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Experiences with pellet reactor softening as pretreatment for inland desalination in the USA

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ABSTRACT

A high water recovery is important in inland desalination. In the nineteen eighties projects in Saudi Arabia applied a treatment train consisting of pellet softening, rapid filtration, RO, brine concentrators and evaporation ponds to achieve zero liquid discharge. In the past few years AwwaRF sponsored research on Zero Liquid Discharge for Inland Desalination. This research was completed in 2007 and concluded that pellet softening was the preferred treatment process of primary RO concentrate to allow subsequent treatment of this concentrate in a secondary RO. Since then a number of projects have been started based on this treatment principle.
Interesting findings are that

1. Softening or desalination of drinking water can significantly reduce the chloride discharge in waste water, because it results in a reduction of the salt usage for self regenerating ion exchange softeners;
2. Pellet softening not only reduces the concentrations of calcium and hydrogen carbonate, but can achieve a significant removal of silica as well.

Use of pellet softening can improve the economic and technical feasibility of inland desalination.

Keywords: Inland desalination; Softening; Pellet reactor; Pre-treatment; Post-treatment; Zero liquid discharge

1. Introduction

Inland desalination is becoming increasingly important in arid and semi arid regions around the world. RO is the state of the art technology for desalination of slightly saline or brackish water. Typically the recovery in inland desalination is limited to between 70% and 80% as a result of the presence of scaling salts such as calcium carbonate, calcium sulfate, barium sulfate and silica. Increasing this recovery is far more important here than in seawater desalination, because the resource is limited and there are significant cost and environmental issues associated with sustainable concentrate management.

Reducing the calcium concentration is generally a prerequisite for an increased recovery. This can be achieved by conventional hot or cold lime softening processes, but these produce wet sludge. Even after dewatering a considerable volume of water is lost with this sludge. For that reason pellet softening is an attractive alternative, because it produces dry pellets instead of wet sludge.

The present article briefly describes pellet softening before discussing experiences in Saudi Arabia with

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pellet softening as pre-treatment before RO and AwwaRF research in the USA into the application of pellet softening for treatment of RO concentrate in order to allow its use as feed water for a secondary RO. Finally the article presents findings in projects currently in the design and construction phases.

2. Pellet softening

The basic principle of pellet softening is heterogeneous primary nucleation of calcium carbonate on the surface of a seed material, contrary to sludge softening processes that are based on homogeneous primary nucleation in the bulk of the water phase. Homogeneous primary nucleation requires a high super saturation of calcium carbonate; small calcium carbonate crystals are formed throughout the water phase [1]. Some growth of these crystals occurs, but still their size remains so small that their sedimentation velocity is a few m/h only, resulting in a large area requirement for sedimentation tanks. From these they are released in the form of a wet voluminous sludge that is hard to dewater.

In pellet softening a low super saturation of calcium carbonate is applied. Here crystallization occurs on surfaces only, because the energy barrier is lower in this situation. These surfaces are supplied in the form of a seed material, most often ordinary silica sand in a fluidized bed. The super saturation is achieved by dosing lime, caustic soda or soda ash in the fluidized bed. As a result of this super saturation a layer of calcium carbonate grows on the surfaces of the seed material, resulting in the formation of pellets with a sand grain in the center and calcium carbonate around it [2].

The fluidization of the bed is achieved by an upward flow of the feed water at a superficial velocity of 80–100 m/h. This upward flow results in hydraulic classification: particles with the highest sedimentation velocities gradually move towards the bottom of the fluidized bed. Calcium carbonate pellets have a higher sedimentation velocity than the seed material. Therefore the largest pellets can be extracted at the reactor bottom. A model of a pellet reactor is presented in Fig. 1.

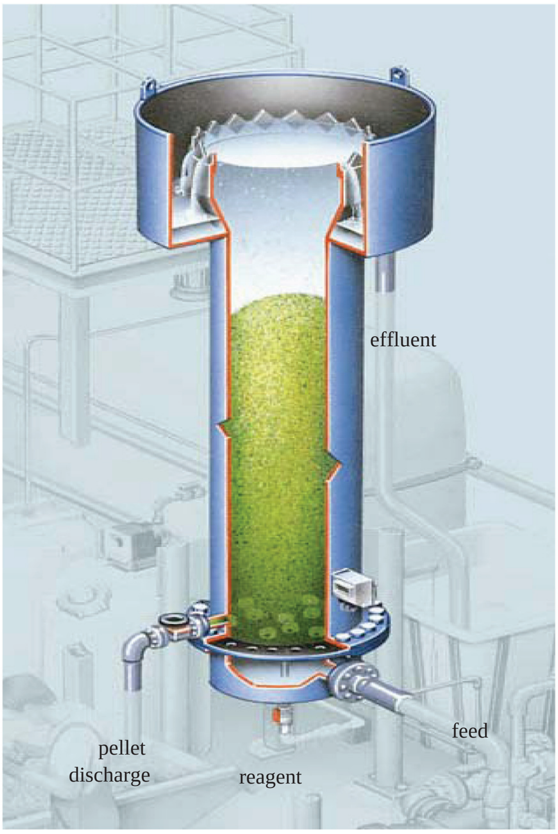

Fig. 1. Model of a pellet reactor.

Research and practice have shown that maximizing the specific surface (m^2 pellet surface per m^3 reactor volume) near the reactor bottom is the key to a successful operation of pellet reactors. This requires an integrated approach of the hydraulic operation, the dosing of base and seed material and the extraction of pellets.

The hydraulic operation of the oldest reactor designs was continuous, but the pellet bed was operated batch wise: the reactor was filled with such an amount of sand that it did not overflow when fluidized. Crystallization resulted in growth of the fluidized bed and pellets were discharged to compensate for this and prevent overflow of the fluidized bed. Ultimately the pellets near the reactor bottom would grow so large that the specific surface area became too low to achieve efficient crystallization. At that time the whole bed would be discharged and the reactor would be filled with a fresh bed of sand.

Modern reactors designs operate the bed in a continuous mode; the bed composition with fresh seed material at the top and full grown pellets at the bottom is kept constant by frequently dosing small batches of seed material and extracting small batches of pellets, usually on the basis of the pressure at the reactor bottom. This enables operation close to the optimum pellet diameter that results in the maximum specific surface area available for crystallization. The latest development is direct control of the pellet diameter on the basis of the differential pressure over the lower section of the fluidized bed [3].

3. Qasim project Saudi Arabia

An early project where pellet softening was applied as pre treatment before RO in inland desalination was

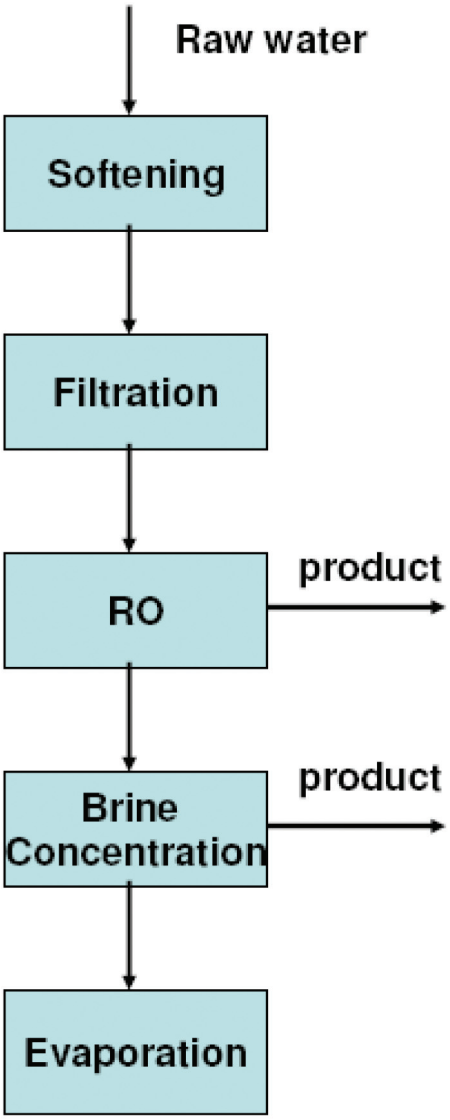

Fig. 2. Block diagram of the process in the Qasim desalination plants.

the Qasim project in Saudi Arabia that was developed by the Ministry of Agriculture and Water in the early eighties. The Qasim Region is located 500 km Northwest of Riyadh. Three plants of 50,000 m^3/d were designed to treat brackish water from the Saq aquifer. The function of the plants was to supply water until the completion of the Jubail-Hail system would supply desalinated seawater to the Region. After the completion of this system the plants would become back-up facilities [4].

The requirement was to produce water that would meet the optimum levels of the Draft Saudi Arabian Standard in order to supply water with a quality similar to desalinated seawater as supplied by the Jubail-Hail scheme. This should be achieved at a recovery of at least 99%.

Calcium sulfate scaling limited the recovery of the RO to 80% without pretreatment. The removal of calcium by pellet softening increased the maximum recovery of the RO to 90%. Pellet softening was preferred over conventional sludge softening system, mainly because the water loss with pellets is virtually zero. Vapor compression was selected to recover 90% of the RO concentrate. A block diagram is presented in Fig. 2.

The first plant of the project to be completed was the one in Unayzah. The design raw water there would require a mixture of caustic soda and soda ash to achieve the required calcium removal, because the water could have a relatively low hydrogen carbonate to calcium ratio. The actual water quality turned out to be more favorable in this respect and in practice dosing caustic soda sufficed.

Reactor effluent turbidity was higher than usual for a caustic soda pellet reactor: > 30 NTU instead of <10 NTU. This way mainly caused by the effect of gas bubbles that were released from the water as its pressure reduced from 50 bar in the aquifer to atmospheric. The negative effects of dissolved gases can be avoided by introducing an aeration step before the pellet reactors.

The pretreatment by softening turned out to be sufficient to achieve the desired recovery of 90% of the RO. The vapor compression brine recovery units were not operated in practice, because the operating costs were considered too high to justify their operation. RO concentrate is sent directly to evaporation ponds.

4. AwwaRF project zero liquid discharge for inland desalination

Increasing population, changing weather patterns, and pollution of renewable water resources have exerted unprecedented demands on water supplies around the world. There is consensus in the water industry that increased use of desalination will be needed to meet world demand for drinking water.

There are extensive brackish water supplies that could be desalinated and used to for drinking water, but often development of brackish sources is hampered by the challenge of managing the concentrate byproduct generated during desalination. The options for concentrate management are as follows:

- Direct discharge;
- Deep well injection;
- Discharge to POTW (Publicly Owned Treatement Works);
- Zero liquid discharge.

The need to protect receiving streams and groundwater sources from increased salinity may preclude concentrate disposal by the first three methods. The alternative is zero liquid discharge (ZLD). In ZLD, concentrate is treated to produce desalinated water and essentially dry salts. Hence, there is no discharge of liquid waste from the process.

Most ZLD applications in operation today treat industrial waste streams using thermal desalination, evaporation ponds, or both. Thermal desalination is a mature technology that has been practiced for over 30 years, particularly in the Middle East. Although there have been design innovations over the years to optimize energy efficiency, thermal desalination remains an energy-intensive process due to the thermodynamic properties of water. Energy requirements for evaporation ponds are minimal, but even in an arid climate ideally suited for natural evaporation, they are expensive to construct and require large land areas.

New ZLD approaches are being investigated that involve treatment of RO concentrate to reduce its precipitation potential followed by a second application of RO to recover more water and reduce concentrate volume. In this manner, the volume of concentrate sent to evaporation ponds or thermal desalination for final separation of salts can be reduced by two to five times, resulting in significantly reduced cost and energy requirements for ZLD.

This ZLD approach is the subject of a recent AWWA Research Foundation (AwwaRF) research project, *Zero Liquid Discharge for Inland Desalination*. The objective of this research was to examine methods for reducing the cost and energy consumption for ZLD desalination [5,6].

The general process train comprises a primary RO system followed by an intermediate concentrate treatment step, secondary RO system, brine concentrator, and evaporation pond. The key to this approach is treatment of primary RO concentrate to reduce its membrane fouling potential, thereby allowing treatment of the concentrate in a secondary RO system for further product water recovery. The system is shown in Fig. 3.

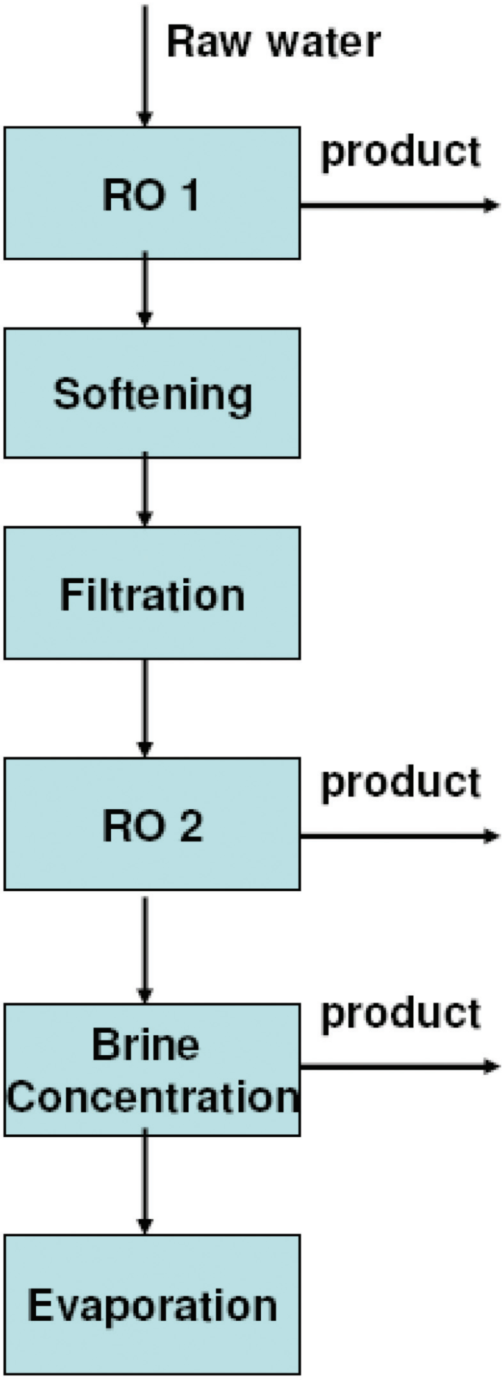

Fig. 3. Block diagram of the process studied in the AwwaRF project.

Bench-scale and pilot-scale tests were conducted to evaluate treatment of concentrate to reduce the membrane fouling potential of RO concentrate. Tests were conducted with five source waters in the Southwestern United States. The test waters included three groundwaters, one surface water, and one reclaimed water. Calcium carbonate, calcium sulfate, barium sulfate, and silica were identified as the scalants that would limit recovery in the secondary RO. Consequently, the concentrate treatment goals were to reduce concentrations of calcium, barium, and silica.

The following concentrate treatment options were evaluated at bench-scale:

- Chemical softening with lime or caustic.
- Fluidized bed crystallization.
- Ion exchange.
- Chemical precipitation with alum.
- Chemical precipitation with sodium aluminate.
- Adsorption with activated alumina (AA).

Based on the bench-scale results, fluidized bed crystallization was the concentrate treatment option selected for evaluation at pilot-scale. The pilot plant included a primary RO, fluidized bed crystallizer, granular media filter, and secondary RO.

Conclusions drawn from this study were as follows:

- Barium was removed in proportion to calcium in all tests with chemical softening and fluidized bed crystallization.
- Relative to chemical softening, treatment goals for calcium and barium were met in fluidized bed crystallization experiments at lower chemical doses and lower pH.
- Silica was not removed effectively by lime or caustic addition in chemical softening or in fluidized bed crystallization at pH less than 10, but it was removed effectively in the pH range of 8–9 when alum or sodium aluminate was added to the fluidized bed crystallizer.
- Calcium removal in the fluidized bed crystallization tests varied among the waters tested. It was found that calcium removal was more effective as the ratio of carbonate to calcium in the water increased.
- The antiscalant in the RO concentrate did not have a cumulative effect in inhibiting crystal formation and calcium removal in the fluidized bed crystallization pilot study. Stable effluent calcium concentrations were observed in experiments that reached 31 h of run time.
- The antiscalant did appear to affect the morphology of the crystals formed. The crystals from the pilot plant were softer and more friable than pellets typically formed in full-scale fluidized bed crystallization applications for softening raw water sources with lower TDS and no antiscalant.

Test results were evaluated to compare the costs of ZLD desalination with the evaluated process to ZLD desalination with the established method of thermal desalination followed by an evaporation pond. Costs projected for the evaluated process were 50–60% of those for thermal desalination followed by an evaporation pond. Energy requirements were estimated to be approximately 70% less.

5. Riverside, California (USA) – Arlington Desalter Expansion

Located in Southern California, approximately 110 km inland from the Pacific Ocean, the Arlington Desalter is a groundwater RO treatment plant originally constructed in the late 1980s. It produces 23,850 m^3/day at a recovery rate of 80%. Concentrate from the RO system (6,060 m^3/day) is discharged into a regional brine line that collects wastewater from other inland desalination plants and transports that water to the Pacific Ocean.

Facing regional water shortages, expansion of the Arlington Desalter is desired, however, the capacity in the reach of the regional brine line that the Arlington Desalter discharges to is at its hydraulic capacity. Therefore, expanded production capacity can only be achieved by increasing the recovery rate of the RO process. Due to the limited land available to build new treatment facilities adjacent to this existing RO treatment plant, pellet softening was identified as an ideal means to treat RO concentrate to remove recovery-limiting salts such as calcium carbonate and silica.

Pilot tests of the process demonstrated that an efficient removal of calcium and silica could be achieved by dosing a mixture of lime and caustic soda to achieve a reactor effluent pH of 9.7. At this pH value still only 10% of the magnesium is removed from the water and the formation of magnesium hydroxide does not interfere with the calcium carbonate crystallization. The main advantage of operating at this relatively high pH value for pellet softening is that over 60% of the silica is removed in the form of calcium silicate (wollastonite, $CaSIO_3$).

The most important water quality characteristics of raw water, primary RO concentrate and secondary RO feed water (= filtered softened water) are shown in Table 1. The achieved water quality after softening and filtering the primary RO concentrate is such that the secondary RO can be operated at a recovery of 65%.

The design of the full scale system on the basis of these pilot test results will be completed later this year.

An interesting observation during the pilot tests was the effect of the pellet diameter. The fluidized bed in the plant was operated in a batch mode and controlled manually. A test run starts with a bed of sand. During the run the pellet size increases.

Fig. 4 shows the reactor effluent turbidity over a filter run. At the start of the run the grain size is below the optimum and at the end is above the optimum. Under these conditions turbidity is far higher than in the middle of the run when the grain size is around the optimum.

Table 1
Water qualities Arlington Desalter pilot study

Constituent	Unit	Primary RO feed	Primary RO concentrate	Secondary RO feed
pH	–	7.3	7.6	9.5
Calcium	mg/l	140	710	25
Magnesium	mg/l	59	265	230
Hydrogen carbonate	mg/l	410	1900	255
Silica	mg/l	47	215	82
Barium	mg/l	0.05	0.18	0.0023
TDS	mg/l	1160	5,300	3850

6. Valencia (California): reducing chloride concentrations without desalination

The Santa Clara River is a 186 km long river in Southern California, North of Los Angeles. Water from this river is used for irrigation. Because some of the crops, especially strawberries and avocados are sensitive to chloride a water quality objective of 100 mg/l chloride was set for the upper Santa Clara River as early as 1978.

Valencia Water Company (VWC) is one of five water purveyors that provide service to the Santa Clarita Valley. VWC provides a blend of local groundwater and imported State Water Project water from Castaic Lake Water Agency. The groundwater has high hardness which has resulted in the widespread use of water softeners. Regeneration of the water softeners results in brine wastewater that is extremely high in chlorides and is identified as a primary cause of discharge to the Santa Clara River from the treatment plant exceeding the 100 mg/l chloride limit.

The Los Angeles Sanitation Data in 2005 indicated that greater than 50% of the chloride received at the wastewater treatment plant was from water softeners (36% self regenerating/16% non-self regenerating water softeners). Further, in a 2005 study conducted by the Santa Clarita Valley Sanitation District and other interested parties, it was found that approximately one third of the overall chloride loading on the Water Reclamation Plants (WRPs) could be eliminated by the removal of automatic residential water softeners [7].

The Santa Clarita Valley Sanitation District has taken and planned a series of measures to control sources of chloride. It even studied the introduction of RO in its wastewater treatment plants to reduce the

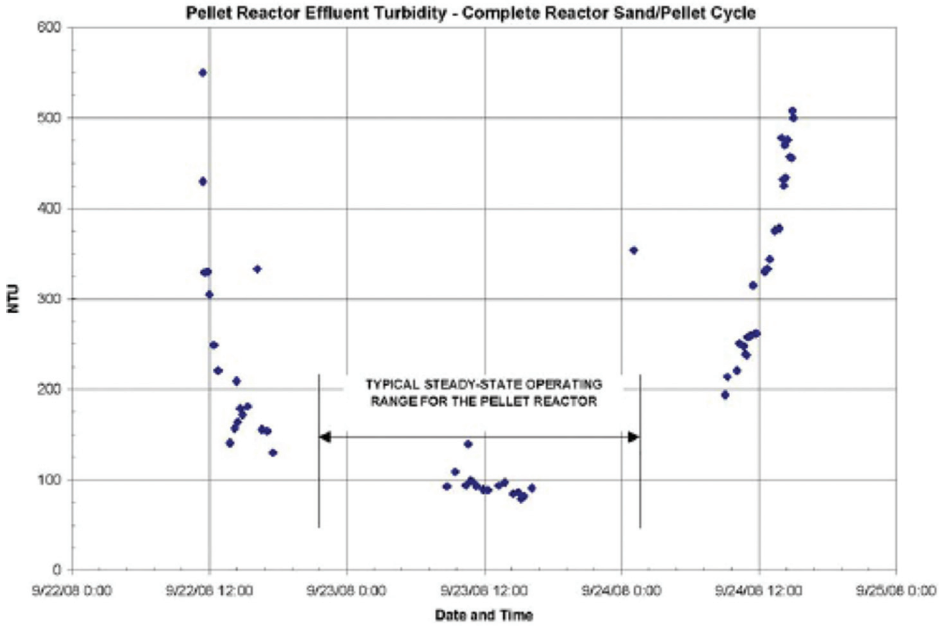

Fig. 4. Pellet reactor effluent turbidity during a test run.

Fig. 5. Pellet reactor in Valencia.

discharge of chloride. Preliminary studies showed that the costs of RO were prohibitive in this situation, most notably the costs for brine transport to the Pacific Ocean.

An important element of the source control measures is the removal of self regenerating water softeners (SRWS). In 2005, at the conclusion of the aforementioned study, the District launched a rebate program that offered residents $ 100 for the removal of their SRWS and $ 150 for removal and replacement with a qualified non-salt alternative unit.

VWC in the Santa Clarita Valley has studied ways to alleviate the water hardness problems of their customers and reduce the chloride discharge to the river. Alternatives studied include ion exchange, membrane treatment, and pellet softening. Ion exchange was considered uneconomical due to the brine discharge and required management (discharge to the Pacific Ocean). Membrane treatment, i.e. reverse osmosis or nano-filtration, also generates a brine wastewater ranging from 15 to 50% that would require discharge. It concluded that pellet softening is the most attractive process to achieve these goals. It is currently operating a groundwater softening demonstration project in the Copperhill area. The goals of this project are to determine consumer attitudes toward per-softened water, establish estimates of cost and overall cost saving to consumers and to quantify the salt reduction in wastewater that is achieved in this way.

The system was installed and has been operational since June 2008. Fig. 5 shows a picture of the plant. Calcium hardness has consistently been reduced from 91 mg/l to 18 mg/l as Ca. Public opinion has been positive and residents receiving the softened water have voluntarily stopped use of home water softeners. As a result the chloride discharged from the community receiving the softened water is significantly reduced. In addition, each residence consumes less water by eliminating the wasted water associated with the water softener regeneration brine; and the cost of soft water for the consumer overall is less.

7. Discussion: advantages and disadvantages of pellet softening compared to sludge softening

An important advantage of pellet softening over sludge softening systems is the production of pellets that dewater easily instead of voluminous sludge that can not be dewatered to over 60% dry solids. An important difference is the fact that pellet softening does not remove magnesium. In situations where pellet softening is used as a pretreatment before RO, magnesium removal in itself is generally not required, because the solubility of magnesium sulfate exceeds that of calcium sulfate by a factor over 10^5 and the solubility of magnesium carbonate exceeds that of calcium carbonate by a factor 10^3. As a consequence scaling of magnesium salts is not an issue in inland desalination in many cases. In these situations pellet softening has the advantage of requiring less chemicals than sludge softening systems.

Silica removal is an issue in many situations. Silica removal by adsorption to magnesium hydroxide is a well known mechanism [8–10] and sludge softening is often applied to achieve this. Experience with silica removal by formation of calcium silicate in pellet softening is limited to the pilot trials for the Arlington Desalter described above. Magnesium removal may be required to achieve sufficient silica removal to allow operation of a subsequent RO at a high recovery. In these situations sludge softening will be the preferred process.

8. Conclusions

Pellet softening has a number of characteristics that make it an attractive candidate for inclusion in treatment schemes for inland desalination:

- It removes calcium, barium and hydrogen carbonate from the water;
- In addition to these well known effects it can also significantly reduce the silica concentration;
- It requires a relatively low dose of chemicals and produces dry pellets instead of wet sludge;
- It functions in the presence of anti-scalants.

Research and practice have proven that It can be used as a pretreatment before RO in order to allow operation at a higher recovery, or as a brine treatment of a primary RO to allow feeding this brine to a secondary RO to raise the overall recovery of the treatment.

Pellet softening does not remove magnesium significantly and will not be the preferred technology in situations where magnesium removal is required.

Controlling the pellet diameter to maximize the specific surface area available for crystallization is key to achieve the optimal results from this process: low effluent super saturation and turbidity and as a consequence low doses of chemicals. Brine treatment applications generally have higher calcium concentrations and therefore higher pellet productions. In these situations the operation of the fluidized bed is even more important.

Central pellet softening by itself can provide an important contribution to salinity control, because it reduces the need for point of use treatment by ion exchange softeners.

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