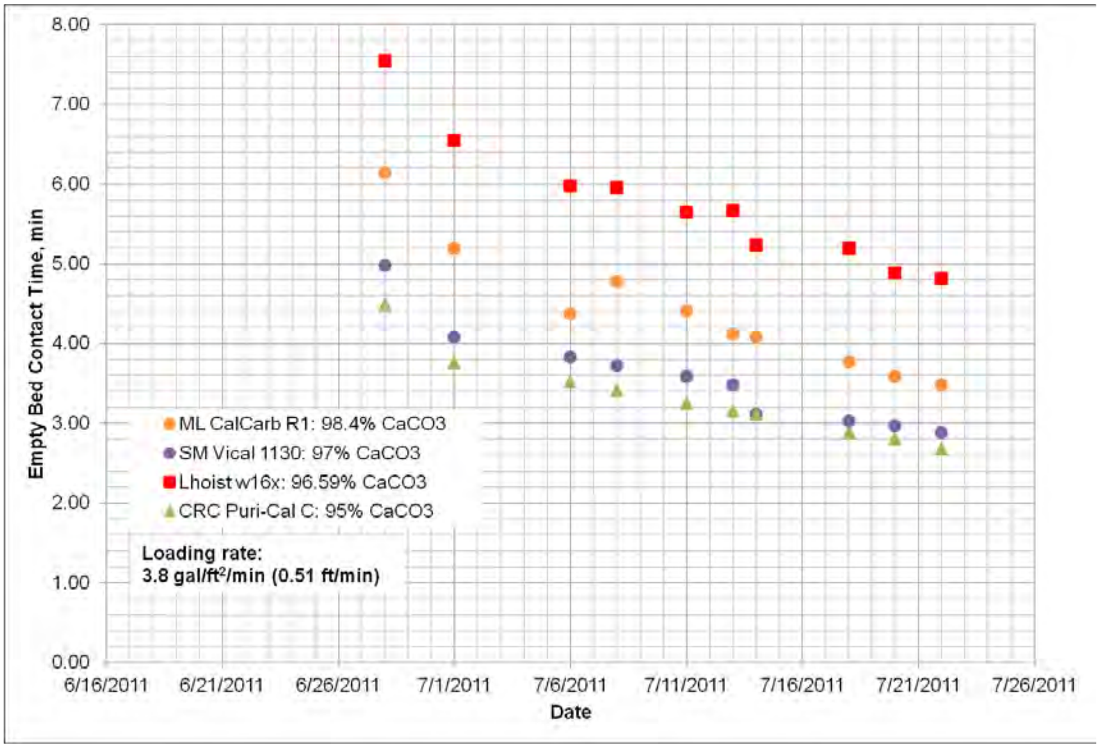

Figure 5.6. **Phase 1: EBCT for 3.8 gpm/ft^2 calcite dissolution at various calcite purities.**

5.2 Phase 2 – Impact of influent loading rate

Based on the test results from Phase 1, CRC Puri-Cal C at 95 percent calcite purity was selected for Phase 2 testing due to its narrow size distribution in the 1 mm range and its low effluent turbidity. The original objective for Phase 2 was to determine the impact of EBCT on finished water quality. As previously discussed, it was operationally difficult to feed calcite continuously to the top of each reactor to maintain a constant bed height. Therefore, a constant EBCT for each column could not be maintained during test runs. However, the influent loading rate to each contactor could be varied easily, and thus provided a way to gauge the impact of the residence time in each column on finished water quality. In Phase 1, only one flow rate at 3.8 gpm/ft^2 (0.5 ft/min) was tested,. Changes in the EBCT were tracked in Figure 5.6. For Phase 2, four additional calcite contactor influent flow rates were tested: – 1.9 gpm/ft^2 (0.26 ft/min):, 5.7 gpm/ft^2 (0.77 ft/min), 9.5 gpm/ft^2 (1.3 ft/min) and 17 gpm/ft^2 (2.3 ft/min).

Phase 2 testing began on July 27, 2011 and lasted for 30 days. Results of the sieve analysis of the calcite particles before and after the dissolution experiments is shown in Figure 5.7. Influent flow rates are inversely proportional to residence time, and as residence time increases, the dissolution rate increases accordingly. In Figure 5.7, at 1.9 gpm/ft^2 (0.26 ft/min), most of the 1-mm particles were able to dissolve slowly and over 95 percent of the calcite samples were in the 0.5-mm size bin after testing. At 5.7 gpm/ft^2 (0.77 ft/min), over 85 percent calcite samples were in the 0.5-mm range, and about 12 percent were in the 0.25-mm range. At 9.5 gpm/ft^2 (1.3 ft/min), the shorter residence time in the columns did not allow the 1-mm samples to dissolve uniformly and about 47 percent of the particles were in the 1-mm range, whereas 50 percent of the particles after testing were retained in the 0.5-mm range. At 17 gpm/ft^2 (2.3 ft/min), the high velocities in the column fluidized the calcite bed and the size of the post-experiment calcite samples ranged from 0.125 to 0.5 mm.

In terms of finished water quality, the results of the average influent and effluent water quality are summarized in Table 5.3. Similar to the Phase 1 results, finished water LSI values were slightly negative, and the CCPP was less than 4 mg/L as $CaCO_3$. As previously discussed, caustic soda would be required to elevate the LSI and CCPP values for anti-corrosion purposes. As residence times in the columns decrease, the rates of calcite dissolution decrease; therefore, more caustic soda would need to be added in the polishing step to achieve the targeted water quality goals. The range of caustic doses increased from 1.5 mg/L to 3.7 mg/L for influent flow rates at 1.9 gpm/ft^2 (0.26 ft/min)to 1.5 to 90 9.5 gpm/ft^2 (1.3 ft/min).

During testing in Phase 2, the Kay Bailey Hutchison Desalination Plant introduced lower salinity wells from their wellfield and a corresponding decrease in the measured conductivity was seen in the influent desalter permeate. Figure 5.8 shows the sudden drop in conductivity during the first week of August 2011. At lower permeate conductivities, the alkalinity and hardness of the influent permeate were reduced by half. To achieve the target water quality, a higher dose of CO_2 should be introduced to the influent permeate to allow more calcite to dissolve and add the necessary calcium hardness and bicarbonate alkalinity into the water. Unfortunately, this change in influent water quality was not noted until after the testing, and therefore the pH settings on the TOMCO_2 system were not adjusted accordingly. Nevertheless, as indicated in the effluent water quality parameters prior to the well changes in Figures 5.9 to 5.13, targeted alkalinity and hardness goals were met. The gray bar in the figures indicates the depletion of CO_2 gas supply on August 12, 2011, and a new tank was restored to the test site three days later, 2011.

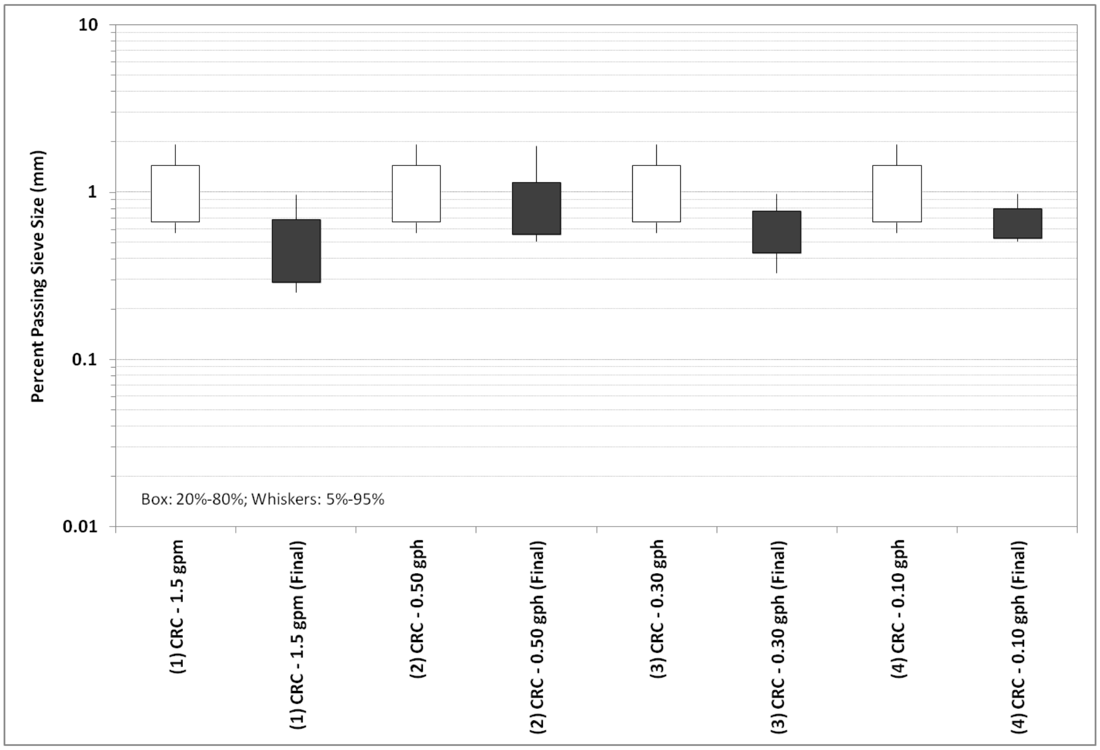

Figure 5.7. **Box-whisker plot of calcite particle size changes in Phase 2.**

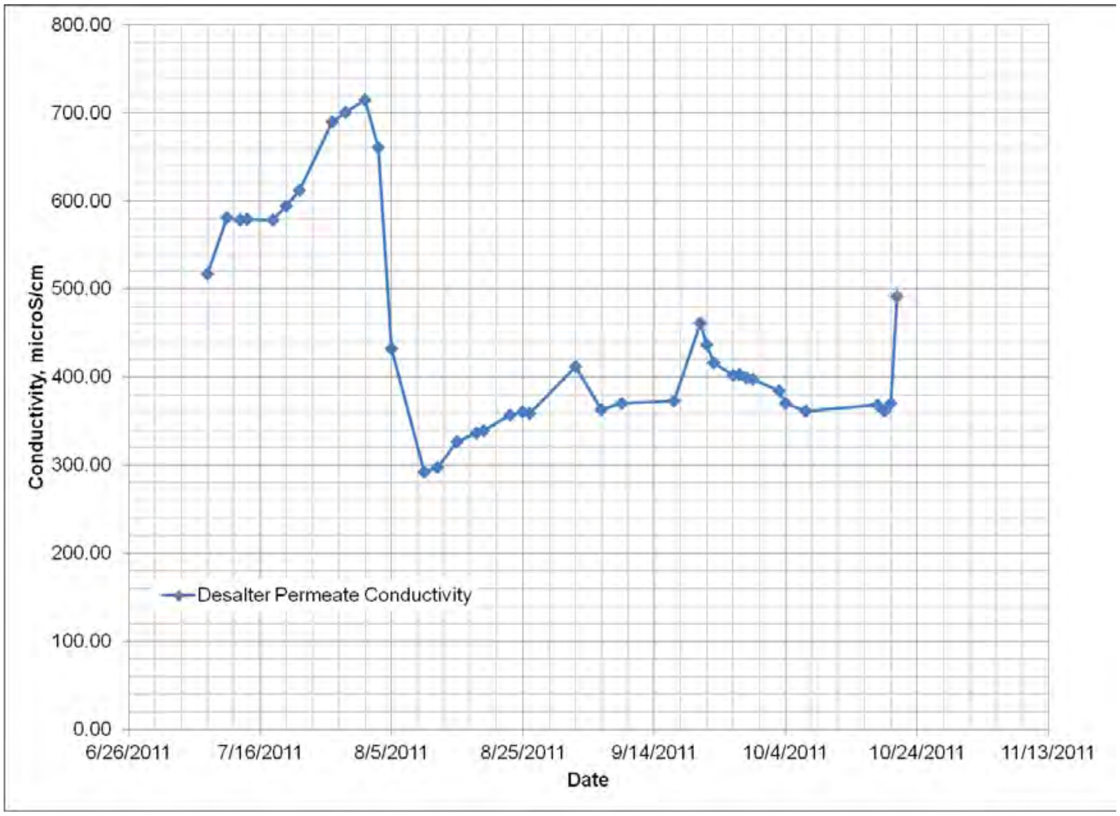

Figure 5.8. **Influent permeate conductivity changes of Kay Bailey Hutchison Desalination Plant in Phase 2.**

Table 5.3. Phase 2 influent and effluent water quality.

				Effluent WQ							
				1.9 gpm/ft^2 (0.26 ft/min)		5.7 gpm/ft^2 (0.77 ft/min)		9.5 gpm/ft^2 (1.3 ft/min)		17 gpm/ft^2 (2.3 ft/min)	
Parameter	**Unit**	**Influent WQ**	**Post CO_2 WQ**		**Post NaOH**		**Post NaOH**		**Post NaOH**		**Post NaOH**
Alkalinity	mg/L as $CaCO_3$	8.75	8.92	56.25	58.13	52.75	54.75	44.42	47.42	43.25	47.88
Hardness	mg/L as $CaCO_3$	7.96	7.33	54.25	54.25	51.58	51.58	43.60	43.60	40.08	40.08
pH	pH unit	6.84	5.98	8.34	8.78	8.36	8.83	8.19	8.96	7.60	8.91
Turbidity	NTU	0.17	0.13	44.88		8.37		0.97		9.60	
Temperature	°C	26.03	26.28	25.49	25.49	25.97	25.97	25.99	25.99	26.06	26.06
Conductivity	µS/cm	464.18	314.31	536.98							
Total Ions + SiO2	mg/L	311.00	210.59	316.58	317.79	361.28	313.43	352.44	300.51	200.16	304.67
TDS (SUM)	mg/L			282.66	284.52	280.45	282.43	271.62	274.53	273.48	278.09
LSI		-3.08	-3.89	0.10	0.56	0.03	0.58	-0.33	0.54	-0.79	0.59
CCPP		-11.06	-39.39	0.51	4.00	0.20	4.17	-1.50	4.21	-4.60	4.25
RI		12.99	13.76	8.14	7.67	8.30	7.67	8.85	7.87	9.18	7.74
Cations											
Calcium	mg/L	< 3	< 3	20.24	20.24	19.96	19.96	15.57	15.57	19.12	19.12
Potassium	mg/L	2.54	2.70	2.28	2.28	2.28	2.28	2.54	2.54	2.29	2.29
Magnesium	mg/L	< 1.5	< 1.5	< 1.5	1.50	< 1.5	1.50	< 1.5	1.50	< 1.5	1.50
Sodium	mg/L	84.07	84.07	83.97	84.83	84.06	84.98	84.07	85.45	83.96	86.09
Aluminum	mg/L	< 0.01	< 0.01	0.05	0.05	0.07	0.07	< 0.01	< 0.01	0.02	0.02
Iron	mg/L	< 0.01	< 0.01	0.05	0.05	0.12	0.12	< 0.01	< 0.01	0.02	0.02
Strontium	mg/L	0.02	0.02	0.22	0.22	0.16	0.16	0.14	0.14	0.13	0.13
Anions											
Silica	mg/L	1.77	1.77	1.91	1.91	1.90	1.90	1.82	1.82	1.87	1.87
Chloride	mg/L	136.50	136.59	135.58	135.58	135.62	135.62	135.93	135.93	135.40	135.40
Fluoride	mg/L	0.07	0.01	0.07	0.07	0.08	0.08	0.06	0.06	0.07	0.07
Nitrate	mg/L	0.33	0.39	0.29	0.29	0.32	0.32	0.48	0.48	0.29	0.29
Sulfate	mg/L	< 3	< 3	< 3	3.00	< 3	3.00	5.65	3.00	< 3	3.00

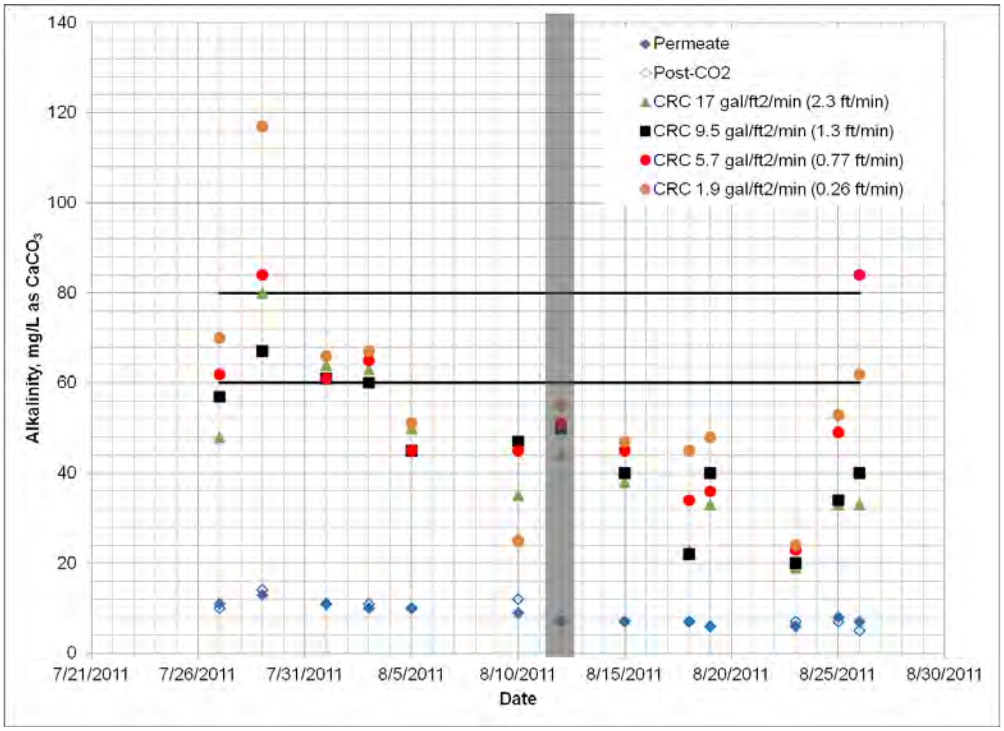

Figure 5.9. **Phase 2: Alkalinity for 1-mm calcite dissolution at various influent flow rates. Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.**

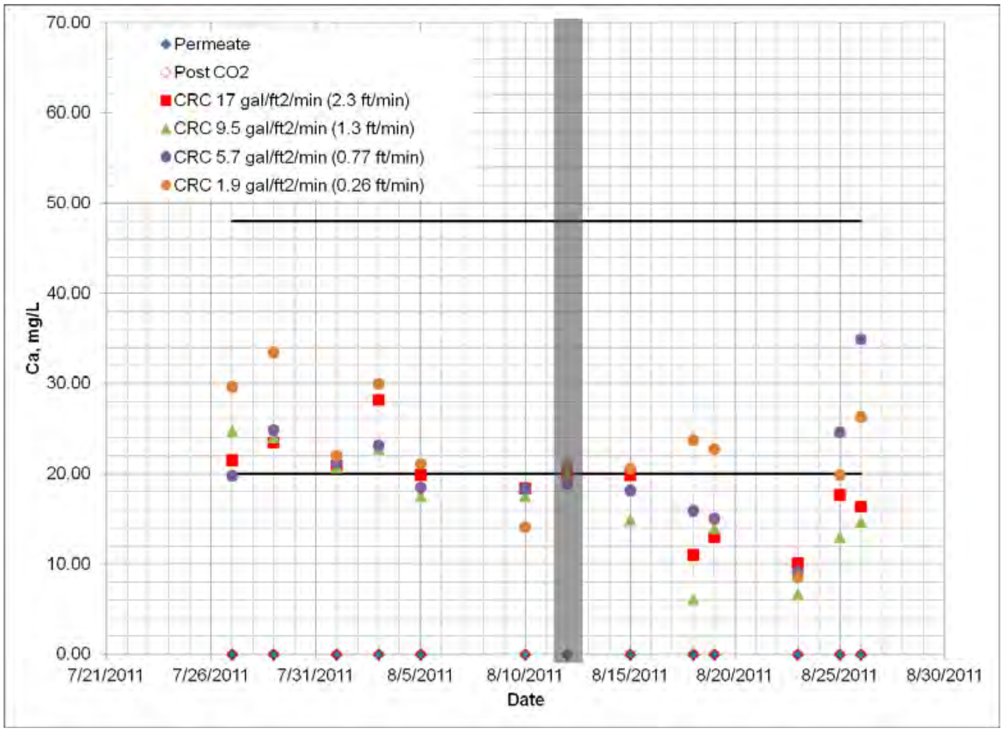

Figure 5.10. **Phase 2: Calcium concentration for 1-mm calcite dissolution at various influent flow rates. Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.**

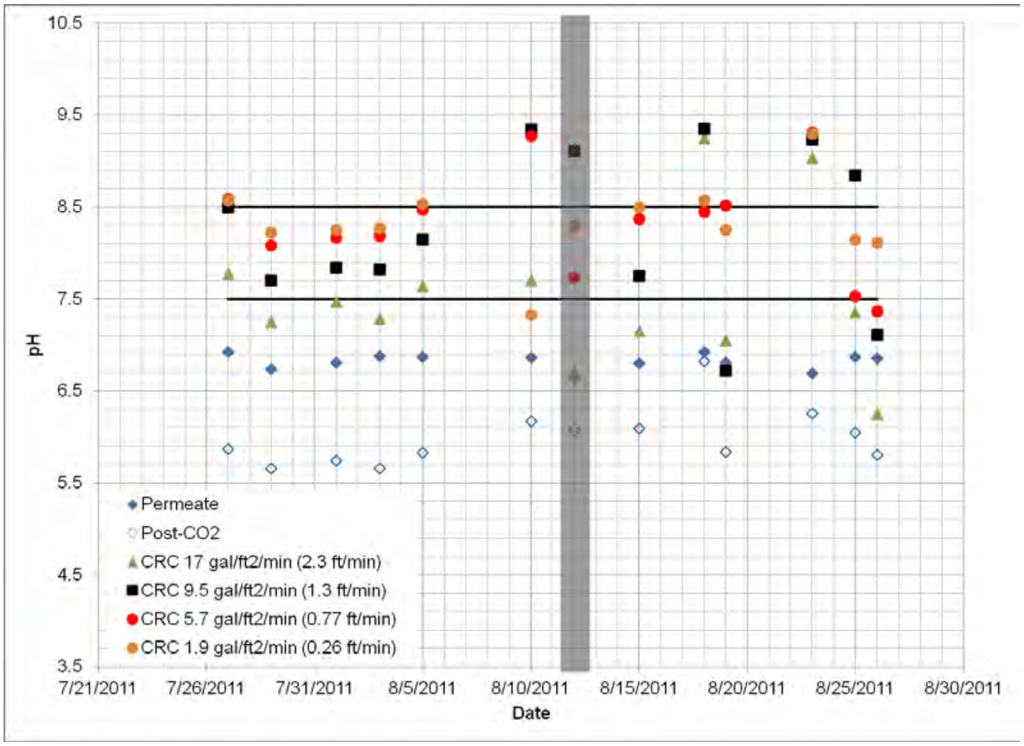

Figure 5.11. **Phase 2: pH for 1-mm calcite dissolution at various influent flow rates. Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.**

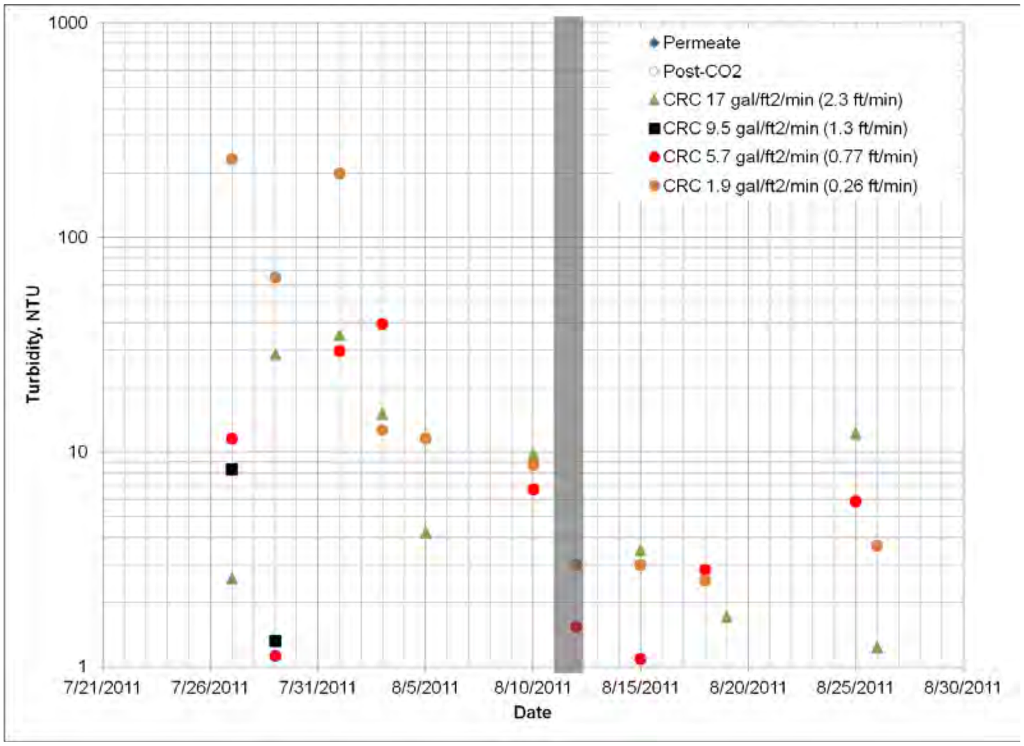

Figure 5.12. **Phase 2: Turbidity for 1-mm calcite dissolution at various influent flow rates. The gray bar in the figures indicates the depletion of CO_2 gas supply.**

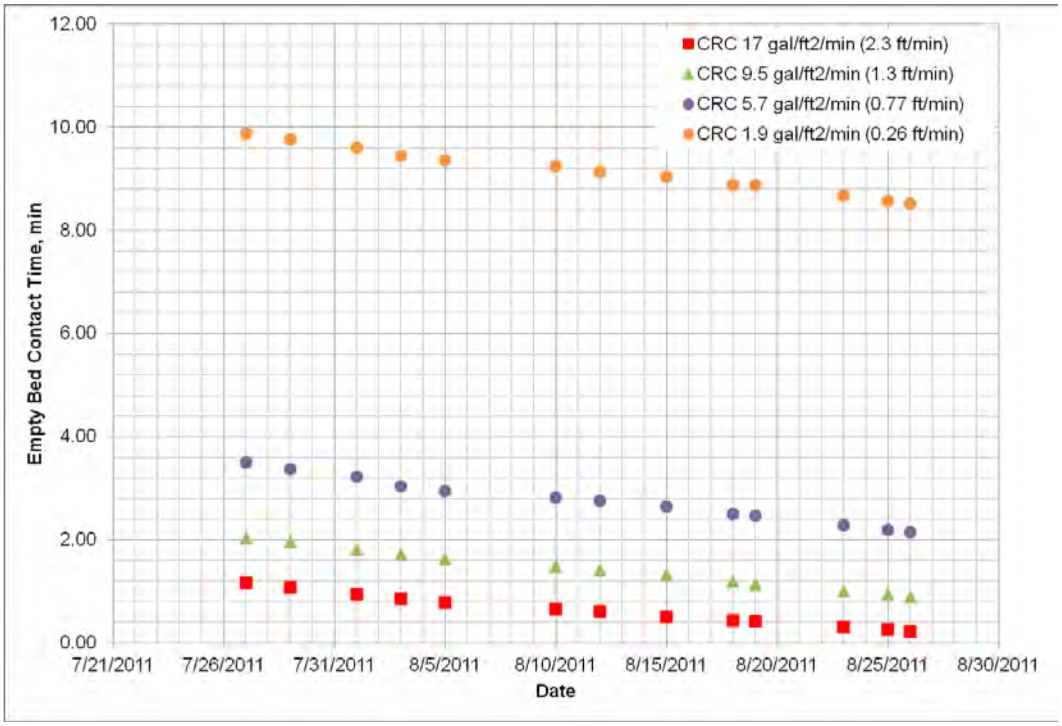

Figure 5.13. Phase 2: EBCT for 1-mm calcite dissolution at various influent flow rates.

Despite the changes in influent permeate water quality, the data shown in Figures 5.9 and 5.10 revealed a trend in the impact of residence time on finished water alkalinity and calcium hardness. At lower loading rates,the longer residence times in the column allowed more calcite to dissolve, and hence more bicarbonate and calcium were introduced into the water. This trend was markedly pronounced in the first week of testing, as shown in Figure 5.11, where the pH of the effluent revealed the effect of contactor residence time. When more bicarbonates were added into the water, the pH was elevated and the results showed that faster flow rates contributed to lower effluent pH values. Also, near the end of Phase 2, the effluent concentrations of calcium and alkalinity appeared to be diminished with EBCTs less than one minute.

The pH of the effluent revealed the effect of contactor residence time on the dissolution of calcite. When more carbonates dissolved into the water (i.e., the alkalinity was higher), the pH was elevated. The results showed that faster flow rates corresponded to lower effluent pH values.

Aside from the impacts on the chemical composition of the effluent, flow rates also influenced the finished water turbidity. Overall, as seen in Figure 5.12, spikes in turbidity readings during startup were noted, but after stable operations were achieved, the effluent turbidity settled to <10 NTU. Within the range of flow rates tested, consistently low turbidities (<4 NTU) were measured for an influent flow rate of 9.5 gpm/ft^2 (1.3 ft/min). The calcite bed fluidization at 17 gpm/ft^2 (2.3 ft/min) resulted in fine calcite particles that washed out of the contactor column and contributed to high turbidity measurements. At 1.9 gpm/ft^2 (0.26 ft/min), it was surmised that the low overflow rate took longer to rinse the initial media of the fines, which resulted in higher turbidity measurements for a longer duration after startup than the other columns. The pilot system was designed to have 2 feet of free board. The results from the Phase 2 experiments indicate that a higher allowance should be made in the full-scale design.

EBCT calculations to track calcite dissolution in the contactors are shown in Figure 5.13. Combined with the alkalinity, calcium hardness, pH and turbidity analysis, it can be deduced that higher EBCT correlates with higher calcium, alkalinity, and pH values in the effluent. In Phase 2, the range of contact times varied from 0.25 minutes to 10 minutes. For practical purposes, it would be desirable to minimize residence time in the contactors to achieve the target water quality. Based on the effluent water quality parameters (turbidity, calcium, alkalinity and pH), the optimum flow rate through the contactors is 9.5 gpm/ft^2 (1.3 ft/min) with contact time of 1 to 2 minutes EBCT.

The concentrations of calcium in the column effluent were correlated with the column influent pH, as shown in Figure 5.14. Based on equilibrium calculations, the concentration of calcium in the column effluent could be increased 20-30 percent by feeding more CO_2 to lower the column influent pH from 6.0 to 5.0.

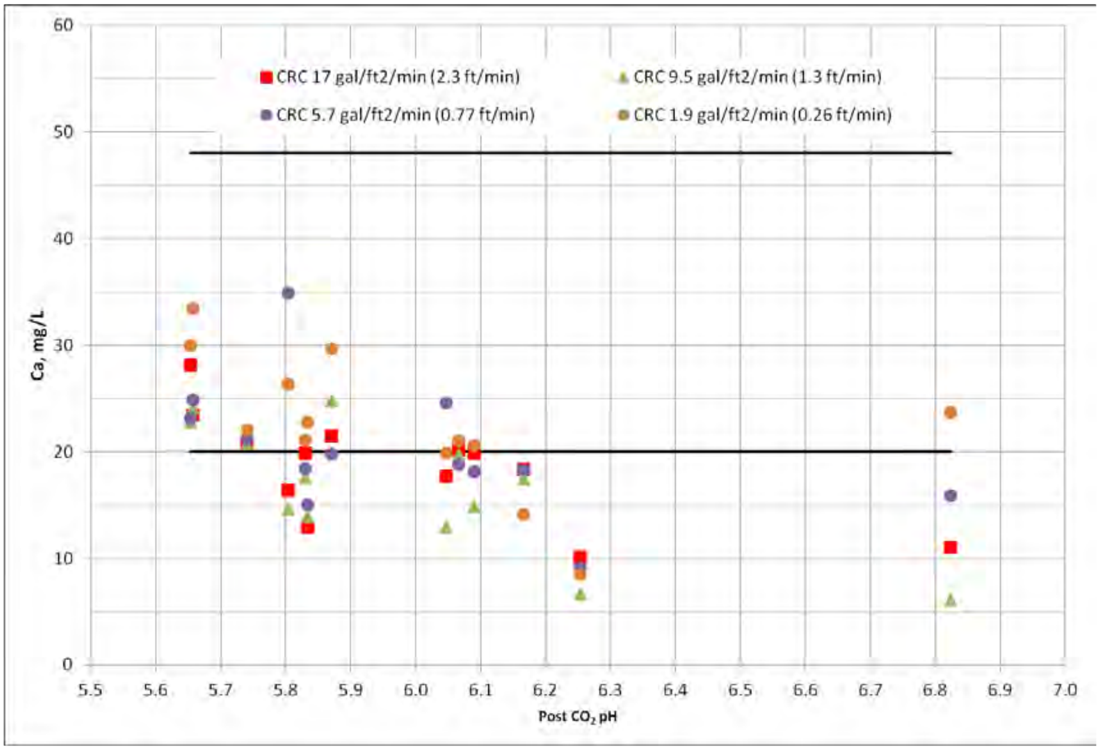

Figure 5.14. **Phase 2: Calcium concentration for 1mm calcite dissolution versus column influent pH.**

5.3 Phase 3 – Impact of calcite particle sizing

As discussed in Section 3.2.1.4, calcite particle size affects the contact surface area and therefore the rate of dissolution and contact time needed to reach equilibrium. Some effects of calcite particle size were alluded to in Section 5.1. In Phase 3 various particle sizes at 95 percent calcite purity from the same manufacturer were tested at a constant influent contactor flow rate of 3.8 gpm/ft^2 (0.51 ft/min). Four calcite products were selected from Imerys, which included *30/50* < *Z White* < XO *White* < *OZ White*, in order of increasing ranking of the particle sizes.

Two sets of data were collected in Phase 3. The first round of testing began on September 2, 2011 and lasted for 3 weeks. Unfortunately, the CO_2 boost pump for the $TOMCO_2$ unit failed on September 2. A replacement was installed on September 9. Data collected from The September 2-6, 2011 was not used in the average influent and effluent water quality analysis in Table 5.4. Pump failure in the first week of testing resulted in only a handful of data points to draw meaningful conclusions from, and it was decided that a second set of Phase 3 testing would be carried out to augment the data. The second set of testing occurred during the last week of October 2011, which lasted a week to avoid interference with the Kay Bailey Hutchison Desalination Plant annual RO clean-in-place operations. As the calcite sizes increased, the required caustic soda dose increased from 1.6 mg/L to 2.7 mg/L to obtain a LSI of 0.5 and a CCPP of over 4 mg/L as $CaCO_3$ for post-polishing.

The sieve analysis conducted before and after testing is shown in Figure 5.14. The sizing information conflicts with the manufacturer's reported size range. The discrepancy between the reported and analyzed particle size ranges are presented in Table 5.5. Based on the size distribution histogram in Figure 5.14, post-experiment calcite samples were observed to be larger than the initial samples. This observation is misleading, given that two separate samples were collected for the sieve analysis. Initial samples were taken from the calcite sample containers, and post-experiment samples were taken from the middle of the calcite contactor columns to average the dissolution effects between the top and bottom of the calcite contactors. It is very likely that the small particles that were measured initially dissolved quickly given the larger surface area, and were washed out of the column as indicated by the spikes in turbidity during startup. When a separate sample post-experimentation was collected, the remaining larger particles were analyzed, and a shift to larger sizes was measured. This suggests that in future experiments, post-experiment samples should be collected from the bottom of the calcite bed (where the immediate changes in calcite particles would be most prominent and indicative of calcite dissolution) as well as the top of the media bed, (to determine how much dissolution is occurring throughout the media bed.

Table 5.4. Phase 3 influent and effluent water quality.

				Effluent WQ							
				30/50		**XO White**		**Z White**		**OZ White**	
Parameter	**Unit**	**Influent WQ**	**Post CO_2 WQ**	**0.29 - 0.59 mm**	**Post NaOH**	**0.40 - 1.2 mm**	**Post NaOH**	**0.40 - 0.84 mm**	**Post NaOH**	**1.4 - 3.4 mm**	**Post NaOH**
Alkalinity	mg/L as $CaCO_3$	7.29	7.00	60.09	62.09	62.29	64.42	58.14	60.89	57.57	60.95
Hardness	mg/L as $CaCO_3$	6.86	6.43	62.43	64.17	64.11	63.97	59.86	62.27	59.00	62.09
pH	pH unit	6.77	5.63	8.21	8.71	8.15	8.68	8.01	8.73	7.84	8.73
Turbidity	NTU	0.14	0.08	0.18		4.19		5.29		0.24	
Temperature	°C	25.73	25.97	25.77	25.77	25.83	25.83	25.83	25.83	25.75	25.75
Conductivity	µS/cm	399.46	400.30	507.86		504.53		497.36		493.59	
Total Ions + SiO2	mg/L	267.64	268.20	308.55	310.01	311.52	313.17	306.29	308.56	305.17	308.34
TDS (SUM)	mg/L			272.01	274.02	273.54	275.67	270.64	273.40	269.70	273.12
LSI		-3.22	-4.36	0.07	0.58	0.02	0.56	-0.16	0.58	-0.34	0.58
CCPP		-11.00	-66.44	0.35	4.05	0.07	4.01	-1.03	4.09	-2.24	4.04
RI		13.20	14.36	8.07	7.55	8.11	7.55	8.33	7.57	8.52	7.58
Cations											
Calcium	mg/L	< 3	< 3	23.20	23.20	23.12	23.12	22.44	22.44	22.37	22.37
Potassium	mg/L	4.23	6.78	3.79	1.50	3.74	1.50	4.32	1.50	3.79	1.50
Magnesium	mg/L	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Sodium	mg/L	80.97	69.65	80.66	81.58	80.83	81.81	80.50	81.77	80.56	82.11
Aluminum	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Iron	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	0.01	< 0.01	< 0.01	< 0.01	0.02	< 0.01
Strontium	mg/L	0.02	0.02	0.05	0.05	0.08	0.08	0.06	0.06	0.06	0.06
Anions											
Silica	mg/L	1.62	1.62	1.68	1.68	1.70	1.70	1.71	1.71	1.73	1.73
Chloride	mg/L	120.73	135.88	121.91	121.91	122.10	122.10	122.11	122.11	122.03	122.03
Fluoride	mg/L	0.05	0.07	0.15	0.15	0.07	0.07	0.07	0.07	0.05	0.05
Nitrate	mg/L	0.38	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	0.21	0.21
Sulfate	mg/L	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3

Table 5.5. Reported and actual Imerys calcite particle sizes.

	30/50	XO White	Z White	OZ White
Reported Sizing (mm)	0.29 - 0.59	0.49-1.2	0.40 - 0.84	1.4 -3.4
Sieve analysis (mm)	0.25 - 1	0.25 - 0.5	1	1 - 2

Figures 5.15 to 5.20 show the alkalinity, calcium hardness, pH, turbidity, and EBCT for both sets of Phase 3 testing, respectively. Similar to Phase 2 testing, turbidity surges during startup were apparent in the first few days of testing in both the first and second round of testing (Figure 5.19). After the contactors had reached stable operations, where turbidity had settled, the measured effluent turbidities were consistently less than 5 NTU, with the sample producing the highest turbidity being XO White. This could be due to the small particle sizes of the XO White, as seen in Phase 1 where use of calcite samples of less than 0.5 mm corresponded to higher initial effluent turbidities. As calcite particle sizes decrease over time during the dissolution process, it was noted that even by the end of the phase, when the calcite beds have been depleted by half its original bed height, the smaller calcite particles did not contribute to turbidity surges in the effluent measurements. The turbidity spikes were only noticeable during startup when the initial flow into the contactors carried over the fines to the effluent stream. The turbidities of the effluent streams settled after a few days and were noticeably stable.

In terms of finished water alkalinity, calcium hardness, and pH, a general trend on the impact that particle sizes had on finished water quality was observed. Larger particles have a smaller surface area-to-volume ratio compared to the smaller particles—more calcite surface contacts the feed water in columns using smaller-particles. Therefore, at the same influent loading rate of 3.8 gpm/ft^2 (0.51 ft/min), less bicarbonate and calcium would dissolve into the water in the larger-particle systems. Within the same size range, 30/50 and XO White behaved interchangeably, but as calcite particle sizes increased from 1 mm (Z White) to 2 mm (OZ White), less calcium and bicarbonate dissolved into the finished water; hence, the effluent pH decreased as particle size increased. No discernible trends were observed in the second set of the testing, mostly because the contactor columns were refilled with new media and did not have enough time to reach stable operating conditions to produce reliable data. Despite smaller particle sizes (0.25 -to-0.5 mm) range contributing to higher finished water turbidities, all tested calcite samples demonstrated that the finished water quality goals were met with the 1-mm particles performing marginally better than the 2-mm particles.

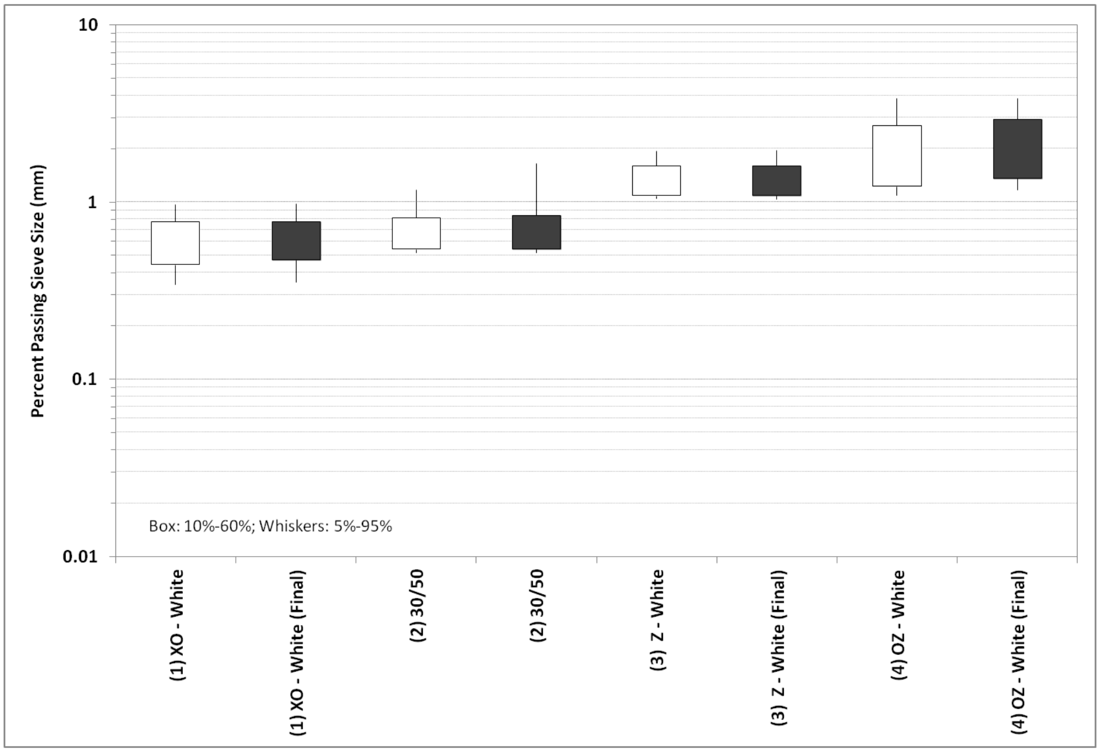

Figure 5.15. **Box-whisker plot of calcite particle size changes in Phase 3.**

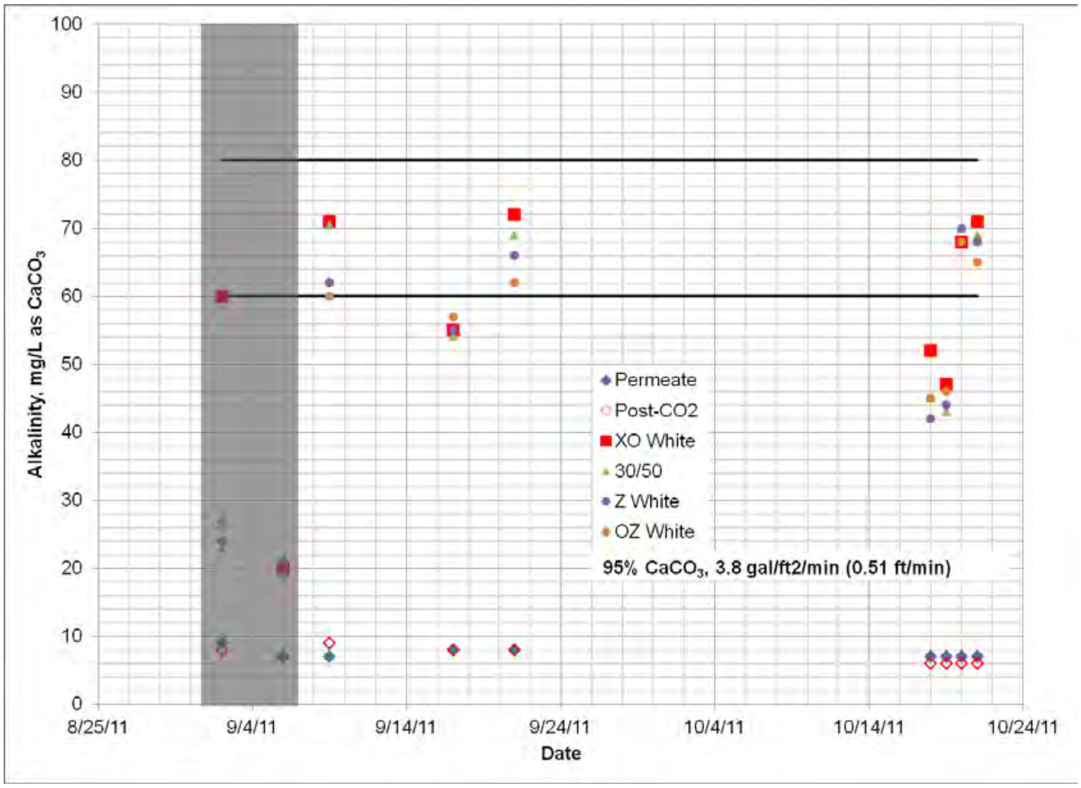

Figure 5.16. **Phase 3: Alkalinity for 95% $CaCO_3$ and 3.8 gpm/ft^2 (0.51 ft/min) calcite dissolution at various particle sizes. Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.**

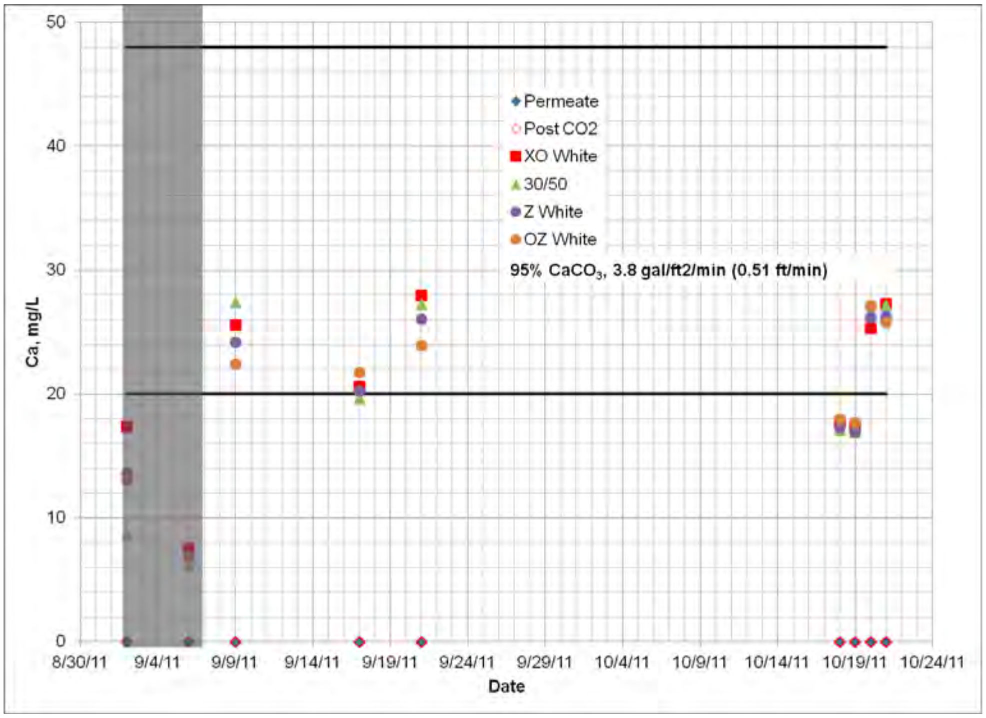

Figure 5.17. Phase 3: Calcium hardness for 95% $CaCO_3$ and 3.8 gpm/ft^2 (0.51 ft/min) 0.33 gpm calcite dissolution at various particle sizes. Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.

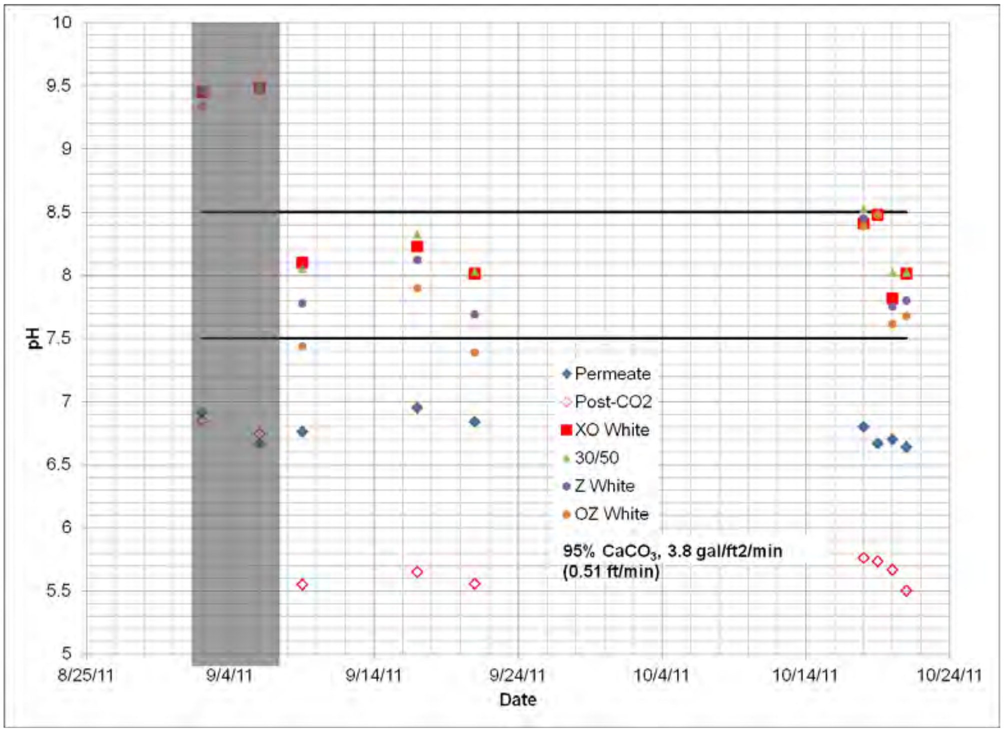

Figure 5.18. Phase 3: pH for 95% $CaCO_3$ and 3.8 gpm/ft^2 (0.51 ft/min) calcite dissolution at various particle sizes Finished water quality goals are represented by the area between the two horizontal lines. The gray bar in the figures indicates the depletion of CO_2 gas supply.

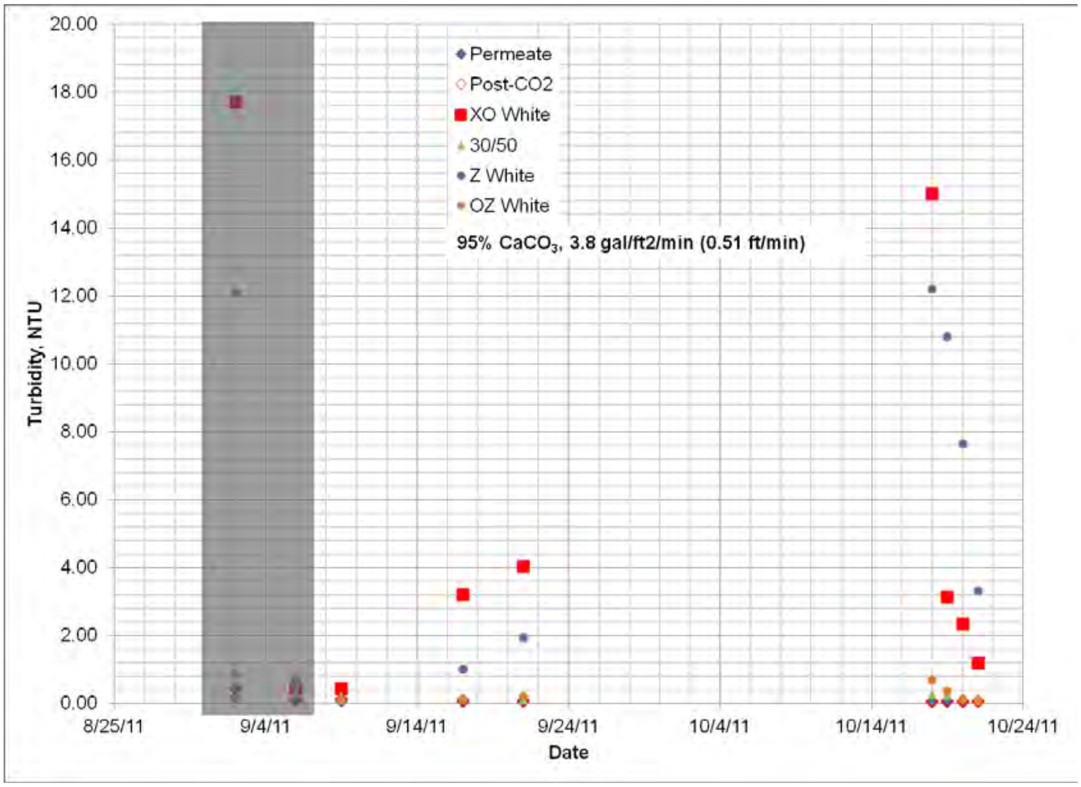

Figure 5.19. **Phase 3: Turbidity for 95% CaCO$_3$ and 3.8 gpm/ft^2 (0.51 ft/min) calcite dissolution at various particle sizes. The gray bar in the figures indicates the depletion of CO$_2$ gas supply.**

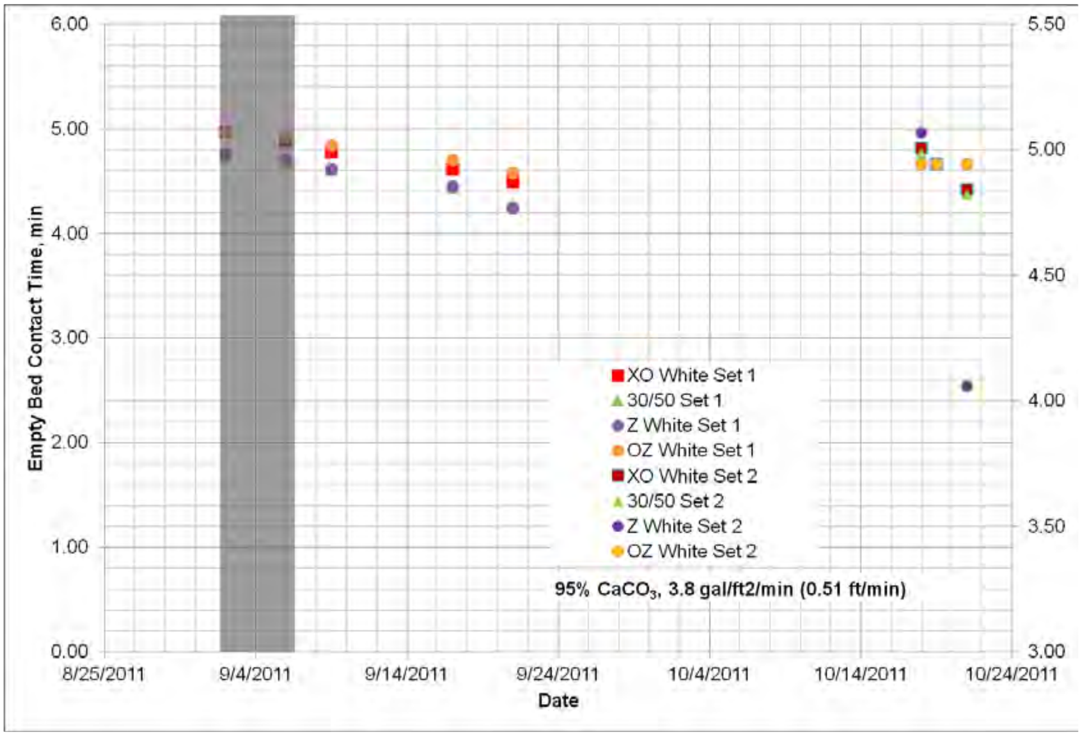

Figure 5.20. **Phase 3: EBCT for 95% CaCO$_3$ and 3.8 gpm/ft^2 (0.51 ft/min) calcite dissolution at various particle sizes. The gray bar in the figures indicates the depletion of CO$_2$ gas supply.**

5.4 Phase 4 – Optimizing treatment conditions

In Phase 1, it was determined that uniform calcite particle sizes exerted more influence on the finished water quality over the range of tested calcite purity. CRC Puri-Cal C at 95 percent purity and SM Vical 1130 at 97 percent purity emerged as favorable candidates for calcite recarbonation. In Phase 2, it was determined that 9.5 gpm/ft^2 (1.3 ft/min) was an optimum flow rate for the calcite dissolution process for the system. In Phase 3, calcite particles in the 1-mm and 2-mm size ranges proved to achieve finished water quality goals with minimum turbidity problems. For Phase 4 of the calcite testing, higher flow rates at 9.5 gpm/ft^2 (1.3 ft/min) and 17 gpm/ft^2 (2.3 ft/min), respectively, were selected for practical implementation. The goal was to demonstrate sufficient calcite dissolution with a high filtration rate for a small area footprint to improve the economics of implementation. In addition to CRC Puri-Cal C and Imerys OZ White and Z White calcite samples, an additional calcite sample derived from RO concentrate softening (Softening Pellet) was tested.

The test matrix was set up to run the 1-mm calcite products (CRC's Puri-Cal C and Imerys Z White) and the Carollo Pellets at 9.5 gpm/ft^2 (1.3 ft/min), and the larger OZ White sample at 17 gpm/ft^2 (2.3 ft/min) to determine the feasibility of using these design conditions. Phase 4 testing began on September 22, 2011 and lasted 2.5 weeks. The shortened testing period was accepted by the Texas Water Development Board to meet the project time constraints. The results of the average influent and effluent water quality are summarized in Table 5.6. As seen in the first three phases of testing, finished water LSI values were slightly negative, and the CCPP was less than 4 mg/L as $CaCO_3$. Caustic soda (NaOH) addition to post-treated water was modeled using RTW software to increase the pH (7.5 to 8.5), elevate the LSI to slightly above zero and maintain a CCPP value between 4 and 10 mg/L as $CaCO_3$ for anti-corrosion purposes.

The Phase 4 post-experiment calcite sample size distribution, shown in Figure 5.21, was observed to be larger than the initial samples—a phenomenon that was illustrated in Phase 3. As with the previous work, it is likely that the small particles that were measured initially dissolved quickly given the larger surface area, and subsequently washed out of the column as indicated by the spikes in turbidity during startup. When a separate sample post-experimentation was collected, the remaining larger particles led to a shift to larger size measurements. The smallest calcite sample tested in Phase 4 was the concentrate-softening pellet at a purity of less than 90 percent. It had an initial size range of 0.063-to-0.5 mm, and dissolution of the small particles during the experimentation shifted the size distribution of the remaining samples to the 0.25-to- 0.5 mm range. However, the effluent was low in pH at the flow rate tested, and a significant amount of caustic (8.1 mg/L) would be required to elevate the pH to , and hence the LSI and CCPP levels to over 0.5 and 4 mg/L as $CaCO_3$, respectively. Post-polishing caustic dose requirements for the CRC Puri-Cal C, Imerys Z White, and Imerys OZ White particles were 3.1 mg/L, 4.0 mg/L, and 5.7 mg/L, respectively.

Table 5.6. Phase 4 Influent and Effluent Water Quality

Parameter	Unit	Influent WQ	Post CO_2 WQ	Effluent WQ							
				Softening Pellets		**CRC Puri-Cal C**		**Imerys Z White**		**Imerys OZ White**	
				9.5 gpm/ft^2 (1.3 ft/min)						17 gpm/ft^2 (2.3 ft/min)	
				Pre-NaOH	**Post NaOH**	**Pre-NaOH**	**Post NaOH**	**Pre-NaOH**	**Post NaOH**	**Pre-NaOH**	**Post NaOH**
Alkalinity	mg/L as $CaCO_3$	6.75	6.80	62.00	72.13	48.50	52.38	43.75	48.75	32.25	39.38
Hardness	mg/L as $CaCO_3$	7.13	6.25	61.20	53.04	48.63	44.74	43.00	39.64	30.88	30.62
pH	pH unit	6.73	5.82	7.16	8.68	7.84	8.89	7.63	8.98	7.28	9.16
Turbidity	NTU	0.10	0.07	2.24		1.60		1.77		5.15	
Temperature	^oC	26.43	26.48	26.34	26.34	26.31	26.31	26.29	26.29	26.29	26.29
Conductivity	µS/cm	401.35	401.37	494.32		485.88		474.98		447.06	
Total Ions + SiO_2	mg/L	268.90	268.92	310.34	324.40	295.94	299.12	288.18	292.66	270.58	277.62
TDS (SUM)	mg/L			271.84	282.40	266.07	269.90	261.13	266.09	250.57	257.57
LSI		-3.28	-4.18	-1.06	0.53	-0.57	0.52	-0.88	0.52	-1.50	0.47
CCPP		-11.14	-43.04	-14.35	4.12	-3.08	4.03	-4.87	4.21	-8.28	4.11
RI		13.29	14.18	9.27	7.62	8.97	7.85	9.39	7.95	10.27	8.22
Cations											
Calcium	mg/L	< 3	< 3	18.75	18.75	15.43	15.43	13.39	13.39	9.78	9.78
Potassium	mg/L	4.02	3.89	3.99	1.50	3.65	1.50	3.73	1.50	3.78	1.50
Magnesium	mg/L	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Sodium	mg/L	63.19	62.09	64.15	68.81	63.12	64.90	63.09	65.39	63.09	66.37
Aluminum	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Iron	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.02	0.02	0.04	0.04
Strontium	mg/L	0.02	0.02	0.12	0.12	0.16	0.16	0.06	0.06	0.05	0.05
Anions											
Silica	mg/L	1.86	1.86	2.07	2.07	1.91	1.91	1.93	1.93	1.94	1.94
Chloride	mg/L	146.92	147.08	140.68	140.68	147.70	147.70	147.65	147.65	147.50	147.50
Fluoride	mg/L	< 0.05	< 0.05	0.06	0.06	< 0.05	0.05	< 0.05	0.05	< 0.05	0.05
Nitrate	mg/L	0.60	0.59	0.45	0.45	0.57	0.57	0.57	0.57	0.57	0.57
Sulfate	mg/L	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3

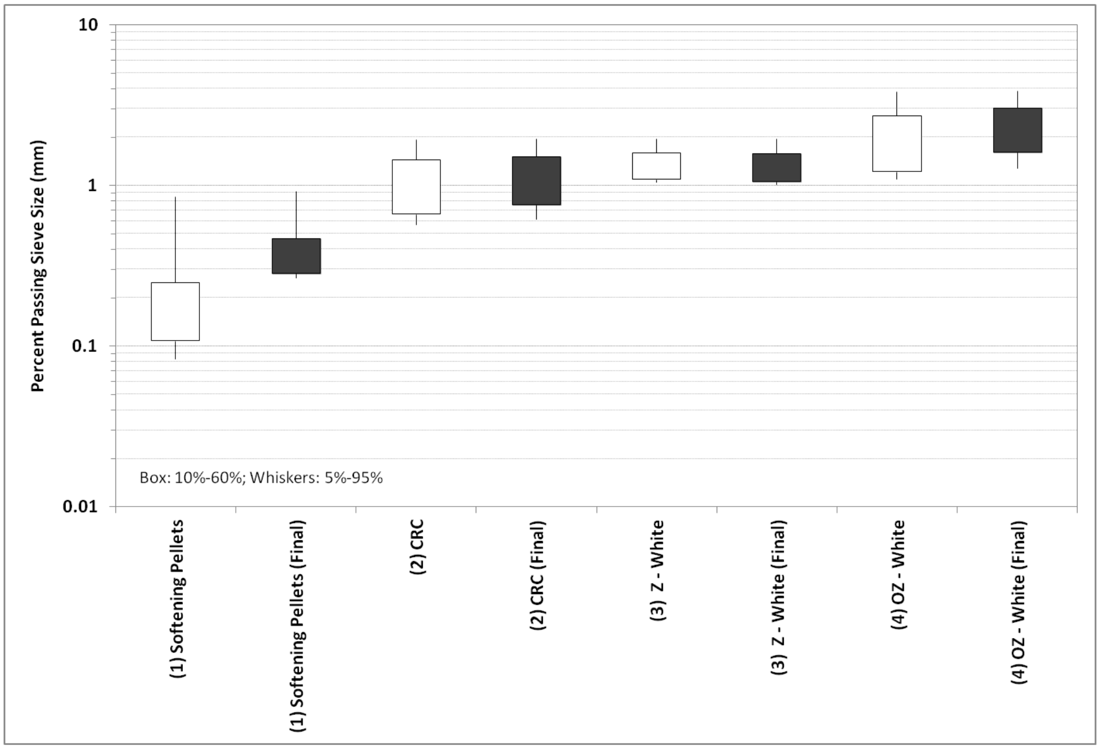

Figure 5.21. Box-whisker plot of calcite particle size changes in Phase 4.

Effluent alkalinity, calcium concentration, pH and turbidity measurements for individual runs are displayed in Figures 5.22 to 5.26. As expected, at a constant flow rate of 9.5 gpm/ft^2 (1.3 ft/min), the smaller Softening Pellets dissolved fastest, followed by CRC Puri-Cal and Imerys Z White. Post-treatment alkalinity and hardness goals were met by the Carollo Pellets and CRC Puri-Cal C at the this flow condition, followed very closely by the Imerys Z White samples. At 17 gpm/ft^2 (2.3 ft/min), the larger Imerys OZ White samples dissolved slower, and the reduction in contact time within the contactor column led to insufficient calcium and bicarbonate dissolution. From the EBCT curve in Figure 5.25, it appeared that contact times between 1.50 to 2 minutes were best for meeting post-treatment water qualities. Operating the reactor at a flow rate of 9.5 gpm/ft^2 (1.3 ft/min) also minimized turbidity spikes, as demonstrated in Phase 2. Amongst the tested calcite samples, CRC Puri-Cal C at 1 mm particle size and 95 percent purity is recommended for calcite post-treatment for the Kay Bailey Hutchison Desalination Plant permeate.

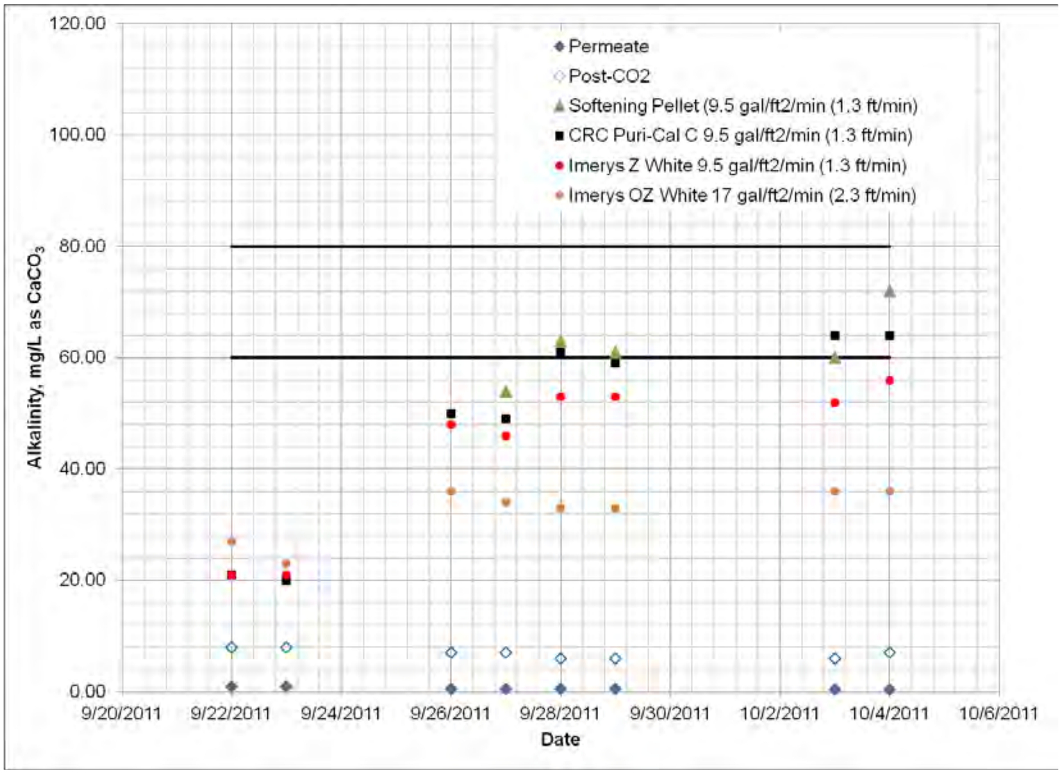

Figure 5.22. **Phase 4: Alkalinity for selected particle size, purity, and flow rate testing. Finished water quality goals are represented by the area between the two horizontal lines.**

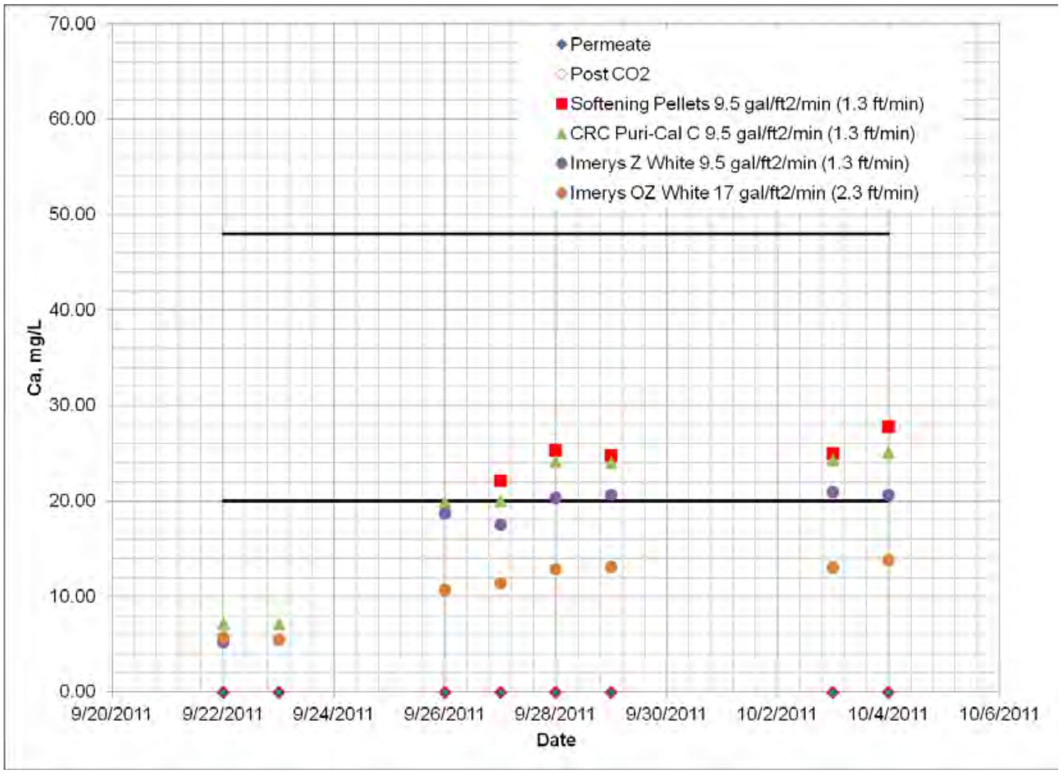

Figure 5.23. **Phase 4: Calcium hardness for selected particle size, purity, and flow rate testing. Finished water quality goals are represented by the area between the two horizontal lines.**

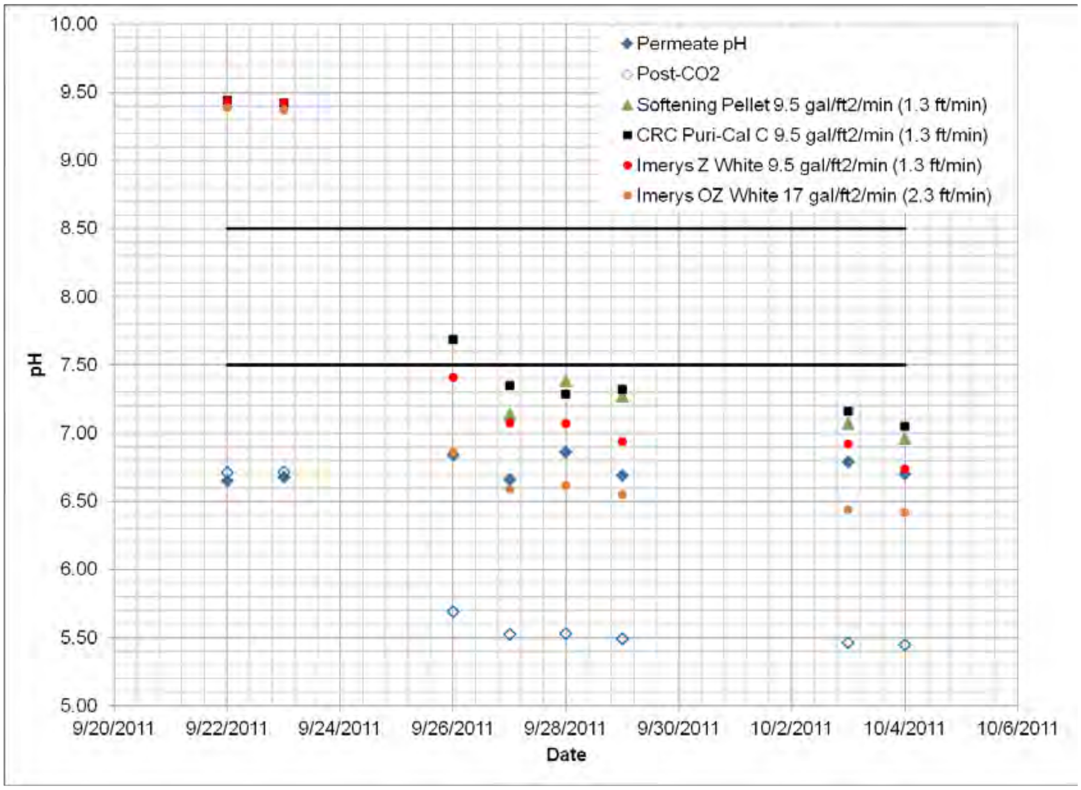

Figure 5.24. **Phase 4: pH for selected particle size, purity, and flow rate testing. Finished water quality goals are represented by the area between the two horizontal lines.**

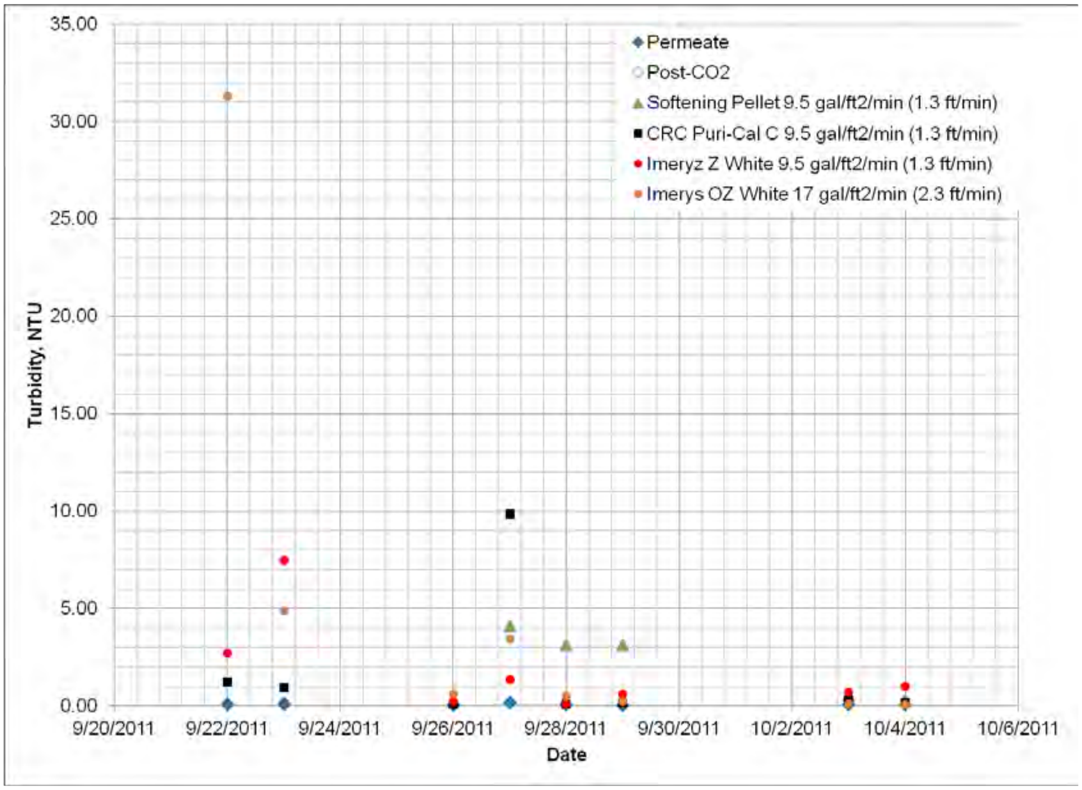

Figure 5.25. **Phase 4: Turbidity for selected particle size, purity, and flow rate testing.**

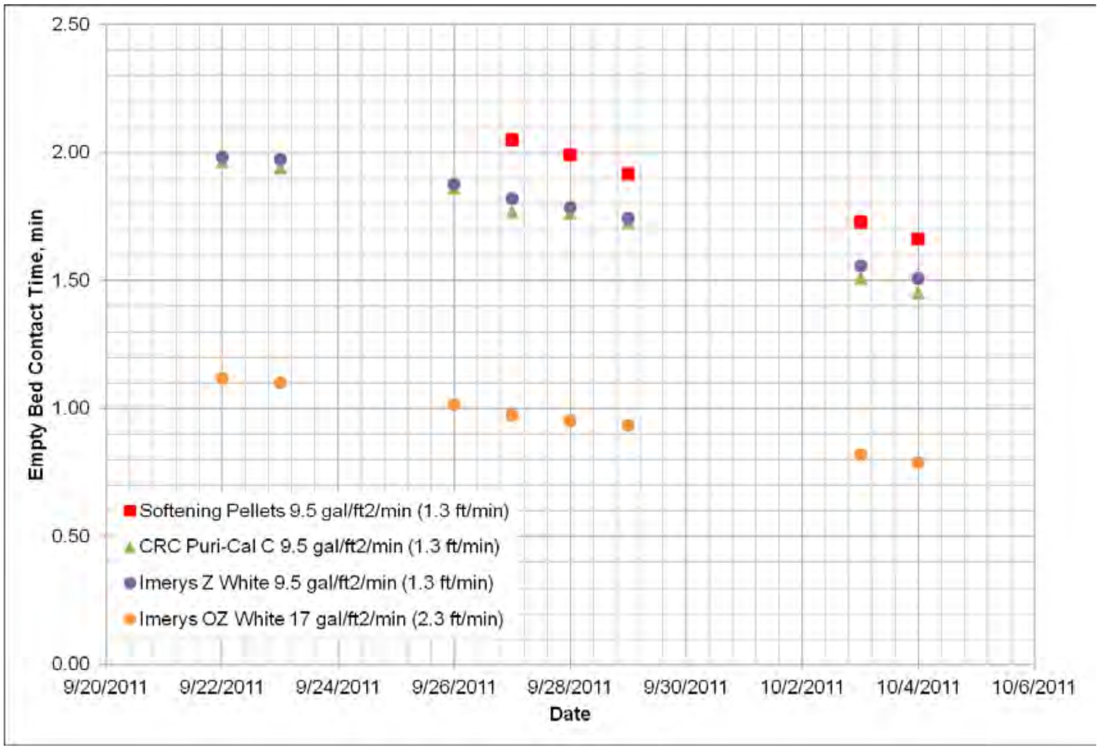

Figure 5.26. **Phase 4: Empty Bed Contact Time (EBCT) for selected particle size, purity, and flow rate testing.**

6 Cost analysis

Table 6.1 provides a conceptual purchased capital cost estimate to implement calcite post-treatment contactors for treatment capacities of 1-, 5-, and 10-MGD plant. These cost estimates were provided by DrinTec Solutions, which produces commercialized upflow calcite contactors for RO permeate post-treatment processes. Their patented process maintains a constant calcite bed height, which simplifies the calcite reload operation by feeding calcite particles continuously using a series of small funnels. Operation and maintenance costs in terms of chemical consumables only are provided in Table 6.2, using the calcite pilot consumption from the Kay Bailey Hutchison Desalination Plant as the basis for cost estimation. A 90 percent online use factor and a 15 percent contingency factor were built into the cost analysis.

7 Conclusions and recommendations

In any calcite dissolution reaction, though it is possible to achieve finished water calcium hardness and alkalinity goals, final polishing by caustic soda dosing is required to elevate the LSI and CCPP indices to above zero and 4 mg/L as $CaCO_3$ for anti-corrosion purposes. This phenomenon was observed for all four phases of upflow calcite contactor testing. The design for the pilot contactors did not allow continuous calcite contactor refill to maintain a constant EBCT, but a constant influent flow rate to the contactor permitted studies on the impact of residence time to be conducted. For full-scale design, an automatic calcite loader should be included to maintain calcite dissolution driving force in the contactor. Fluctuations in the influent water quality should be monitored constantly with reliable field measurements so operators can adjust CO_2 dosing to meet finished water quality goals. During pilot testing, it was observed that turbidity spikes during startup was a consistent occurrence, due to fines present in the initial calcite loading in the contactors. The continuous decrease in particle sizes during the dissolution process after the initial turbidity surges did not contribute to increased turbidities in the effluent measurements. For normal operations, to avoid turbidity surges during calcite material loading, the following recommendations are suggested:

- Install a system to pre-wash calcite particles to remove fines.
- Design for redundant calcite contactors, whereby one contactor is pre-washed and at standby, so that interruptions to operations are minimized when the depleted contactor is refreshed with new calcite.

Calcite samples obtained from different manufacturers were highly varied in their particle size distribution. From the study, it was determined that samples with a narrow size distribution outperformed those with broad distributions in terms of effluent turbidities. For practical applications, the effective size (d_{10}) and the uniformity (d_{60}/d_{10}) should be specified. The results of this study indicated that 1 mm calcite particles at an effective size of 0.66-0.67 mm with a uniformity coefficient of 2.16-2.17 produced low effluent turbidities. Specific conclusions for each of the phases are summarized below.

7.1 Impact of calcite purity on effluent water quality

In Phase 1, calcite particles in the 1-mm size range (manufacturer-reported) were tested at a fixed influent flow rate of 3.8 gpm/ft^2 (0.51 ft/min) across a range of calcite purities from 95 to 98 percent. The experimental results indicated that within the tested range of calcite purities, there was no discernible impact on effluent water quality in terms of pH, alkalinity, or calcium hardness. Sieve analysis conducted for the tested particles and effluent turbidity suggested that calcite particles that are less than 0.5 mm could contribute to high turbidities. An influent loading rate of 3.8 gpm/ft^2 (0.51 ft/min) resulted in EBCTs ranging from 3 to 8 minutes. At this loading rate there was more than enough contact time in the calcite contactors to reach equilibrium. Of the tested calcite products, CRC Puri-Cal C was selected as a candidate sample for subsequent testing in Phase 2 due to its narrow size distribution (around 1 mm) and low effluent turbidity.

Table 6.1. Capital cost for commercial DrinTec System and TOMCO$_2$ carbon dioxide feed system.

Capacity	Quantity	Description	Dimensions	Unit Budgetary Price	Sub-Total	Total
1 MGD						
	3	FRP vessels	2.04 m Diameter x 5.00 Tall (including built-in silo for constant calcite feed)	$26,900.00	$80,700.00	
	1	CO$_2$ System	15 lb/hr 1-1/2" pressurized solution feed panel and 6 ton storage tank (includes electric vaporizer, pressure regulator, controls, diffuser assembly)	$150,000.00	$150,000.00	
	1	Building	700 sq. Ft	$150/sq. ft	$105,000.00	
	1	Electrical/ Controls	n/a	10%	$33,570.00	
	1	Interconnecting Piping	n/a	15%	$50,355.00	
						$419,625.00
	1	Engineering	n/a	15%	$62,943.75	
	1	Legal/ Administration	n/a	10%	$41,962.50	
	1	Contingency	n/a	15%	$62,943.75	
						$587,475.00
5 MGD						
	3	Concrete Cells	3 m x 7 m (4.5 m for contactor bed height)	$98,420.40	$492,102.00	
	1	CO$_2$ System	70 lb/hr 2" pressurized solution feed panel and 18 ton storage tank (includes electric vaporizer, pressure regulator, controls, diffuser assembly)	$190,000.00	$190,000.00	
	1	Building	1800 sq/ft	$150/sq. ft	$270,000.00	
	1	Electrical/ Controls	n/a	10%	$95,210.20	
	1	Interconnecting Piping	n/a	15%	$142,815.30	
						$1,190,127.50
	1	Engineering	n/a	15%	$178,519.13	
	1	Legal/ Administration	n/a	10%	$119,012.75	
	1	Contingency	n/a	15%	$178,519.13	
						$1,666,178.50

Table 6.1. Capital cost for commercial DrinTec System and TOMCO$_2$ carbon dioxide feed system.

Capacity	Quantity	Description	Dimensions	Unit Budgetary Price	Sub-Total	Total
10 MGD						
	6	Concrete Cells	3 m x 7 m (4.5 m for contactor bed height)	$98,420.40	$984,204.00	
	1	CO$_2$ System	140 lb/hr 3" pressurized solution feed panel and 38 ton storage tank (includes electric vaporizer, pressure regulator, controls, diffuser assembly)	$245,000.00	$245,000.00	
	1	Building	3300 sq ft	$150/sq. ft	$495,000.00	
	1	Electrical/ Controls	n/a	10%	$172,420.40	
	1	Interconnecting Piping	n/a	15%	$258,630.60	
						$2,155,255.00
	1	Engineering	n/a	15%	$258,630.60	
	1	Legal/ Administration	n/a	10%	$172,420.40	
	1	Contingency	n/a	15%	$258,630.60	
						$2,844,936.60

Note:
Preliminary cost estimate may vary from actual cost due to field conditions and construction market

Table 6.2. Annual O&M for chemical consumables.

		Treatment capacity (MGD)					
Description	**Unit**	**1**		**5**		**10**	
Calcite Consumption	kg/day	184	209	920	1046	1841	2092
	lb/day	405	460	2025	2301	4049	4602
	lb/year	133026	151166	665131	755831	1330262	1511662
	$/ton	345	345	345	345	345	345
	$/lb	0.1725	0.1725	0.1725	0.1725	0.1725	0.1725
	$/year	**$22,948**	**$26,077**	**$114,736**	**$130,381**	**$229,471**	**$260,762**
CO_2 consumption	lb/hr	10	14	52	69	104	139
	lb/day	250	333	1,250	1,667	2,500	3,333
	lb/year	82,124	109,499	410,622	547,496	821,245	1,094,993
	$/lb	0.15	0.15	0.15	0.15	0.15	0.15
	$/year	**$12,319**	**$16,425**	**$61,594**	**$82,125**	**$123,187**	**$164,249**
Caustic Soda	mg/L	2.4	3.1	2.4	3.1	2.4	3.1
	lb/day	20	26	100	129	200	258
	lb/year	6575	8493	32876	42465	65752	84930
	$/lb	0.88	0.88	0.88	0.88	0.88	0.88
	$/year	**$5,787**	**$7,474**	**$28,932**	**$37,370**	**$57,863**	**$74,739**
Subtotal	$/year	$41,054	$49,976	$205,262	$249,876	$410,521	$499,750
Total (incl 15% contingency)	**$/year**	**$47,212**	**$57,472**	**$236,051**	**$287,357**	**$472,099**	**$574,713**

7.2 Impact of influent flow rate on effluent water quality

In Phase 2, the objective was to determine the impact of influent loading rates from 1.9 gpm/ft^2 (0.26 ft/min) to 17 gpm/ft^2 (2.3 ft/min) on effluent water quality. CRC Puri-Cal C was used as the test sample. The experiment results indicated that as flow rate increases, contact time between the influent permeate and the calcite particles decreases, and the dissolution rate also decreases. The longer the contact time, the higher the amount of calcium and bicarbonate were introduced to the effluent (i.e., the higher the concentrations of calcium and alkalinity rose). At the highest influent flow rate, 17 gpm/ft^2 (2.3 ft/min), the velocity of the flow fluidized the calcite bed within the contactors and led to calcite particle blow out. The optimum loading rate that achieved the effluent water quality goals was 9.5 gpm/ft^2 (1.3 ft/min). The optimum contact time was 1.5 to 2.5 minutes in the contactor columns.

7.3 Impact of particle sizes on effluent water quality

In Phase 3, the objective was to determine the impact of calcite particle sizes (0.25 to 2 mm) on effluent water quality. Four calcite products from the same manufacturer were selected, all with the same calcite purity of 95 percent and tested at the same flow rate of 3.8 gpm/ft^2 (0.51 ft/min). Smaller calcite particles in the contactor bed resulted in higher surface area, which led to a higher rate of calcite dissolution and hence, more calcium and bicarbonate added to the water. Calcite particles that were less than 0.5 mm with a broad size distribution contributed more to high effluent turbidities, and 1-mm particles produced marginally better effluent water qualities compared to the 2-mm particles.

7.4 Optimized treatment conditions

For Phase 4 of calcite testing, higher flow rates at 9.5 gpm/ft^2 (1.3 ft/min) and 17 gpm/ft^2 (2.3 ft/min) were tested with the candidate calcite samples selected from Phases 1 to 3. The goal was to demonstrate sufficient calcite dissolution with a high filtration rate for a small area footprint to improve the economics of implementation. The tested calcite samples were CRC Puri-Cal C and Imerys Z White in the 1-mm range, the 2-mm Imerys OZ White, and an additional calcite sample derived from RO concentrate softening (Carollo Pellet) as a means for reuse.

Of the four products tested, the smallest calcite sample in Phase 4 was the Softening Pellets at a purity of less than 90 percent. At a constant flow rate of 9.5 gpm/ft^2 (1.3 ft/min), the smaller S Pellets dissolved faster, followed by CRC Puri-Cal and Imerys Z White, and lastly by OZ White. Phase 4 test results confirmed that contact times between 1.50 and 2 minutes were best for meeting post-treatment water qualities. Operating the reactor at a flow rate of 9.5 gpm/ft^2 (1.3 ft/min) also minimized turbidity spikes, as demonstrated in Phase 2. Amongst the tested calcite samples, CRC Puri-Cal C at 1 mm and 95 percent purity would be recommended for calcite post-treatment of the permeate from the Kay Bailey Hutchison Desalination Plant.

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Appendix A:
Calcite Dissolution Model

Calcite dissolution model

As $CaCO_3$ dissolves, particle size, bed depth, bed porosity, flow velocity and pressure drop in the contactor change with time. Limestone dissolution rate models have been developed to encompass these variables for contactor design. The U.S. EPA published a limestone dissolution rate study in 1995 that was developed at Syracuse University (Letterman, 1995) for the design of limestone contactors. For a contactor operating at steady state, the calcite dissolution process can be modeled by Equation 1 through 3, as given below.

$$r = k_0 a\left(C_{eq} - C\right) \qquad \text{(Equation 1)}$$

Where r is the calcium carbonate dissolution rate (moles per liter/centimeter^2/seconds), C_{eq} is the equilibrium calcium ion concentration (moles per liter), C is the bulk calcium concentration (moles per liter), a is the area of $CaCO_3$ per unit volume of fluid (centimeter^{-1}), and k_0 is the overall dissolution rate constant (centimeter/second).

The overall dissolution rate constant, k_0, is governed by both a mass transfer rate constant (k_m) and a first-order surface reaction rate constant (k_s).

$$k_o = \left(\frac{1}{k_m} + \frac{1}{k_s}\right)^{-1} \qquad \text{(Equation 2)}$$

This model assumes that the rate of dissolution is controlled by two resistances that act in series: a surface reaction that controls the release of calcium from the solid and a mass transfer resistance that controls the rate of calcium transport between the solid surface and the bulk solution (Letterman, 1995).

$$N_D \frac{d^2C}{dZ^2} - \varepsilon \frac{dC}{dZ} + r\theta = 0 \qquad \text{(Equation 3)}$$

Where N_D is the dimensionless axial dispersion number, Z is the dimensionless depth, ε is the porosity of the calcite particles (assumed to be 0.4 for random packing configuration), and θ is the mean fluid residence time (in seconds).

By substituting Equation 1 into 3, the steady-state model that relates the depth of calcite required in the contactor to the desired effluent water chemistry, influent water chemistry, calcite particle size and shape, bed porosity, water temperature and superficial velocity is defined by:

$$\frac{C_{eq} - C_{bL}}{C_{eq} - C_{b0}} = \exp\left\{-\frac{k_0 aL\varepsilon}{U_s} + \left(\frac{k_0 aL\varepsilon}{U_s}\right)^2 N_D\right\} \qquad \text{(Equation 4)}$$

Where C_{b0} is the calcium concentration in the influent of a contactor (moles per liter), C_{bL} is the calcium concentration in the effluent of a contactor (moles per liter), L is the overall depth of a contactor (centimeter), and U_s is the superficial velocity of the fluid (centimeter/second).

The interfacial area, a, can be calculated by Equation 1.

$$a = \frac{6(1-\varepsilon)}{d\varepsilon\psi} \qquad \text{(Equation 5)}$$

Where *d* is the diameter of the calcite particle, and ψ is the sphericity of the calcite particle (assumed to be 0.8). For any particle, the sphericity may be calculated using Equation 2.

$$\psi = \frac{\pi d^2}{S} \qquad \text{(Equation 6)}$$

Where *S* is the actual surface area of the particle. For an irregular media like calcite, *d* may be estimated using the effective size from a standard sieve analysis and *S* may be determined by adsorption measurements or measurement of pressure drop in a bed of particles.

Based on this kinetic model, a computer program called DESCON (http://rdletter.mysite.syr.edu/software.html) was developed. In 2003, the mathematical code used for the DOS-based DESCON program was incorporated into an Excel® spreadsheet program-- "Calcite Bed Contactor – Corrosion Control and Treatment Process Analysis Program.xls" (Schott, 2002).

Calcite dissolution rate models developed by Letterman and other published authors (Plummer et al., 1979 and Yamauchi et al., 1987) were compared by Hasson et al. in 2006 (Hasson et al, 2006) and the paper reported that some researchers assumed that the dissolution process was controlled by surface chemical reactions while others assumed a mass transfer controlled process. Different mass transfer models were adopted in each of the published studies. Due to the lack of consensus in the mechanisms of calcite dissolution published in literature, lab and pilot testing is recommended prior to the design of full-scale calcite contactors.

Appendix B:
Entities the TWDB Calcite Post-Treatment Demonstration Project Study Benefits

LIST OF ENTITIES THE TWDB CALCITE POST-TREATMENT DEMONSTRATION PROJECT STUDY BENEFITS

Typically, brackish groundwater RO permeate is blended with feed water to provide appropriate pH, alkalinity and hardness adjustment of finished water to prevent distribution infrastructure corrosion. The use of upflow calcite contactors for post-treatment of RO permeate is an emerging method to provide non-corrosive finished water without the use of feed water bypass blending. This study provides reverse osmosis system designers, engineers, federal, state and local regulators a better understanding of upflow calcite reactor technology design.

Upflow calcite contactors provide a permeate post-treatment option for existing and future reverse osmosis facilities that have challenges with meeting their finish water quality goals. This study will benefit stakeholders involved in seawater desalination facilities (for example, cities of Brownsville and Laguna Madre) as well as high TDS brackish desalting facilities where post treatment blending may be limited. The study may also benefit other applications for membrane treatment such as advanced wastewater reuse and groundwaters with specific feed water constituents that limit bypass blending to achieve finish water goals (for example, San Antonio Water System and City of San Angelo). These groundwaters may contain high concentrations of one or a combination of the following: nitrates, arsenic, and radionuclides.

Appendix C:
Upflow Calcite Contractor Study Protocol

Upflow Calcite Contactor Pilot Study Protocol

Final

by

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Wen Yi Shih, Ph.D.
Bradley Sessions

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Austin, Texas 78711-3231
April 2012

Texas Water Development Board

Report #1004831105

Upflow Calcite Contactor
Pilot Study Protocol

by
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Carollo Engineers, Inc.

April 2012

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1 Introduction

1.1 Background

Tightening restrictions on the use of freshwater resources and lack of traditional water sources have led to increasing usage of reverse osmosis membrane technologies to tap into brackish water resources. The reverse osmosis process removes dissolved solids from a source water, including calcium and bicarbonate/carbonate ions. The resulting reverse osmosis permeate will typically have unacceptably low levels of calcium hardness and alkalinity. Without additional treatment, the reverse osmosis permeate would be unappealing aesthetically, poorly buffered against changes in pH, and aggressive to infrastructure components.

Typically, pH adjustment and the addition of calcium and alkalinity to reverse osmosis permeate are required prior to distribution. A corrosive reverse osmosis permeate is "stabilized" to protect downstream pipelines and storages, usually by blending with reverse osmosis feed water, chemical dosing, and lime/calcite dissolution to maintain a permeate pH between 6.8 and 8.1 to meet potable water specifications. Blending the reverse osmosis permeate with feed water is currently the most common approach to stabilizing a reverse osmosis finished water in the United States. However, this approach may be limited by high concentrations of nitrates, arsenic, radionuclides, and other regulated contaminants in the source water.

The use of upflow contactors is recognized in Europe and the Caribbean to be an emerging method of post-treatment of reverse osmosis permeate to provide a non-blended, stable, non-corrosive, finished water. Nevertheless, design criteria to develop these systems is not well-established in the United States. In Task 1 of this study, a summary of the state of the technology, a preliminary assessment of calcite sources in the United States, and an evaluation of gaps in the available information was presented to the Texas Water Development Board as Component A of the Draft Final Report. Based on this information provide in this summary, the following protocol was developed to perform a pilot investigation to provide guidance criteria to optimize upflow calcite contactor design.

1.2 Purpose and objectives

The purpose of this document is to present an experimental plan to evaluate upflow calcite contactor design parameters for optimization of reverse osmosis permeate stabilization. The major objectives of this testing are to:

- Evaluate three design parameters: empty-bed contact time, particle size, and calcite purity.
- Evaluate up to two (2) possible synergistic combinations of the above design parameters.
- Evaluate particle size reduction during upflow calcite contactor operations.
- Analyze calcite particles from up to five (5) select contactors for the presence of adsorbed inorganic foulants on the particles.

2 Finished water quality goals

Based on the applicable state and federal regulations and current knowledge in engineering practice, finished water quality goals were established for permeate stabilization by upflow calcite contactors (Table 2-1).

Table 2-1 Finished water quality goals.

Parameter	Unit	TCEQ SMCL[a]	Finished water quality goal	Basis for goal
pH	---	> 7	7.0 – 8.5	National Secondary Drinking Water Regulations
Alkalinity	milligram per liter as $CaCO_3$	---	60 - 80	D'Antonio et al. 2008
Calcium	milligram per liter as $CaCO_3$	---	50 - 120	World Health Organization, 2004 and Birnhack et al. 2008
Langlier Saturation Index	---	Non-corrosive	> 0	Lahav and Birnhack, 2007
Ryznar Index	---	Non-corrosive	< 10	Lahav and Birnhack, 2007
Calcium Carbonate Precipitation Potential	milligram per liter as $CaCO_3$	---	4 - 10	Lahav and Birnhack, 2007

[a] Secondary Maximum Contaminant Limit

3 Pilot testing location

Pilot testing for the upflow calcite contactors will be conducted in the CHIWAWA Laboratory at the Kay Bailey Hutchison Plant in El Paso, Texas. The facility has an area that is used for research. A 6-foot by 12-foot section of this area is available and will be adequate to locate the equipment for this pilot study. The permeate is fed at 4 – 4.5 pounds per square inch to the research area by a 2-inch pipe with a steel ball valve on the end of it. Single-phase power at 110 volts is available on-site.

4 Testing protocol

4.1 Process flow diagram

An overall process flow diagram for the testing is presented in Figure 4-1. Permeate from the Kay Bailey Hutchison Desalination Plant will be supplied to the pilot at 20 gallons per minute and 4 – 4.5 pounds per square inch. A centrifugal pump will be used to increase the permeate pressure for use in the upflow calcite contactor pilot plant. A side-stream of permeate and compressed carbon dioxide (CO_2) will be used to generate a carbonic acid solution. This solution will be injected into the permeate to lower its pH from 6.8 to 5.5 to condition the water for calcite dissolution. The pH of the acidified permeate will be controlled by a pH probe with a feedback loop to the Carbonic Acid Solution Feed Panel. The acidified permeate will be split between four upflow calcite contactors operating in parallel for each experiment. This will allow up to four conditions to be in operation with the same 'history' of feed water quality. The effluents from each upflow contactor will be combined and sent to a waste drain at the Kay Bailey Hutchison Plant.

Design criteria for the various major testing equipment and an experimental plan are presented in the following sections.

4.2 Process testing equipment

The following section includes calcite selection and technical specifications for the major process testing equipment:

- Upflow Contactors
- CO_2 Injection System

4.2.1 Design criteria for upflow contactors

Design criteria and experimental conditions for the pilot-scale upflow contactor columns are presented in Table 4-1. A total of four contactor will be operated in parallel for each set of experiments presented below.

Table 4-1 Upflow contactor design criteria and experimental conditions.

Parameter	**Unit**	**Value**
Columns	---	4
Column diameter : particle diameter	---	> 100:1
Calcite height : column diameter	---	> 1:1
Column dimensions (D x H)	inches x inches	4 x 72
Cross-sectional area	square feet	0.087
Calcite height	inch(es)	30
Hydraulic loading rate	gallons per minute per square foot	2 – 20
Empty bed contact time	minutes	0.2 – 10
Sample ports	---	Common and individual influents and individual effluents

4.2.2 Design criteria for CO_2 injection system

One injection system will be used to lower the pH of the permeate before it is split into the four upflow calcite contactors. Design criteria for the CO_2 injection are presented in Table 4-2. The pH will be controlled with an online pH meter and feedback control loop. The design is based on the availability of equipment to meet the needs of this testing.

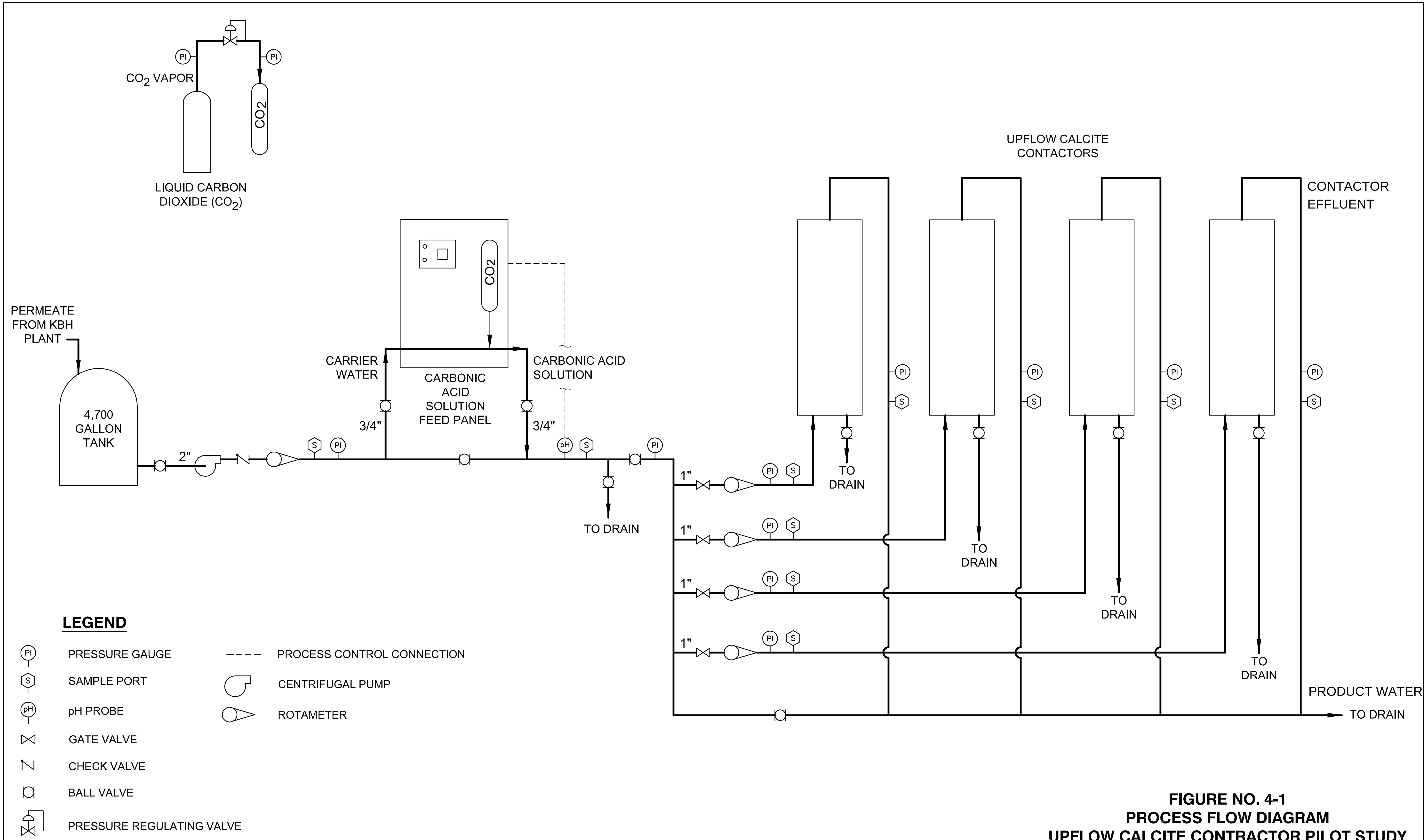

FIGURE NO. 4-1
PROCESS FLOW DIAGRAM
UPFLOW CALCITE CONTRACTOR PILOT STUDY
TEXAS WATER DEVELOPMENT BOARD

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Table 4-2 CO_2 injection system design criteria.

Parameter	**Unit**	**Value**
pH control	---	Automatic
CO_2 injection rate, maximum	pounds per hour	5
CO_2 inlet pressure	pounds per square inch	55 - 60
Carrier water flowrate, minimum	gallons per minute	5
Panel dimensions (L x H)	inches x inches	42 x 46
Panel mount	---	Free standing
Carrier water connection	inch(es)	3/4 FPT, 304 S.S.
Solution outlet connection	inch(es)	3/4 FPT, 304 S.S.
CO_2 vapor inlet connection	inch(es)	1/4 FPT, 304 S.S.
CO_2 storage container	---	Liquefied gas cylinders
CO_2 per storage container	pounds	400

4.2.3 Calcite selected for upflow contactor tests

Seven calcite products from four manufacturers have been selected for testing. The properties of each calcite product is presented in Table 4-3. These calcites were selected to achieve a range of particle sizes and purities for testing.

Table 4-3 Properties of calcite[a] selected for testing.

		Calcite Manufacturers			
Description	**Unit**	**Imerys**	**Columbia River Carbonates**	**Specialty Chemicals, Inc.**	**Mississippi Lime**
Product Name	---	40-200™ NSF 30-50™ NSF Z White™ NSF OZ White™ NSF	Puri-Cal C™	Vical 1200	CalCarb®R1
Nominal Particle Size	millimeter	0.075, 0.3, 0.84, 1.4	1.0	1.0	1.19
NSF Certified	---	Yes	Yes	Yes	Yes
$CaCO_3$ Content	percent	95	95	97	98.4
$MgCO_3$ Content	percent	Not reported	3	1.4	0.8
Other Reported Impurities	---	SiO_2	Not Reported	Fe_2O_3	SiO_2, Fe_2O_3, Al_2O_3, S

Note:

[a] Based on manufacturer's information.

4.3 Experimental plan

The experimental plan includes testing upflow calcite contactors for reverse osmosis permeate stabilization by varying empty bed contact time, calcite purity, and calcite particle size. Experimental matrices and sampling and analysis plans for each are presented below.

4.3.1 Experimental matrix for upflow calcite contactor testing

Four experiments will be conducted to determine design criteria for reverse osmosis permeate stabilization (Table 4-4). The first three sets of experiments involve varying one of three design parameters: calcite particle size, calcite purity, and empty bed contact time. The fourth set of experiments will use up to two combinations of selected values for these parameters to validate synergies in the operation of an upflow calcite contactor. Operating conditions for each experiment are presented in Table 4-5.

Table 4-4 Experimental plan for upflow calcite contactor testing

Experiment	Description	Purpose	Approximate duration
1	Vary calcite particle size while keeping empty bed contact time and calcite purity constant	Determine the optimum calcite particle size for permeate stabilization	1 month
2	Vary calcite purity while keeping empty bed contact time and calcite particle size constant	Determine appropriate calcite purity for permeate stabilization	1 month
3	Vary empty bed contact time while keeping calcite particle size and purity constant	Determine the minimum empty bed contact time for optimum permeate stabilization	1 month
4	Up to two combinations of empty bed contact time, particle size, and purity will be selected for testing	Validate synergy of up to two combinations of operating conditions for permeate stabilization	1 month

4.3.2 Sample and analysis plan for upflow calcite contactor testing

Water quality parameters will be sampled and analyze according to the plan presented in Table 4-6. Calcite particles, before and after each experiment, will be sampled and analyzed according the plan presented in Table 4-7. These samples will be used to evaluate the change in particle size distribution and composition for each operating condition. Operational parameters that will be monitored are presented in Table 4-8.

Table 4-5 Operating conditions for upflow calcite contactor pilot study.

Parameter	Units	Experiment 1	2	3	4
Upflow contactors	---	4	4	4	2
Calcite depth/contactor	in.	30	30	30	30
Calcite volume/contactor	ft^3	0.87	0.87	0.87	0.87
Calcite particle size	mm.	0.075 – 1.4	TBD[a]	TBD[a]	TBD[a]
Calcite purity	% $CaCO_3$	95.0	95.0 – 98.4	TBD[a]	TBD[a]
Empty bed contact time	min.	5	5	2 - 8	TBD[a]
Flowrate	gpm	8	8	3.3 – 13	TBD[a]
Hydraulic loading rate	gpm/ft^2	23	23	9.4 – 37.1	TBD[a]
Contactor influent pH	---	5.5	5.5	5.5	5.5

Notes:
[a] The apparent optimum from the preceding experiment will be used to select this parameter.

Table 4-6 Sampling and analysis plan[a] for water quality.

Parameter	Reverse osmosis permeate	Acidified permeate	Upflow contactor effluents 1	2	3	4	Lab
pH	3/W	3/W	3/W	3/W	3/W	3/W	On-site
Temperature	3/W	3/W	3/W	3/W	3/W	3/W	On-site
Conductivity	3/W	3/W	3/W	3/W	3/W	3/W	On-site
Turbidity	3/W	3/W	3/W	3/W	3/W	3/W	On-site
Alkalinity	1/M	3/W	3/W	3/W	3/W	3/W	University of Texas at El Paso
Calcium	1/M	3/W	3/W	3/W	3/W	3/W	University of Texas at El Paso
Magnesium	1/M	3/W	3/W	3/W	3/W	3/W	University of Texas at El Paso
Total dissolved solids	1/M	1/M	1/M	1/M	1/M	1/M	University of Texas at El Paso
Aluminum	---	2/W	2/W	2/W	2/W	2/W	University of Texas at El Paso
Arsenic (III)	2/W	2/W	2/W	2/W	2/W	2/W	University of Texas at El Paso
Arsenic (V)	2/W	2/W	2/W	2/W	2/W	2/W	University of Texas at El Paso
Iron, total	2/W	2/W	2/W	2/W	2/W	2/W	University of Texas at El Paso
Iron, ferrous	2/W	2/W	2/W	2/W	2/W	2/W	On-site

Parameter	Reverse osmosis permeate	Acidified permeate	Upflow contactor effluents 1	2	3	4	Lab
Silica	1/M	1/W	1/W	1/W	1/W	1/W	University of Texas at El Paso
Total organic carbon	1/M	---	---	---	---	---	University of Texas at El Paso
Gross alpha/beta	1	---	---	---	---	---	Contract
Radium-226	1	---	---	---	---	---	Contract
Radium-228	1	---	---	---	---	---	Contract
Radon-222	1	---	---	---	---	---	Contract

Notes:
[a] W: Week; M: Month

Table 4-7 Sample and analysis plan for calcite particle testing.

Experiment	Description	Particle Size Distribution[a] Before pilot operation	Particle Size Distribution[a] After pilot operation	XRD[a] Before pilot operation	XRD[a] After pilot operation
1	Vary calcite particle size while keeping empty bed contact time and calcite purity constant	4	4	1	4
2	Vary calcite purity while keeping empty bed contact time and calcite particle size constant	4	4	4	4
3	Vary empty bed contact time while keeping calcite particle size and purity constant	1	4	1	4
4	Up to two combinations of empty bed contact time, particle size, and purity will be selected for testing	2	2	2	2
---	Laboratory	University of Texas at El Paso		Contract	

Notes:
[a] Each value represents the number of samples that will be collected. For example, four calcite samples (one from each contactor) will be collected before and after an experiment for particle size distribution.

Table 4-8 **Operational parameters monitoring plan[a] for upflow calcite contactor testing.**

Parameter	Units	CO_2 Bottle	Reverse osmosis permeate	Upflow contactors 1	2	3	4
Flowrate	Gallons per minute	---	3/W	3/W	3/W	3/W	3/W
Headloss	Pounds per square inch	---	---	3/W	3/W	3/W	3/W
Pressure	Pounds per square inch	3/W	3/W	---	---	---	---

Notes:
[a] W: Week

4.3.3 Corrosivity modeling

Based on the effluent water quality from each pilot upflow calcite contactor, the corrosivity of each will be evaluated using an Excel spreadsheet to calculate the Langlier Saturation Index, Ryznar Index, and Calcium Carbonate Precipitation Potential.

5 Quality management

Quality management is an integral part of this study; the data collected on site will be used to verify the performance of the testing units. The analytical testing equipment will be calibrated and maintained as described in the section below. The analytical testing performed by the off-site laboratory will use the methods listed in the tables below.

5.1 Calibration schedule

The calibration schedule is presented in Table 5-1. Any contract laboratory used during this study will calibrate analytical laboratory equipment according to the applicable Environmental Protection Agency or Standard Method for each analysis. A quality control report will be included with the water quality data analysis.

Table 5-1 **Instrument calibration schedule.**

Instrument	Frequency	Method
Flow Meters (transducers and display)	1 per month	Graduated cylinder and stop watch
Pressure gauge (dials)	Beginning of study	
Bench-top conductivity meters(1)	Every time sample is run	Verify with standard
Online pH Meters(1)	Beginning of study	Verify with bench top unit
Bench-top pH meters (1)	Every time sample is run	Verify with buffer

Instrument	Frequency	Method
Field turbidity kits (1)	Every time sample is run	Verify with standard
Chemical feed pumps	3 per week	Check of tank volume versus hour meter on pilot plant

Notes:
1. Texas Commission on Environmental Quality 290.46 (s) indicates the frequency or verification method.

5.1.1 Water quality testing methods

A summary of water quality parameters and respective testing methodologies that will be used over the course of the study are presented in Table 5-2.

Table 5-2 Water quality monitoring parameters and methods.

Parameter	Method
General	
Temperature	SM 2550
pH	EPA 150.1
Alkalinity	SM 2320
Turbidity	SM 2130
Total dissolved solids	SM 2540C
Conductivity	SM 2510
Total hardness	SM 3500-Mg
Total organic carbon	SM 5310B or SM 5310D
Particle size distribution	ASTM D422
Inorganic Chemicals	
Aluminum	SM 3120 or SM 3125
Arsenic (III) and (V)	SM 3125
Calcium	SM 3120 or SM 3125
Magnesium	SM 3120 or SM 3125
Iron (total)	SM 3120 or SM 3125
Silica, milligrams per liter	SM 3120 or SM 3125
Sulfate, milligrams per liter	SM 4500-SO_4^{2-}
Radionuclides	
Gross alpha emitters	EPA 900.0/900.1
Gross Beta Particle and Photon Emitters	EPA 900
Radium-226	EPA 903
Radium-228	EPA 904
Radon	SM 7500RN

5.2 Roles and responsibilities

The purpose of this section is to define the roles and responsibilities of the parties involved in the pilot testing study. The material discussed in the section is presented in the following order:

1. Carollo Responsibilities
2. University of Texas at El Paso Responsibilities
3. Health and Safety
4. Spill Control/Clean-up/Equipment Repair

A matrix presenting specific roles, responsibilities, and key assignments is presented in Table 5-3.

Table 5-3 Overall roles and responsibilities matrix.

Task	Carollo staff	University of Texas at El Paso staff
Overall test design	Primary	
Test facilities setup	Primary	Secondary
Test facility start-up	Primary	
Field sampling	Primary	Secondary
Laboratory analysis	Secondary	Primary
Data collection	Primary	Secondary
Data reduction	Primary	
Quality assurance/quality control	Primary	Secondary

5.2.1 Carollo Engineers responsibilities

Based on the scope of services in the contract with TWDB, Carollo will provide the following during the operation phase of the testing system:

1. Test, commission, and adjust the pilot plant equipment to ensure that it meets the requirements of the testing protocol.
2. Provide chemicals necessary for pretreatment.
3. Monitor performance of equipment and collate data.
4. Carollo will provide personnel three times per week (Mondays, Wednesdays, and Fridays) to collect samples for chemical analysis and verify operation of the pilot.
5. Provide maintenance for the pilot facility over the life of the project.
6. Review and analyze pilot plant and analytical performance data over the life of the project.
7. Meet with TWDB staff.

5.2.2 University of Texas at El Paso responsibilities

Based upon our understanding of the project, University of Texas at El Paso will provide the following:

1. Provide chemical analysis of water samples collected from the pilot plant
2. Provide particle size analysis of select calcite particle samples collected from the pilot plant
3. Provide quality management procedures for analyses conducted at University of Texas at El Paso. Provide comments on performance and analytical data collected in a timely manner to keep the project on schedule
4. Provide analytical results in a timely manner to keep the project on schedule.

5.2.3 Health and safety

All chemical usage on the testing site will be in accordance with the safety policies of the CHIWAWA Laboratory at the Kay Bailey Hutchison Plant. Key items related to health and safety issues are summarized as follows:

1. Carollo will be considered as “Authorized” personnel for Kay Bailey Hutchison Plant Research Laboratory for this project.
2. Carollo will provide Material Safety Data Sheets for the chemicals brought on site.
3. Carollo will provide secondary containment for chemical storage tanks.
4. Adequate lighting will be provided in the proposed site area for off-hours response.
5. All personnel working on this project will be instructed on the location and proper use of the shower and eyewash systems at the Kay Bailey Hutchison Plant Research Laboratory.
6. The project site area will require use of safety glasses; however, hard hats will not be necessary.

5.2.4 Spill control/clean-up/equipment repair

All chemical storage and dosing tanks that may be used on-site will be double contained. All product and waste stream spills from the testing units will be directed to an appropriate waste drain. The testing units have been designed to minimize the potential for major spills. However, in case of significant equipment or piping failure causing a large spill of solids or chemicals, Carollo will perform clean up and arrange for piping repairs.

5.2.5 Contact Information

The contact information for the project team members from various organizations is presented in the Table 5-4.

Table 5-4 Contact information for project team members.

Name	Phone Number	E-mail Address
TWDB		
Saqib Shirazi	(512) 463-7932	Saqib.Shirazi@twdb.state.tx.us
Jorge Arroyo	(512) 475-3003	Jorge.Arroyo@twdb.state.tx.us
Carollo Engineers		
Bradley Sessions	(208) 376-2288	bsessions@carollo.com
Justin Sutherland	(512) 453-5383	jsutherland@carollo.com
Paul Walker	(512) 453-5383	pwalker@carollo.com
University of Texas at El Paso		
Shane Walker	(915) 747-5000	wswalker2@utep.edu
Malynda Cappelle	(915) 747-5000	macappelle@utep.edu

Appendix D:
Radionuclides Report for Kay Bailey Hutchinson Desalter Permeate

Pace Analytical Services, Inc.
1638 Roseytown Road - Suites 2,3,4
Greensburg, PA 15601
(724)850-5600

December 07, 2011

Mr. Justin Sutherland
Carollo Engineers
8911 Capital of Texas Hwy N
Suite 2200
Austin, TX 78759

RE: Project: 8487A.00
Pace Project No.: 3056519

Dear Mr. Sutherland:

Enclosed are the analytical results for sample(s) received by the laboratory on October 26, 2011. The results relate only to the samples included in this report. Results reported herein conform to the most current TNI standards and the laboratory's Quality Assurance Manual, where applicable, unless otherwise noted in the body of the report.

If you have any questions concerning this report, please feel free to contact me.

Sincerely,

Carin A. Ferris

Carin Ferris for
Jacquelyn Collins
jacquelyn.collins@pacelabs.com
Project Manager

Enclosures

CERTIFICATIONS

Project:	8487A.00
Pace Project No.:	3056519

Pennsylvania Certification IDs

1638 Roseytown Road Suites 2,3&4, Greensburg, PA 15601
Alabama Certification #: 41590
Arizona Certification #: AZ0734
Arkansas Certification
California/NELAC Certification #: 04222CA
Colorado Certification
Connecticut Certification #: PH 0694
Delaware Certification
Florida/NELAC Certification #: E87683
Guam/PADEP Certification
Hawaii/PADEP Certification
Idaho Certification
Illinois/PADEP Certification
Indiana/PADEP Certification
Iowa Certification #: 391
Kansas/NELAC Certification #: E-10358
Kentucky Certification #: 90133
Louisiana/NELAC Certification #: LA080002
Louisiana/NELAC Certification #: 4086
Maine Certification #: PA0091
Maryland Certification #: 308
Massachusetts Certification #: M-PA1457
Michigan/PADEP Certification
Missouri Certification #: 235
Montana Certification #: Cert 0082
Nevada Certification
New Hampshire/NELAC Certification #: 2976
New Jersey/NELAC Certification #: PA 051
New Mexico Certification
New York/NELAC Certification #: 10888
North Carolina Certification #: 42706
Oregon/NELAC Certification #: PA200002
Pennsylvania/NELAC Certification #: 65-00282
Puerto Rico Certification #: PA01457
South Dakota Certification
Tennessee Certification #: TN2867
Texas/NELAC Certification #: T104704188-09 TX
Utah/NELAC Certification #: ANTE
Virgin Island/PADEP Certification
Virginia Certification #: 00112
Washington Certification #: C1941
West Virginia Certification #: 143
Wisconsin/PADEP Certification
Wyoming Certification #: 8TMS-Q

SAMPLE SUMMARY

Project: 8487A.00
Pace Project No.: 3056519

Lab ID	Sample ID	Matrix	Date Collected	Date Received
3056519001	**KBH Permeate 1-3**	Drinking Water	10/25/11 10:30	10/26/11 10:00
3056519004	**KBH Permeate 4-6**	Drinking Water	10/25/11 17:40	10/26/11 10:00

SAMPLE ANALYTE COUNT

Project: 8487A.00
Pace Project No.: 3056519

Lab ID	Sample ID	Method	Analysts	Analytes Reported
3056519001	**KBH Permeate 1-3**	EPA 900.0	EHH	2
		EPA 903.1	SLA	1
		EPA 904.0	AMK	1
3056519004	**KBH Permeate 4-6**	SM 7500Rn-B	LAL	1

PROJECT NARRATIVE

Project:	8487A.00
Pace Project No.:	3056519

Method: **SM 7500Rn-B**
Description: 7500RnB Radon
Client: Carollo Engineers
Date: December 07, 2011

General Information:
1 sample was analyzed for SM 7500Rn-B. All samples were received in acceptable condition with any exceptions noted below.

Hold Time:
The samples were analyzed within the method required hold times with any exceptions noted below.

Method Blank:
All analytes were below the report limit in the method blank with any exceptions noted below.

Laboratory Control Spike:
All laboratory control spike compounds were within QC limits with any exceptions noted below.

Matrix Spikes:
All percent recoveries and relative percent differences (RPDs) were within acceptance criteria with any exceptions noted below.

Duplicate Sample:
All duplicate sample results were within method acceptance criteria with any exceptions noted below.

Additional Comments:

PROJECT NARRATIVE

Project:	8487A.00
Pace Project No.:	3056519

Method: **EPA 900.0**
Description: 900.0 Gross Alpha/Beta
Client: Carollo Engineers
Date: December 07, 2011

General Information:
1 sample was analyzed for EPA 900.0. All samples were received in acceptable condition with any exceptions noted below.

Hold Time:
The samples were analyzed within the method required hold times with any exceptions noted below.

Method Blank:
All analytes were below the report limit in the method blank with any exceptions noted below.

Laboratory Control Spike:
All laboratory control spike compounds were within QC limits with any exceptions noted below.

Matrix Spikes:
All percent recoveries and relative percent differences (RPDs) were within acceptance criteria with any exceptions noted below.

Duplicate Sample:
All duplicate sample results were within method acceptance criteria with any exceptions noted below.

Additional Comments:

PROJECT NARRATIVE

Project:	8487A.00
Pace Project No.:	3056519

Method: **EPA 903.1**
Description: 903.1 Radium 226
Client: Carollo Engineers
Date: December 07, 2011

General Information:
1 sample was analyzed for EPA 903.1. All samples were received in acceptable condition with any exceptions noted below.

Hold Time:
The samples were analyzed within the method required hold times with any exceptions noted below.

Method Blank:
All analytes were below the report limit in the method blank with any exceptions noted below.

Laboratory Control Spike:
All laboratory control spike compounds were within QC limits with any exceptions noted below.

Matrix Spikes:
All percent recoveries and relative percent differences (RPDs) were within acceptance criteria with any exceptions noted below.

Duplicate Sample:
All duplicate sample results were within method acceptance criteria with any exceptions noted below.

Additional Comments:

PROJECT NARRATIVE

Project:	8487A.00
Pace Project No.:	3056519

Method: **EPA 904.0**
Description: 904.0 Radium 228
Client: Carollo Engineers
Date: December 07, 2011

General Information:
1 sample was analyzed for EPA 904.0. All samples were received in acceptable condition with any exceptions noted below.

Hold Time:
The samples were analyzed within the method required hold times with any exceptions noted below.

Method Blank:
All analytes were below the report limit in the method blank with any exceptions noted below.

Laboratory Control Spike:
All laboratory control spike compounds were within QC limits with any exceptions noted below.

Matrix Spikes:
All percent recoveries and relative percent differences (RPDs) were within acceptance criteria with any exceptions noted below.

Duplicate Sample:
All duplicate sample results were within method acceptance criteria with any exceptions noted below.

Additional Comments:

This data package has been reviewed for quality and completeness and is approved for release.

ANALYTICAL RESULTS

Project: 8487A.00
Pace Project No.: 3056519

Sample: KBH Permeate 1-3 **Lab ID: 3056519001** Collected: 10/25/11 10:30 Received: 10/26/11 10:00 Matrix: Drinking Water
PWS: Site ID: Sample Type:

Parameters	Method	Act ± Unc (MDC)	Units	Analyzed	CAS No.	Qual
Gross Alpha	EPA 900.0	**-0.725 ± 0.839 (2.91)**	pCi/L	11/16/11 09:30	12587-46-1	
Gross Beta	EPA 900.0	**1.23 ± 0.997 (2.11)**	pCi/L	11/16/11 09:30	12587-47-2	
Radium-226	EPA 903.1	**0.190 ± 0.305 (0.447)**	pCi/L	11/19/11 11:07	13982-63-3	
Radium-228	EPA 904.0	**1.98 ± 0.535 (0.843)**	pCi/L	12/05/11 12:03	15262-20-1	

Sample: KBH Permeate 4-6 **Lab ID: 3056519004** Collected: 10/25/11 17:40 Received: 10/26/11 10:00 Matrix: Drinking Water
PWS: Site ID: Sample Type:

Parameters	Method	Act ± Unc (MDC)	Units	Analyzed	CAS No.	Qual
Radon	SM 7500Rn-B	**260.2 ± 37.5 (46.5)**	pCi/L	10/27/11 18:31	10043-92-2	

QUALITY CONTROL DATA

Project:	8487A.00
Pace Project No.:	3056519

QC Batch:	RADC/9957	Analysis Method:	SM 7500Rn-B
QC Batch Method:	SM 7500Rn-B	Analysis Description:	7500Rn B Radon
Associated Lab Samples:	3056519004		

METHOD BLANK: 360215 Matrix: Water

Associated Lab Samples: 3056519004

Parameter	Act ± Unc (MDC)	Units	Analyzed	Qualifiers
Radon	11.6 ± 19.1 (32.2)	pCi/L	10/27/11 17:48	

QUALITY CONTROL DATA

Project: 8487A.00
Pace Project No.: 3056519

QC Batch: RADC/10099
QC Batch Method: EPA 900.0
Analysis Method: EPA 900.0
Analysis Description: 900.0 Gross Alpha/Beta
Associated Lab Samples: 3056519001

METHOD BLANK: 363633
Matrix: Water
Associated Lab Samples: 3056519001

Parameter	Act ± Unc (MDC)	Units	Analyzed	Qualifiers
Gross Alpha	-0.677 ± 0.613 (2.16)	pCi/L	11/16/11 09:29	
Gross Beta	-0.081 ± 0.732 (1.89)	pCi/L	11/16/11 09:29	

QUALITY CONTROL DATA

Project: 8487A.00
Pace Project No.: 3056519

QC Batch: RADC/10107
QC Batch Method: EPA 904.0
Analysis Method: EPA 904.0
Analysis Description: 904.0 Radium 228
Associated Lab Samples: 3056519001

METHOD BLANK: 364141
Matrix: Water
Associated Lab Samples: 3056519001

Parameter	Act ± Unc (MDC)	Units	Analyzed	Qualifiers
Radium-228	0.959 ± 0.540 (0.969)	pCi/L	12/05/11 11:55	

QUALITY CONTROL DATA

Project: 8487A.00
Pace Project No.: 3056519

QC Batch:	RADC/10117	Analysis Method:	EPA 903.1
QC Batch Method:	EPA 903.1	Analysis Description:	903.1 Radium-226

Associated Lab Samples: 3056519001

METHOD BLANK: 364173 Matrix: Water

Associated Lab Samples: 3056519001

Parameter	Act ± Unc (MDC)	Units	Analyzed	Qualifiers
Radium-226	0.135 ± 0.458 (0.884)	pCi/L	11/19/11 09:27	

QUALIFIERS

Project:	8487A.00
Pace Project No.:	3056519

DEFINITIONS

DF - Dilution Factor, if reported, represents the factor applied to the reported data due to changes in sample preparation, dilution of the sample aliquot, or moisture content.

ND - Not Detected at or above adjusted reporting limit.

J - Estimated concentration above the adjusted method detection limit and below the adjusted reporting limit.

MDL - Adjusted Method Detection Limit.

S - Surrogate

1,2-Diphenylhydrazine (8270 listed analyte) decomposes to Azobenzene.

Consistent with EPA guidelines, unrounded data are displayed and have been used to calculate % recovery and RPD values.

LCS(D) - Laboratory Control Sample (Duplicate)

MS(D) - Matrix Spike (Duplicate)

DUP - Sample Duplicate

RPD - Relative Percent Difference

NC - Not Calculable.

SG - Silica Gel - Clean-Up

U - Indicates the compound was analyzed for, but not detected.

N-Nitrosodiphenylamine decomposes and cannot be separated from Diphenylamine using Method 8270. The result reported for each analyte is a combined concentration.

Act - Activity

Unc - Uncertainty

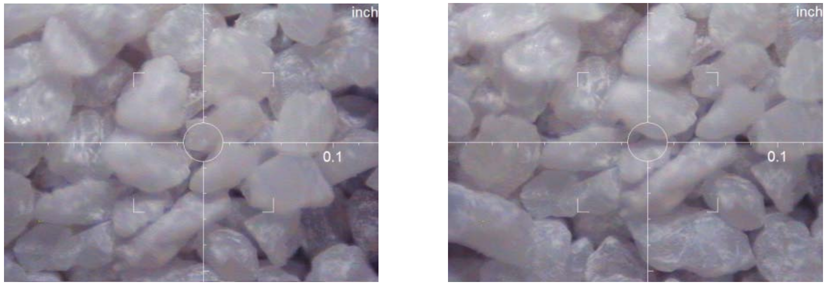
(MDC) - Minimum Detectable Concentration

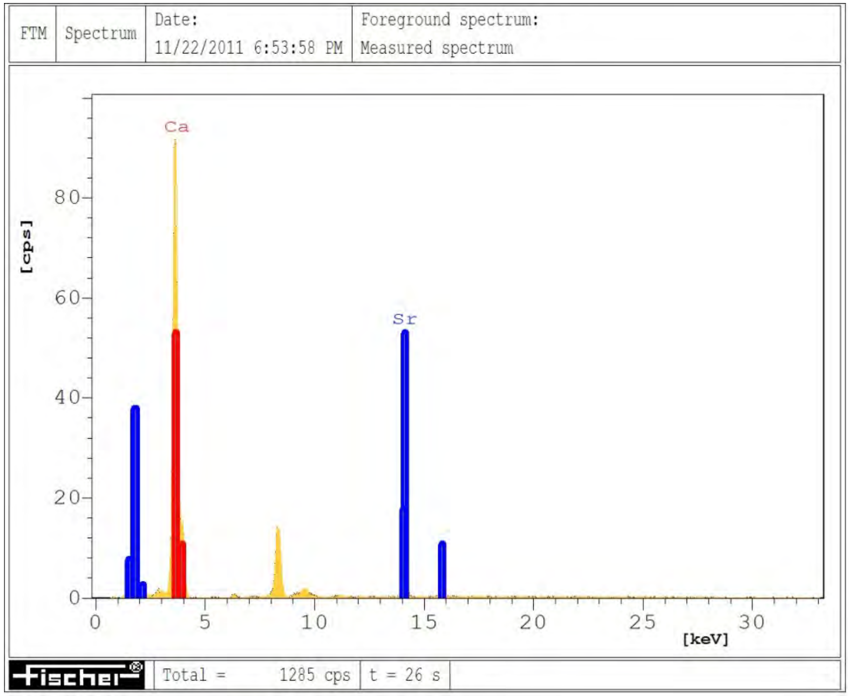
Pace Analytical is TNI accredited. Contact your Pace PM for the current list of accredited analytes.

Appendix E:
XRF Results for Calcite Particles

Phase I

Initial Media of Columbia River





FTM | Spectrum | Date: 11/22/2011 6:53:58 PM | Foreground spectrum: Measured spectrum

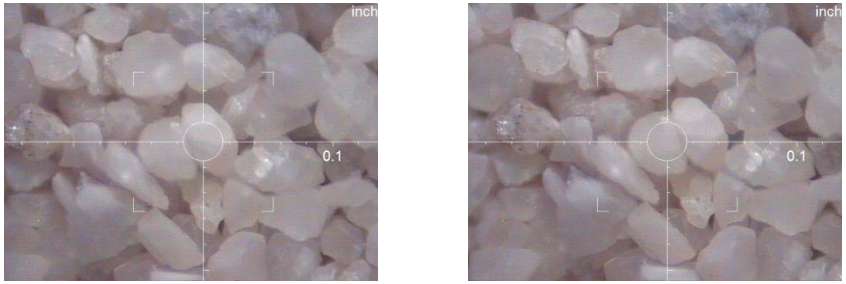
Fischer | Total = 1285 cps | t = 26 s

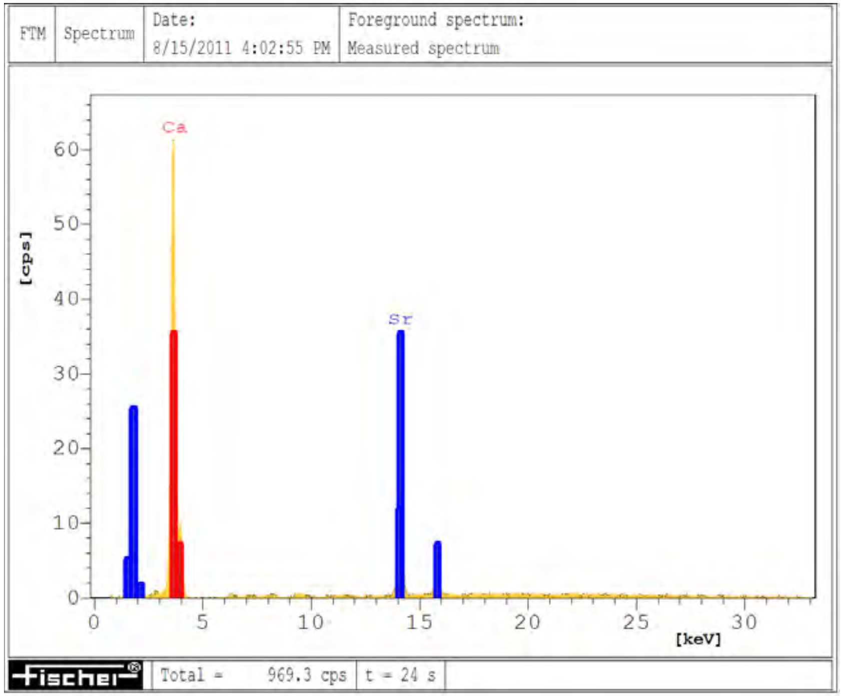
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)    Prim. Filter = --
Collimator 3 =   0.60 Dm.    Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Final Media of Columbia River





FTM | Spectrum | Date: 8/15/2011 4:02:55 PM | Foreground spectrum: Measured spectrum

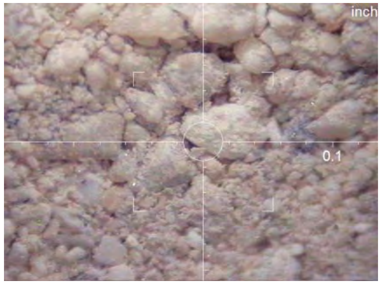
Fischer | Total = 969.3 cps | t = 24 s

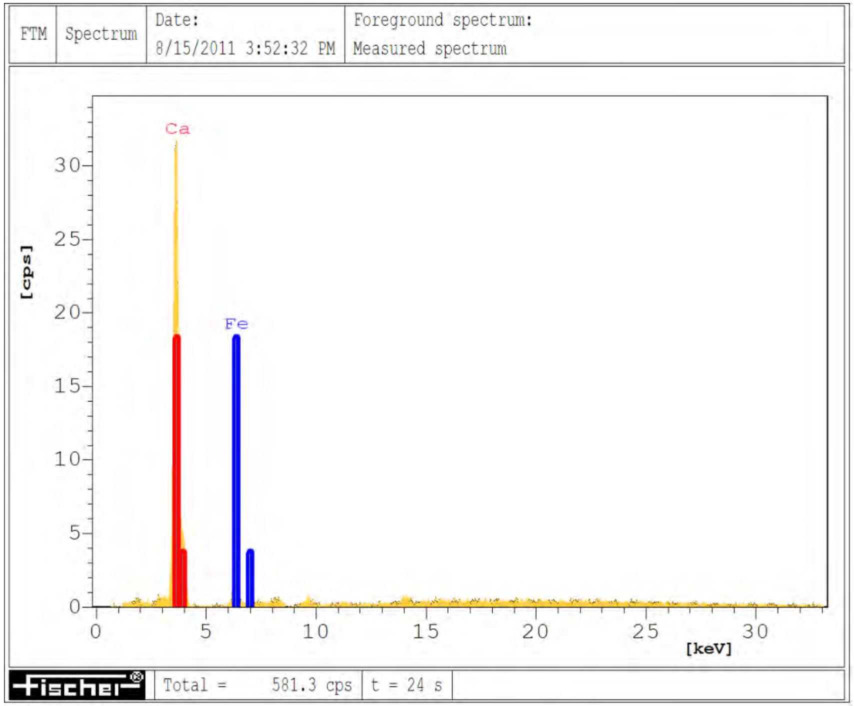
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)    Prim. Filter =  Ni10
Collimator 3 =   0.60 Dm.    Anode current 235 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Initial Media of Lhoist



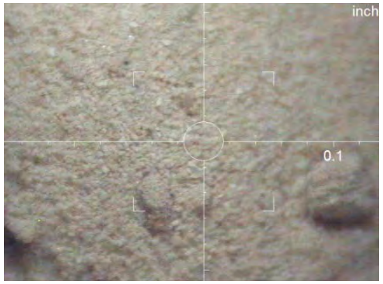

FTM | Spectrum | Date: 8/15/2011 3:52:32 PM | Foreground spectrum: Measured spectrum

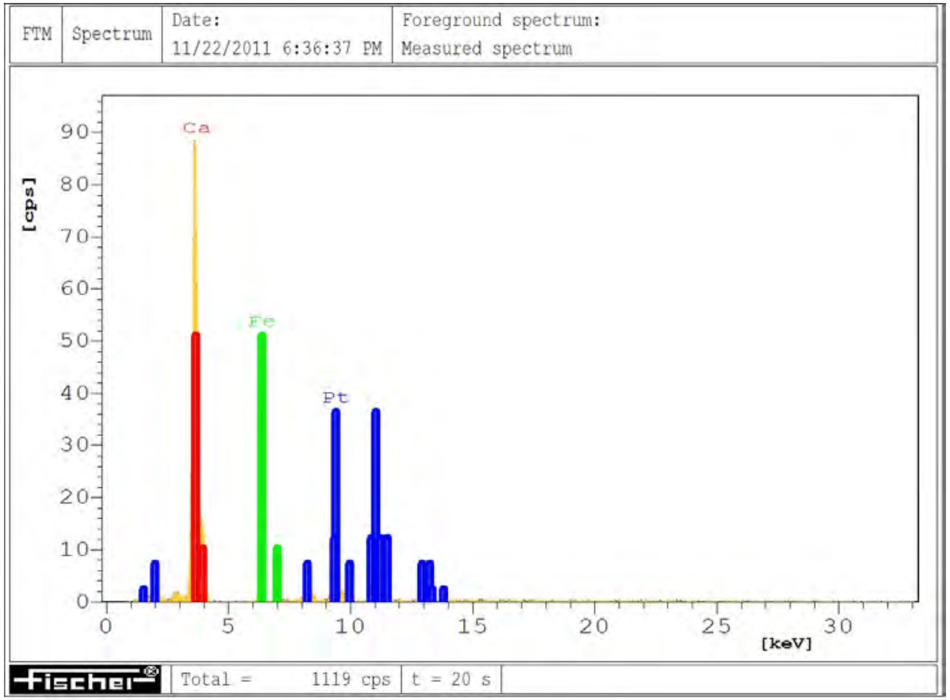
Total = 581.3 cps | t = 24 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = Ni10
Collimator 3 = 0.60 Dm. Anode current 235 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Final Media of Lhoist



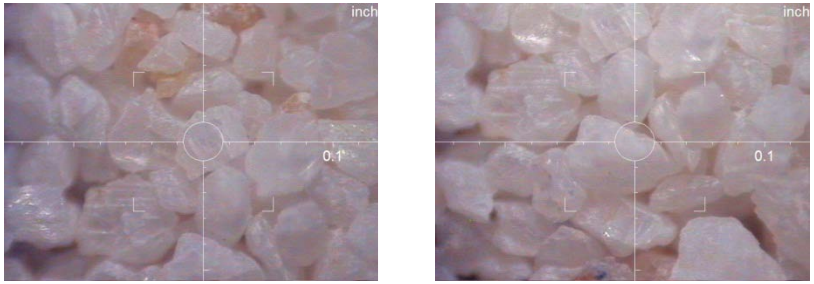

FTM | Spectrum | Date: 11/22/2011 6:36:37 PM | Foreground spectrum: Measured spectrum

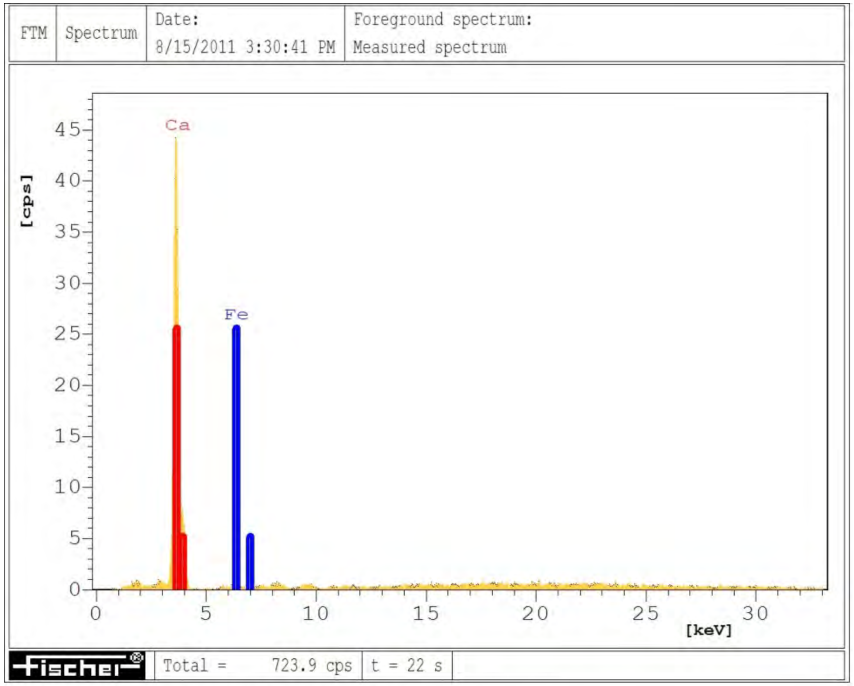
Total = 1119 cps | t = 20 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Initial Media Vical





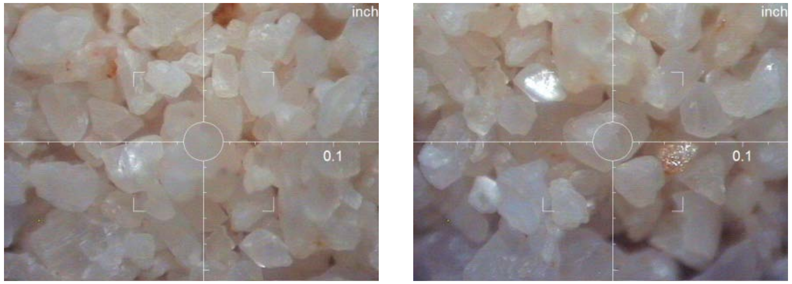
FTM | Spectrum | Date: 8/15/2011 3:30:41 PM | Foreground spectrum: Measured spectrum

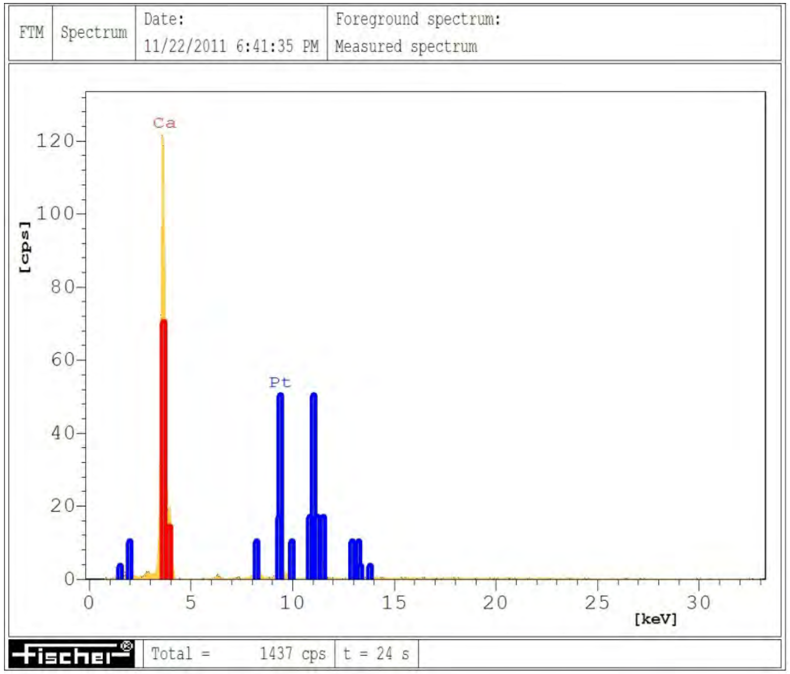
Total = 723.9 cps | t = 22 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter = Ni10
Collimator 3 = 0.60 Dm.   Anode current 235 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Final Media Vical





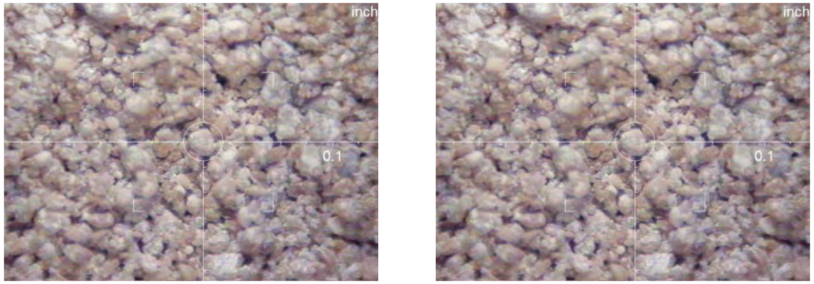
FTM | Spectrum | Date: 11/22/2011 6:41:35 PM | Foreground spectrum: Measured spectrum

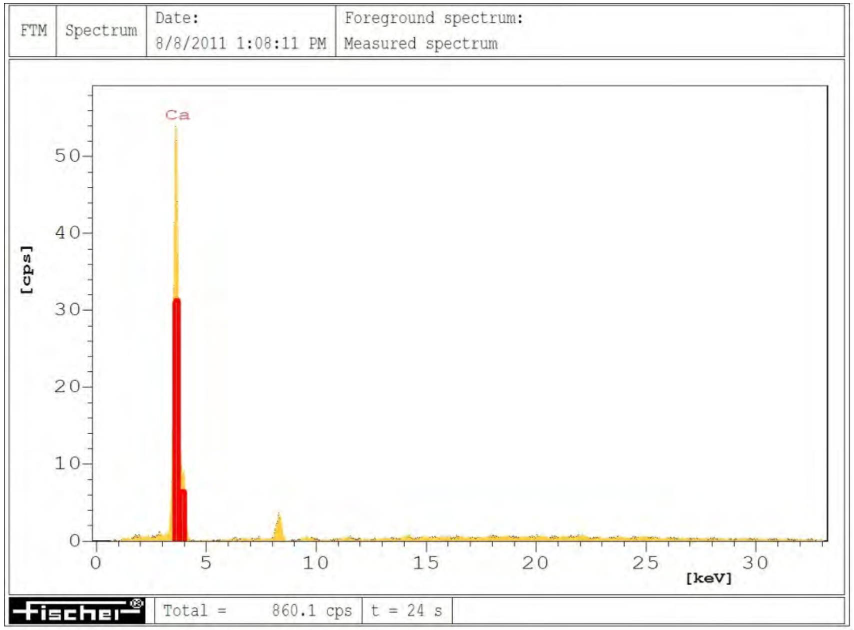
Total = 1437 cps | t = 24 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter = --
Collimator 3 = 0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Initial Phase of Mississippi River





FTM | Spectrum | Date: 8/8/2011 1:08:11 PM | Foreground spectrum: Measured spectrum

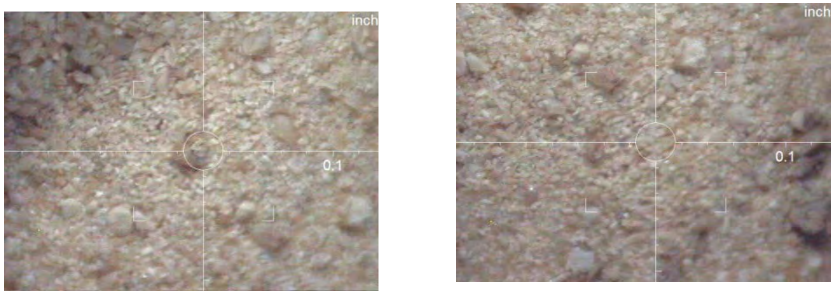
Total = 860.1 cps | t = 24 s

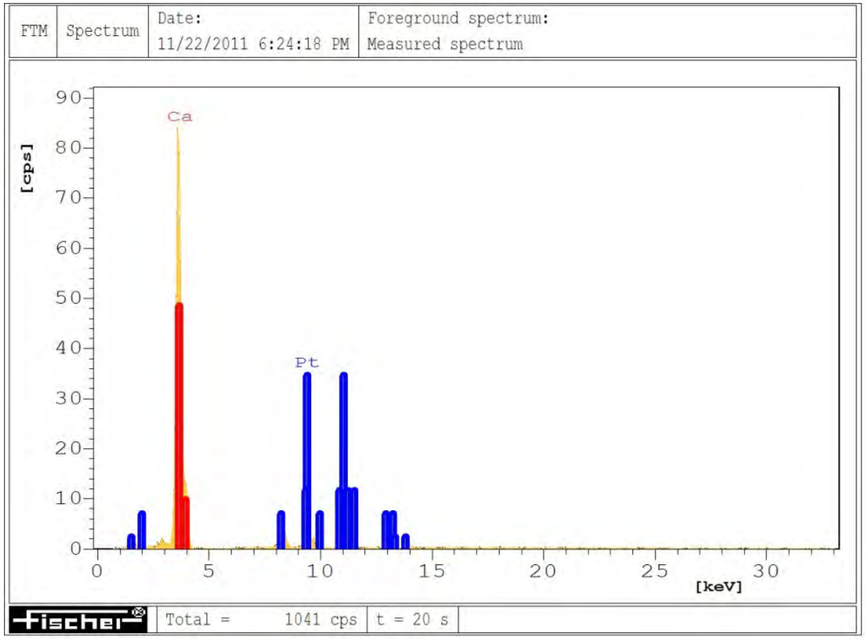
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter =  Ni10
Collimator 3 =  0.60 Dm.   Anode current 235 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Final Phase of Mississippi River





FTM | Spectrum | Date: 11/22/2011 6:24:18 PM | Foreground spectrum: Measured spectrum

Total = 1041 cps | t = 20 s

```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter = --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

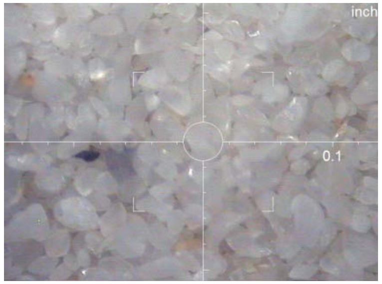
🟨 Foreground: Measured spectrum

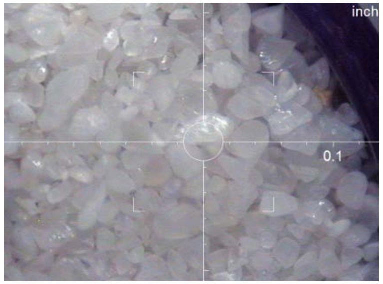
Mississippi River Analysis Element

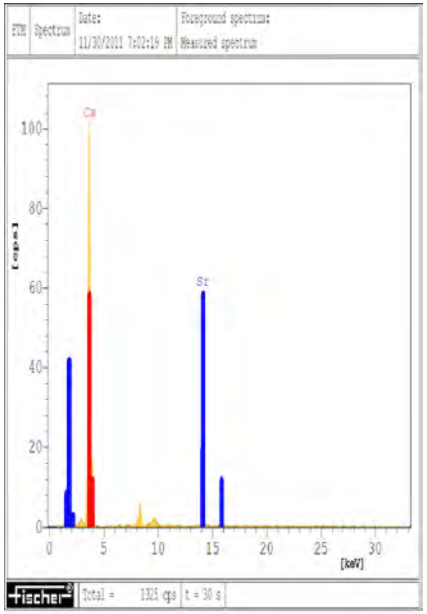
- Principal Element: Calcium
- Secondary Element: Iron

Phase II

Colum 1 Final





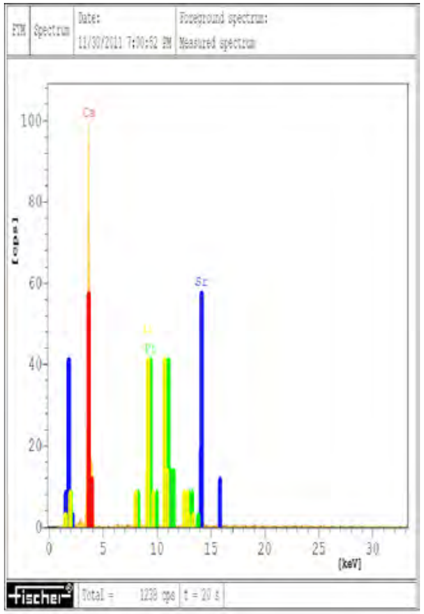

FTM | Spectrum | Date: 11/30/2011 7:02:19 PM | Foreground spectrum: Measured spectrum

Total = 1325 cps | t = 30 s

```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum


FTM | Spectrum | Date: 11/30/2011 7:30:52 PM | Foreground spectrum: Measured spectrum

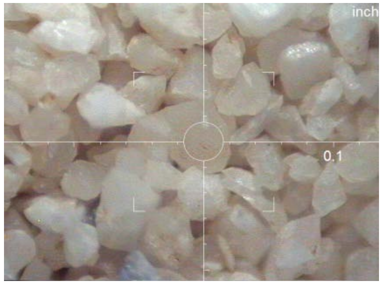
Total = 1238 cps | t = 20 s

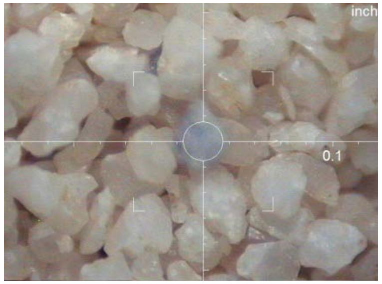
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

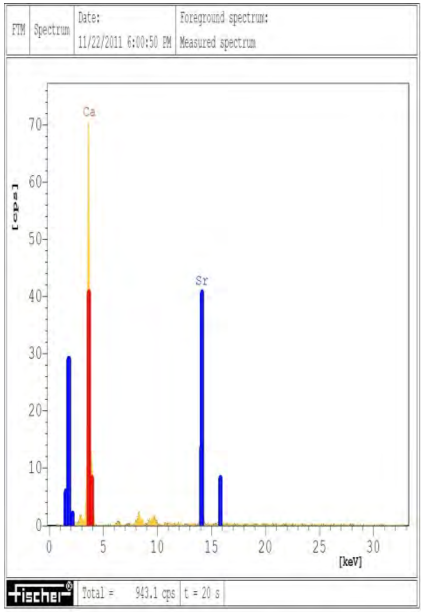
List of spectra:

🟨 Foreground: Measured spectrum

Colum 2 final





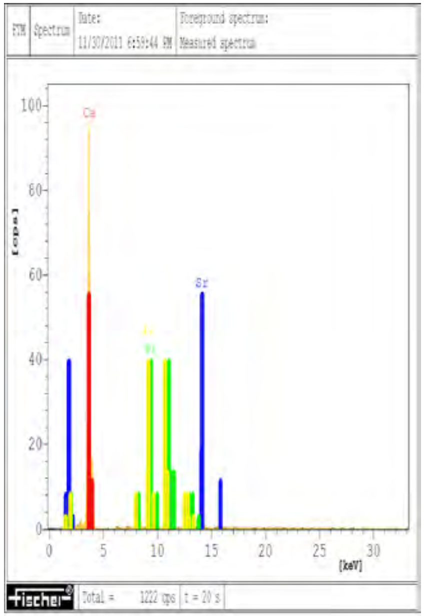

FTM | Spectrum | Date: 11/22/2011 6:00:50 PM | Foreground spectrum: Measured spectrum

Total = 943.1 cps | t = 20 s

```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum


FTM | Spectrum | Date: 11/30/2011 6:59:44 PM | Foreground spectrum: Measured spectrum

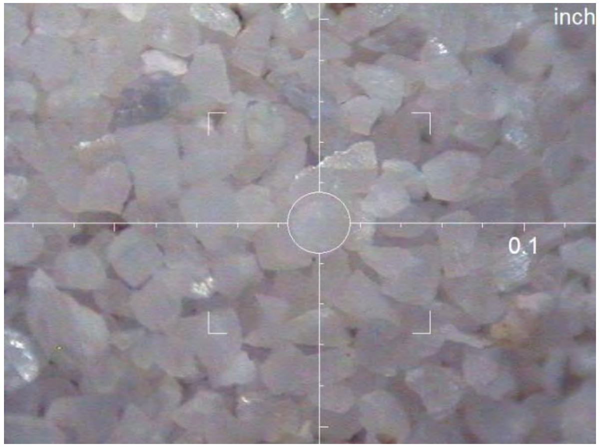
Total = 1222 cps | t = 20 s

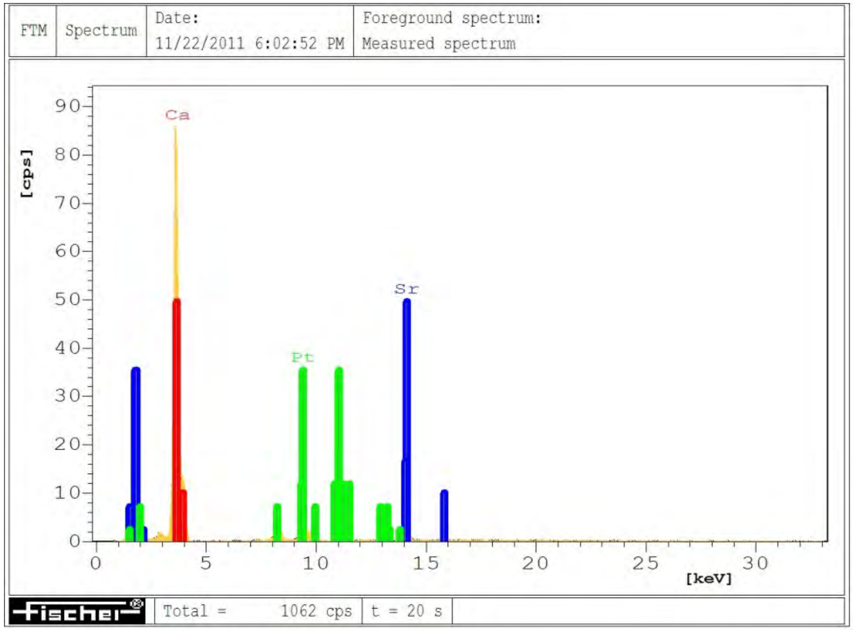
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Colum 3 Final





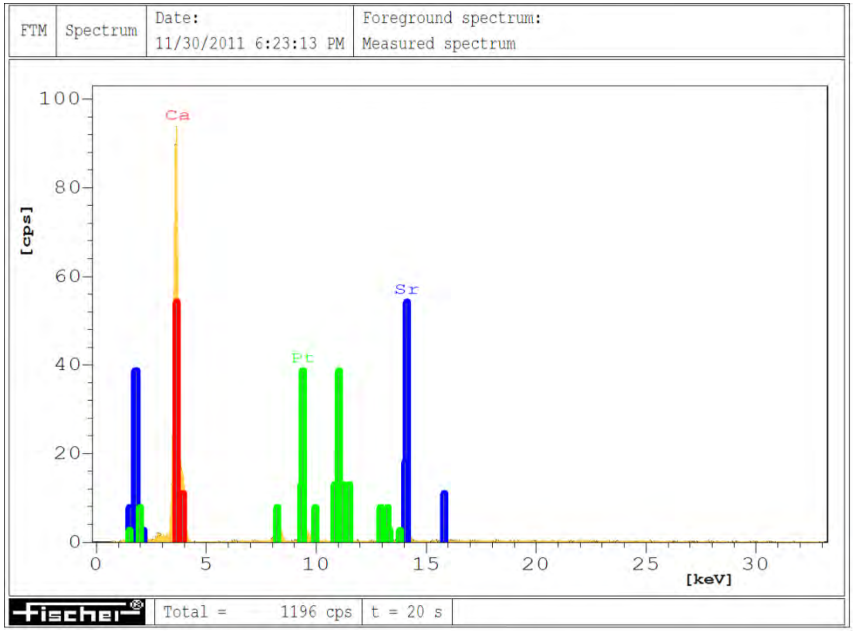
FTM | Spectrum | Date: 11/22/2011 6:02:52 PM | Foreground spectrum: Measured spectrum

Total = 1062 cps | t = 20 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Colum 4 Final



FTM | Spectrum | Date: 11/30/2011 6:23:13 PM | Foreground spectrum: Measured spectrum

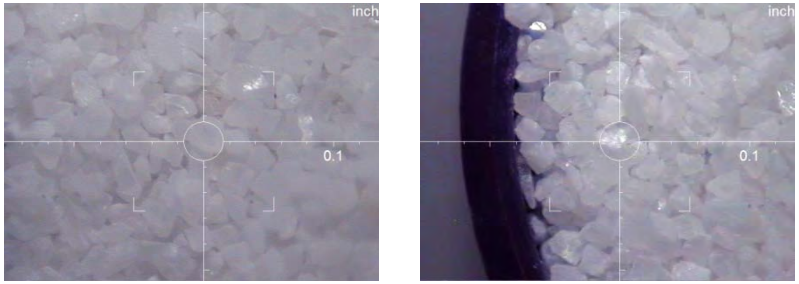
Total = 1196 cps | t = 20 s

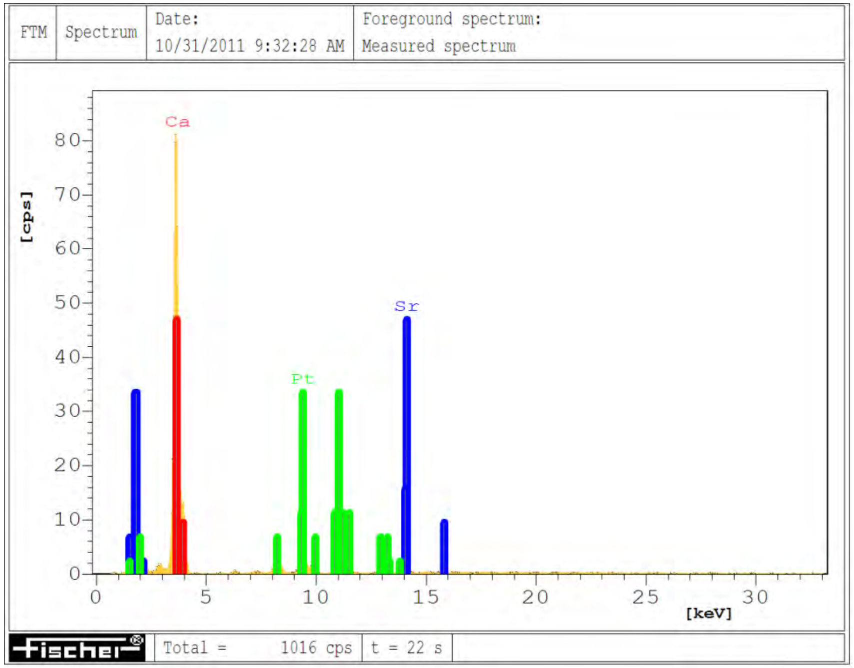
Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Phase III

Initial Media xo-white





FTM	Spectrum	Date: 10/31/2011 9:32:28 AM	Foreground spectrum: Measured spectrum

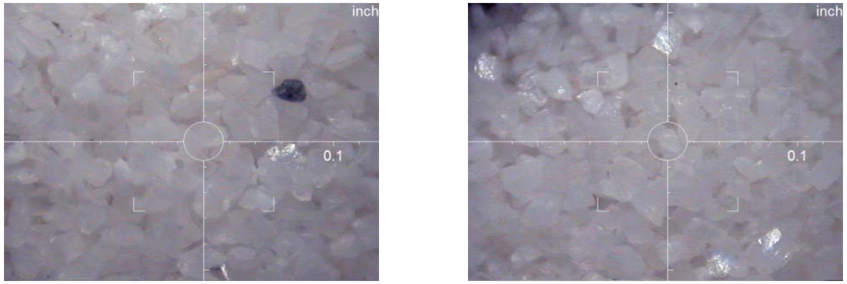
Total = 1016 cps | t = 22 s

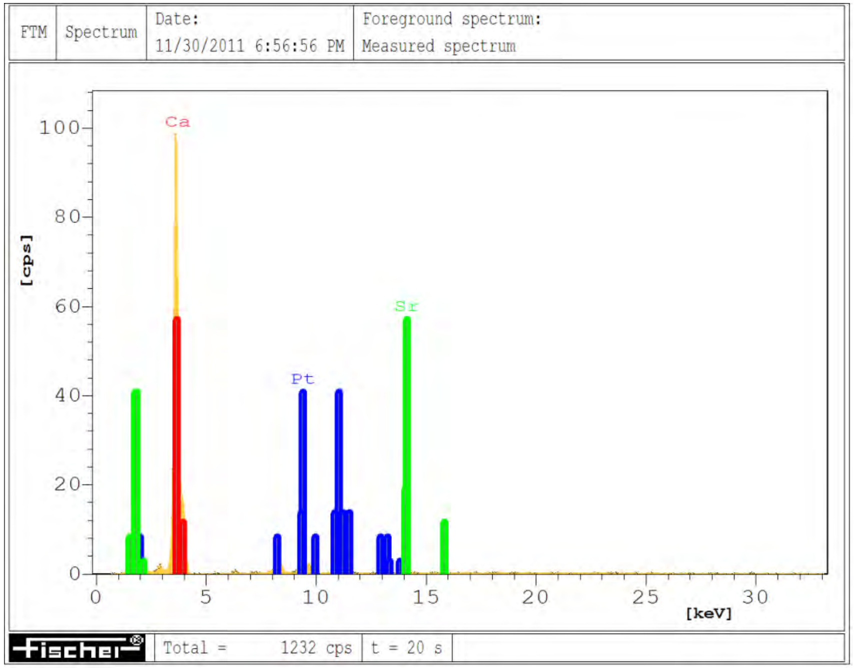
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter = --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Final Media xo-white





FTM	Spectrum	Date: 11/30/2011 6:56:56 PM	Foreground spectrum: Measured spectrum

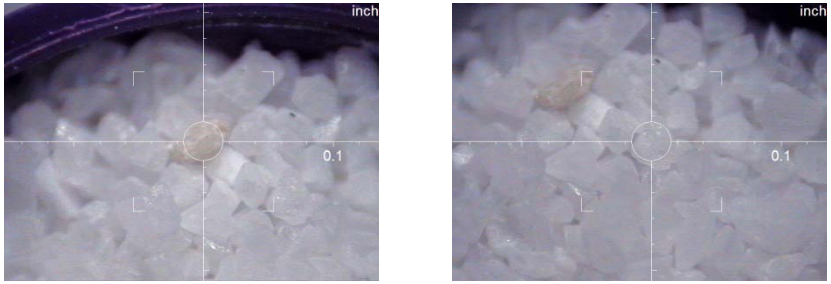
Total = 1232 cps | t = 20 s

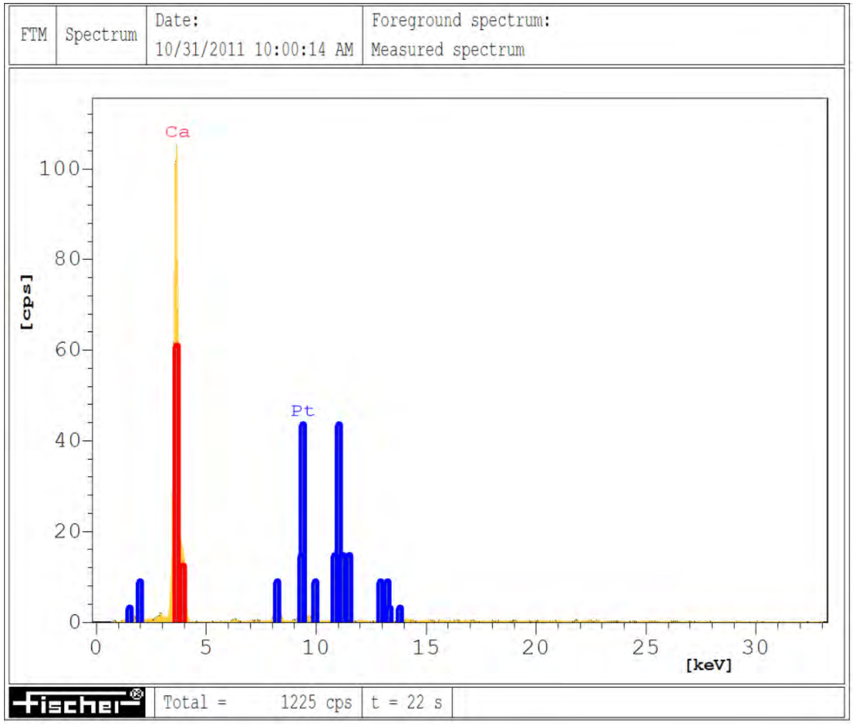
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter = --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Initial Media 30/50





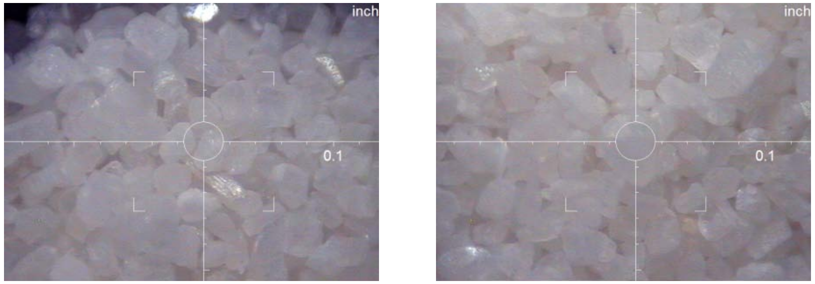
FTM | Spectrum | Date: 10/31/2011 10:00:14 AM | Foreground spectrum: Measured spectrum

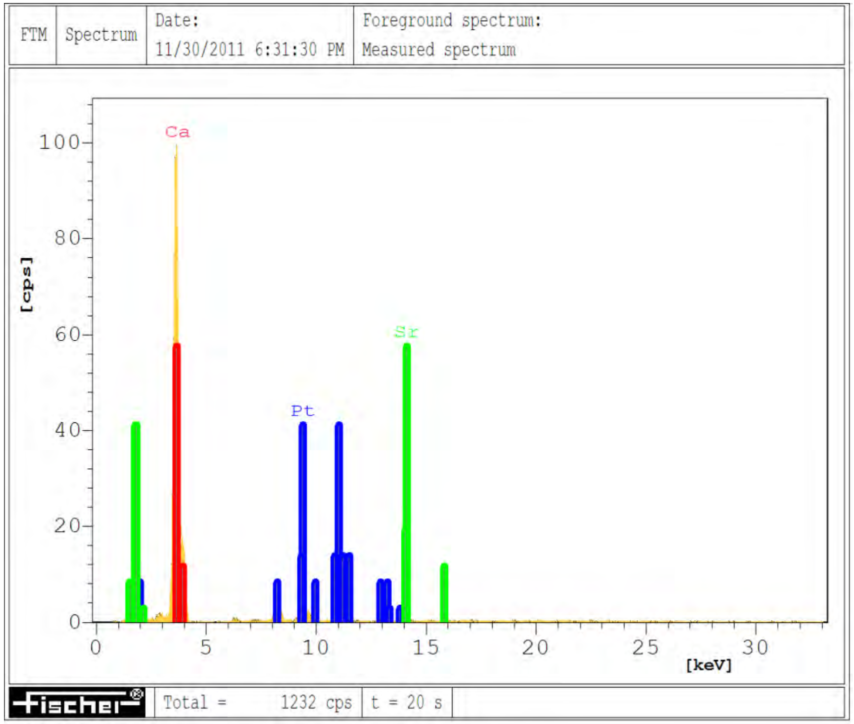
Fischer | Total = 1225 cps | t = 22 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Final Media 30/50





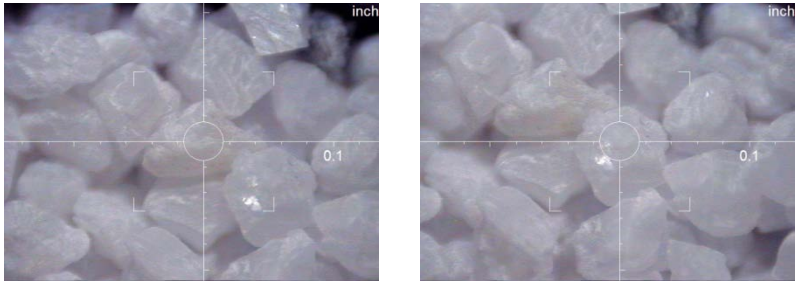
FTM | Spectrum | Date: 11/30/2011 6:31:30 PM | Foreground spectrum: Measured spectrum

Fischer | Total = 1232 cps | t = 20 s

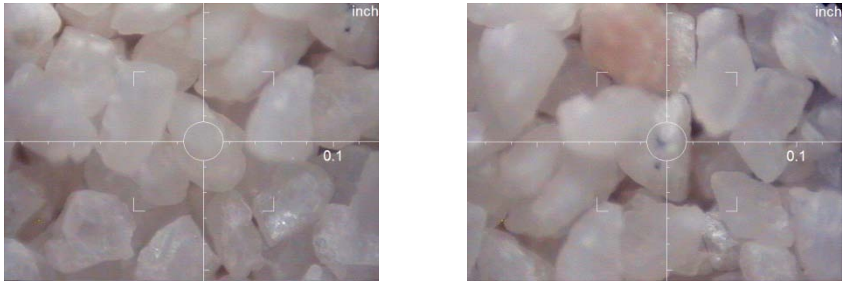
Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

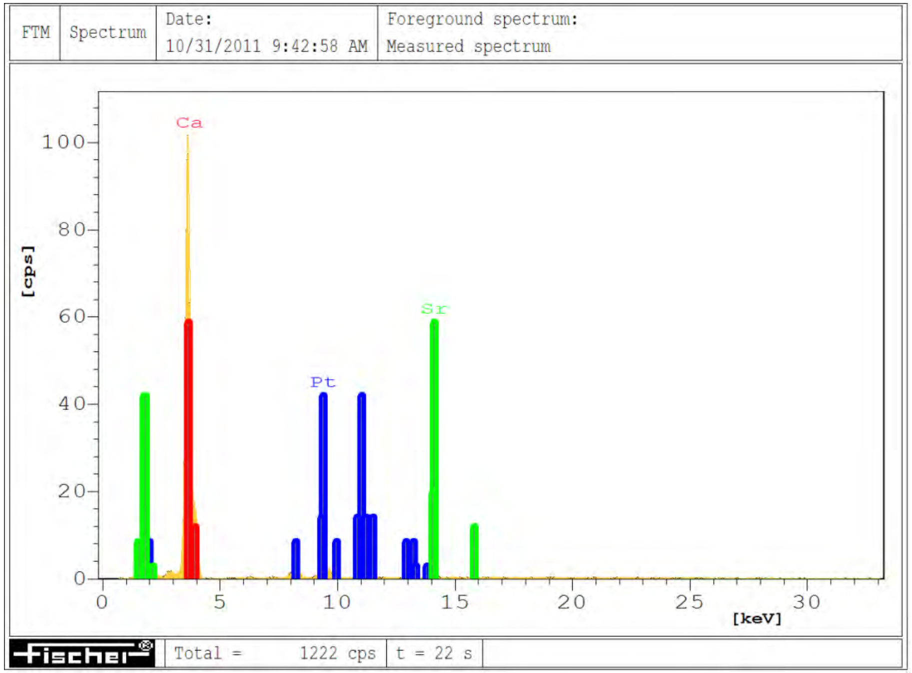
List of spectra:
🟨 Foreground: Measured spectrum

Initial Media z-white



Final Media z-white



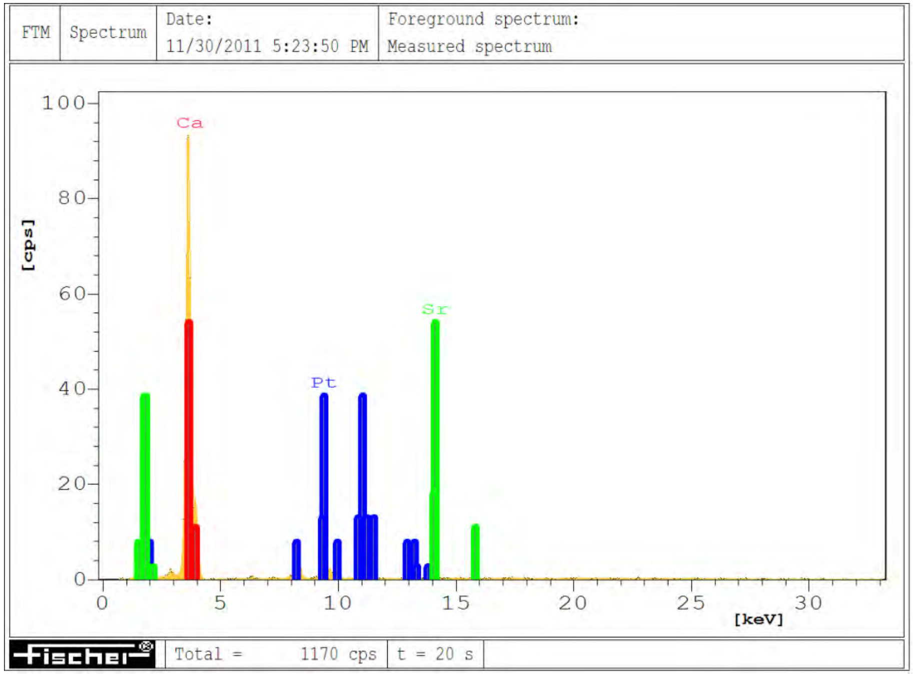


FTM	Spectrum	Date: 10/31/2011 9:42:58 AM	Foreground spectrum: Measured spectrum

Total = 1222 cps | t = 22 s

```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
         Foreground: Measured spectrum
```



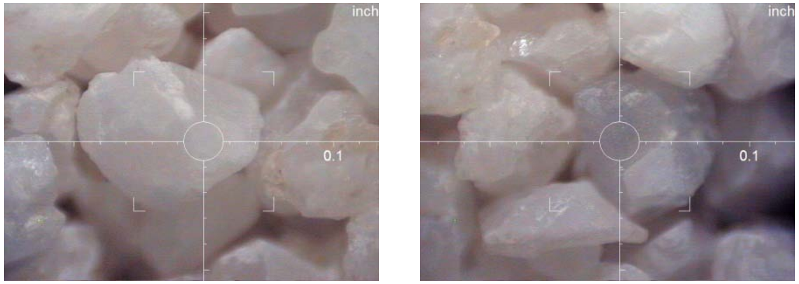
FTM	Spectrum	Date: 11/30/2011 5:23:50 PM	Foreground spectrum: Measured spectrum

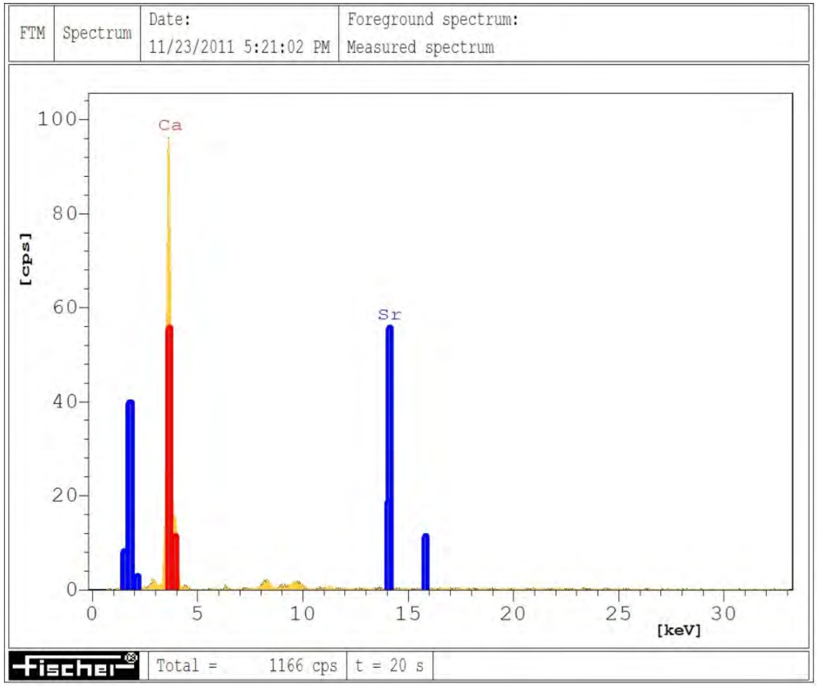
Total = 1170 cps | t = 20 s

```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)   Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
         Foreground: Measured spectrum
```

Initial Media oz-white





FTM	Spectrum	Date: 11/23/2011 5:21:02 PM	Foreground spectrum: Measured spectrum

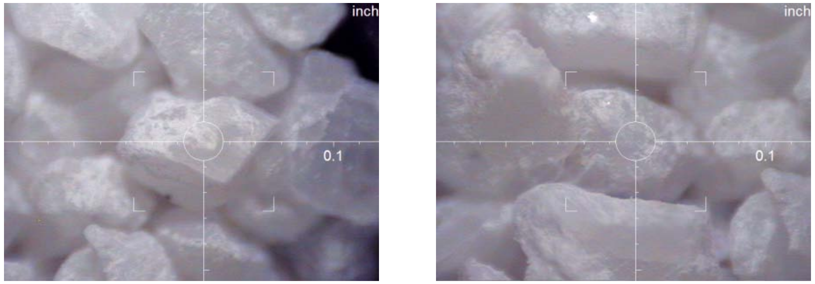
Total = 1166 cps | t = 20 s

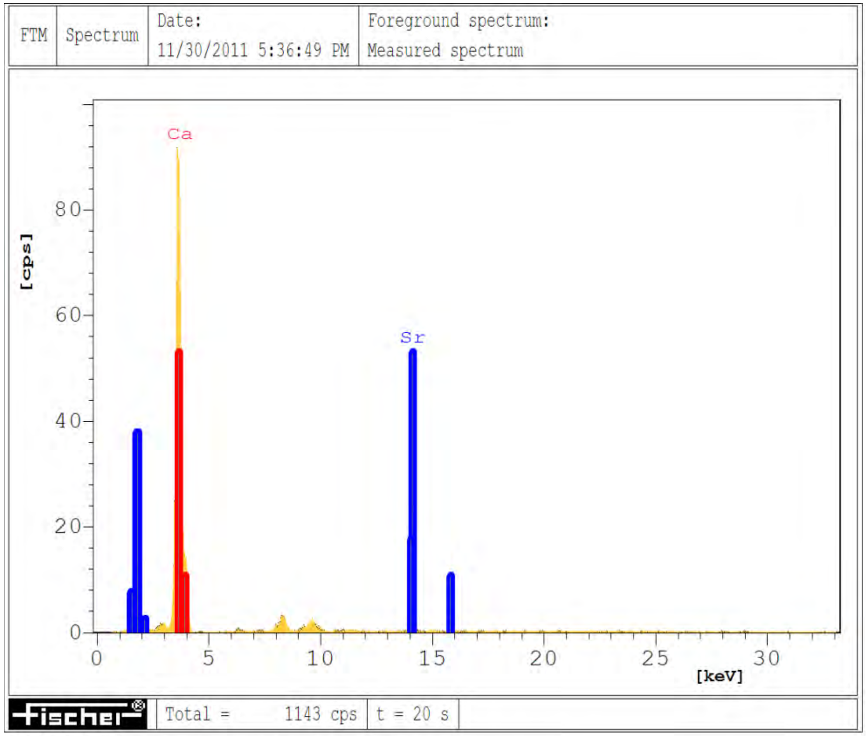
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

List of spectra:

🟨 Foreground: Measured spectrum

Final Media oz-white





FTM	Spectrum	Date: 11/30/2011 5:36:49 PM	Foreground spectrum: Measured spectrum

Total = 1143 cps | t = 20 s

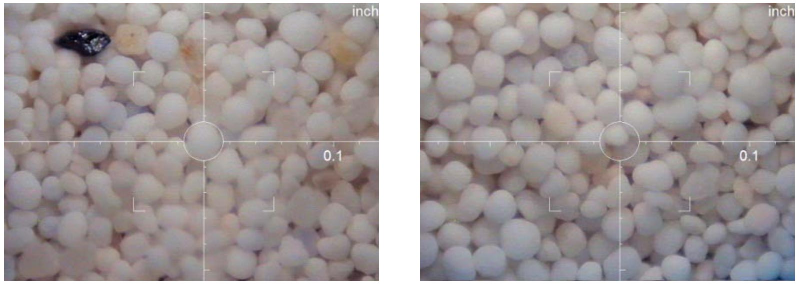
```
Meas. para. (foreground spectrum):
High voltage = 50 kV (875)  Prim. Filter =  --
Collimator 3 =  0.60 Dm.   Anode current 128 uA
Meas. distance = -0.002 inch
```

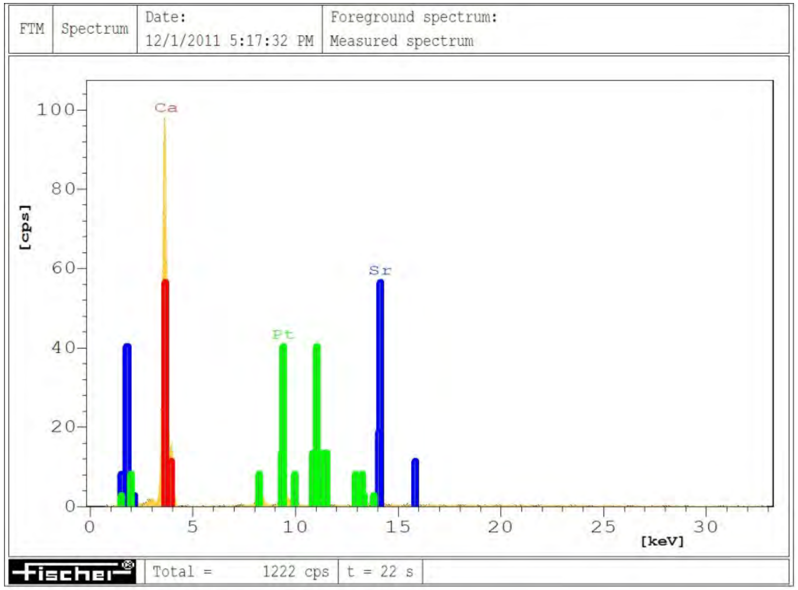
List of spectra:

🟨 Foreground: Measured spectrum

Phase IV

Initial Phase





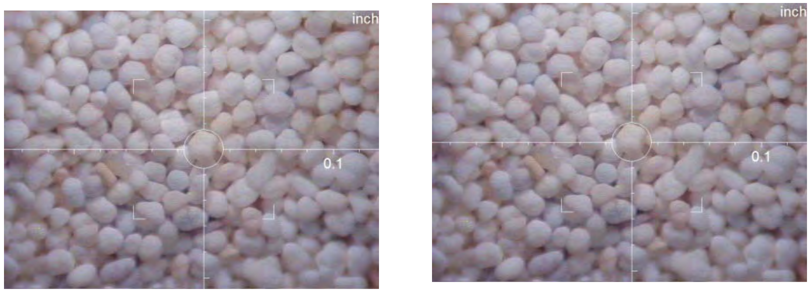
FTM | Spectrum | Date: 12/1/2011 5:17:32 PM | Foreground spectrum: Measured spectrum

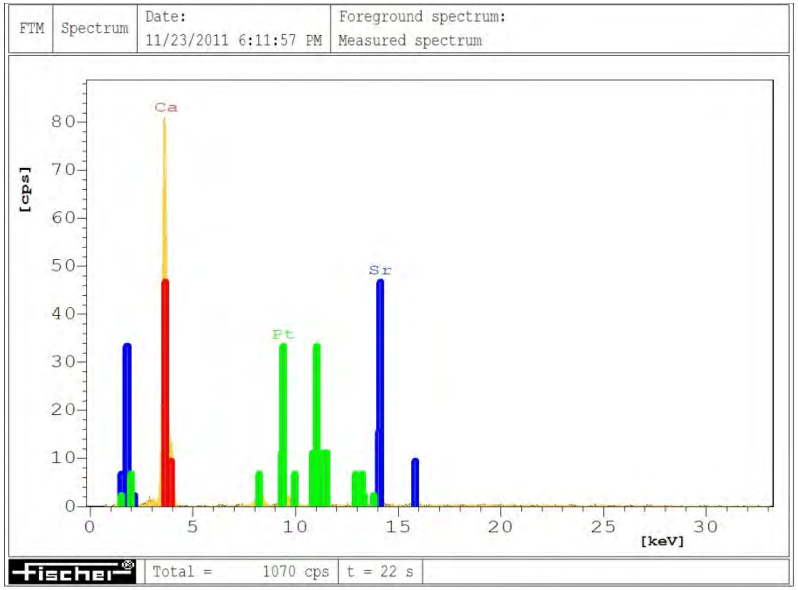
Total = 1222 cps | t = 22 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Final Phase





FTM | Spectrum | Date: 11/23/2011 6:11:57 PM | Foreground spectrum: Measured spectrum

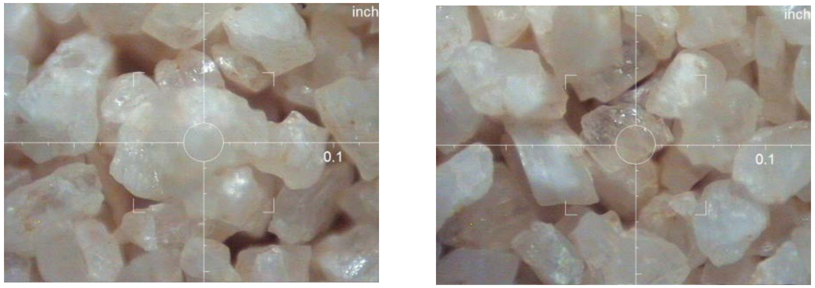
Total = 1070 cps | t = 22 s

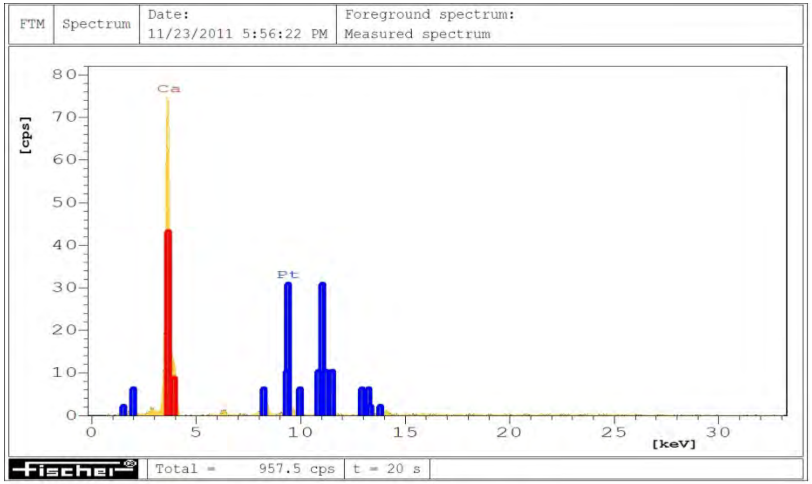
Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Phase 4 Final Phases

Final media for Columbia River





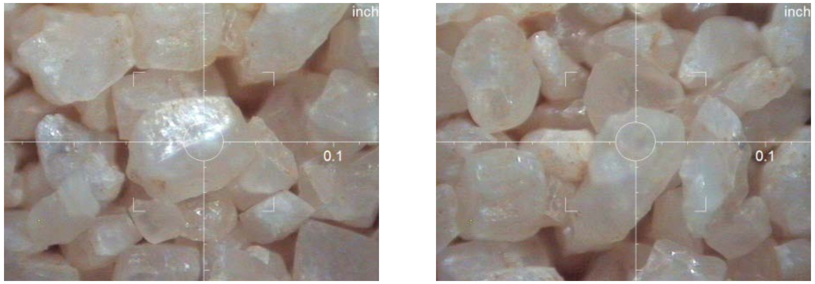
FTM | Spectrum | Date: 11/23/2011 5:56:22 PM | Foreground spectrum: Measured spectrum

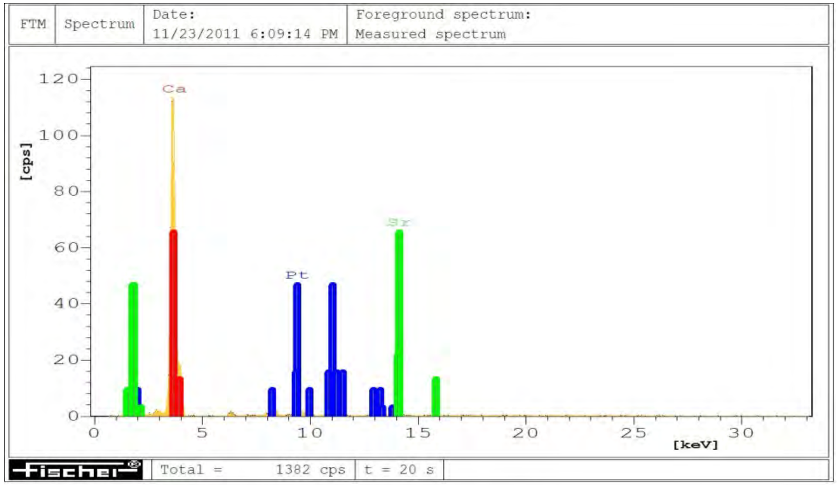
Total = 957.5 cps | t = 20 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum

Final media for Z- white





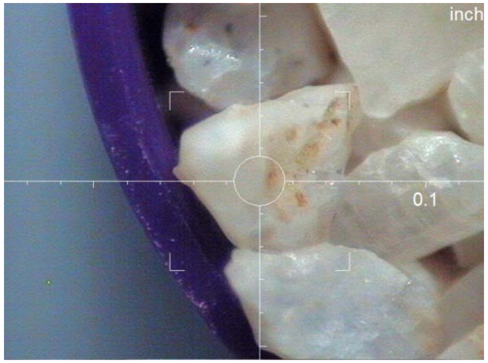
FTM | Spectrum | Date: 11/23/2011 6:09:14 PM | Foreground spectrum: Measured spectrum

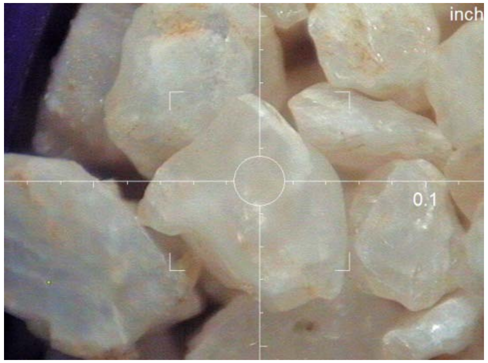
Total = 1382 cps | t = 20 s

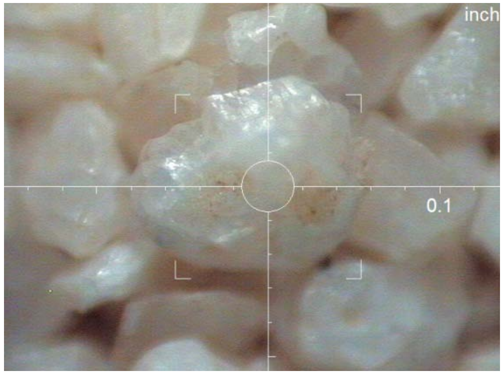
Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

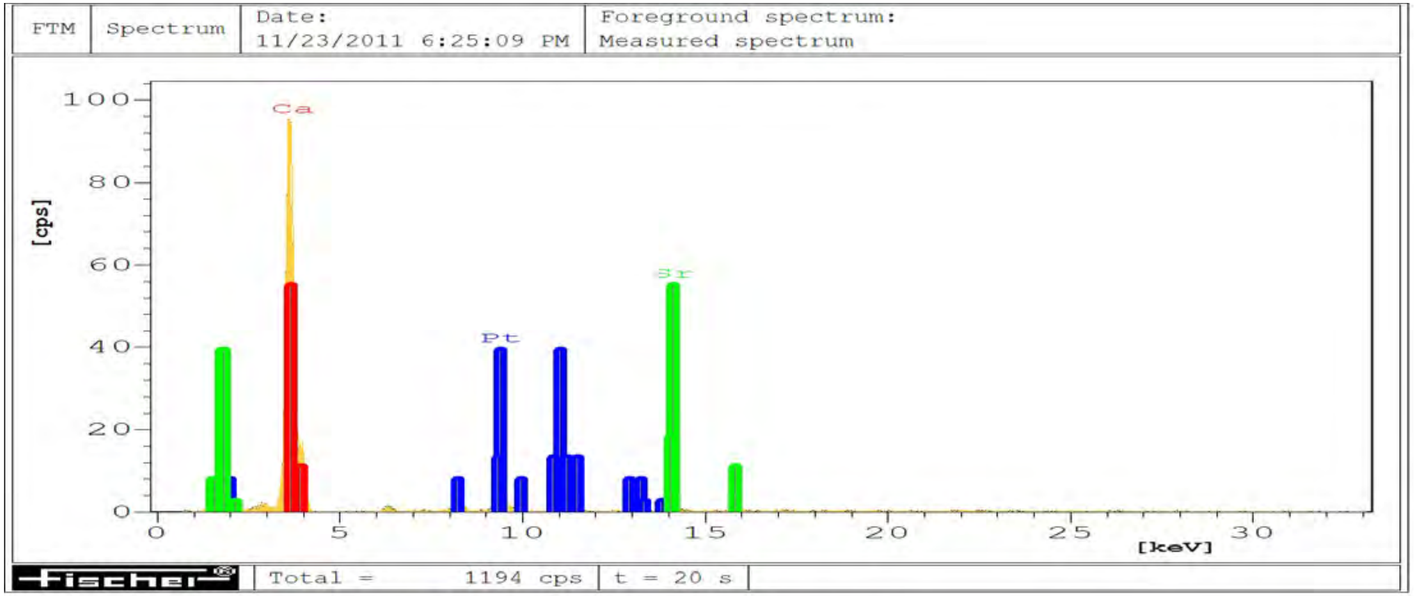
List of spectra:
🟨 Foreground: Measured spectrum

OZ- White








FTM | Spectrum | Date: 11/23/2011 6:25:09 PM | Foreground spectrum: Measured spectrum

Total = 1194 cps | t = 20 s

Meas. para. (foreground spectrum):
High voltage = 50 kV (875) Prim. Filter = --
Collimator 3 = 0.60 Dm. Anode current 128 uA
Meas. distance = -0.002 inch

List of spectra:
🟨 Foreground: Measured spectrum