# THE ROLES OF PELLET REACTOR SOFTENING IN INLAND DESALINATION

Gerard van Houwelingen[1], Rick Bond[2], Luc Kox[3]
1. DHV, Amersfoort, The Netherlands
gerard.vanhouwelingen@dhv.com
2. Black & Veatch, Kansas City, USA
bondrg@bv.com
3. Luc Kox, DHV Australia, Perth, WA
luc.kox@dhv.com

ABSTRACT

Near zero liquid discharge is an important design objective in inland desalination. Pellet reactor softening has been applied as pretreatment before RO and as stand alone process for inland desalination, depending on the salinity of the groundwater.
Research sponsored by the Water Research Foundation (WRF) in the USA in 2007 concluded that pellet reactor softening is the preferrred treatment process of first stage RO concentrate to allow subsequent treatment of this concentrate in a second stage RO.
The feasibility of this process was confirmed by pilot plant in research for the Arlington desalter in California.

## 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 discharging the concentrate flow is an environmental issue that can only be solved at high costs.

Reducing the calcium concentration is 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.

Pellet softening can be applied in inland desalination in three different ways:

1) As a stand alone process in situations where salinity slightly exceeds the standard;
2) As pretreatment before RO;
3) As treatment of primary RO concentrate in order to allow treatment in a secondary RO.

## 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, De Han et al., 2007. 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, Van Dijk et at., 1991.

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 figure 1.

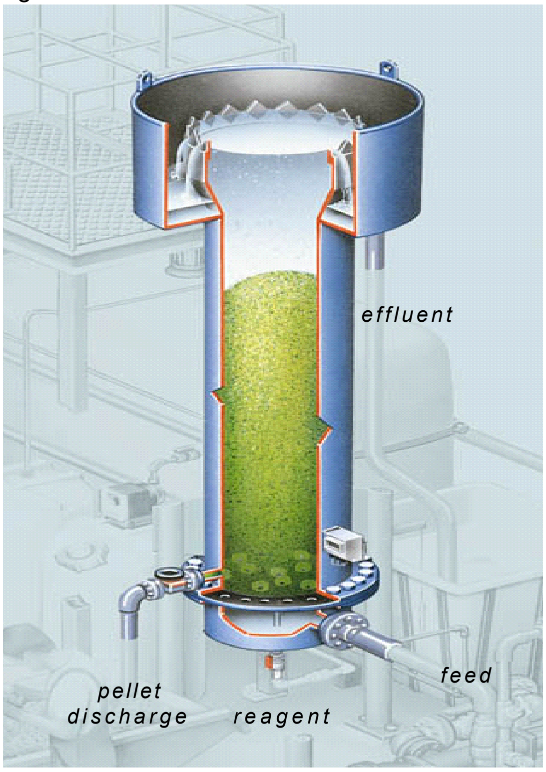


*Figure 1: Model of a pellet reactor*

Research and practice have shown that maximizing the specific surface (m2 pellet surface per m3 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 reactors 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 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 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 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 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, Van Schagen, 2009.

NEERABUP: GROUNDWATER SOFTENING

Neerabup Groundwater Treatment Plant is located North of Perth close to the shore of the Indian Ocean. It extracts groundwater from a series of wells before it would flow into the ocean. The most relevant characteristics of the water quality are presented in table 1.

*Table 1: Raw Water Quality and Standards*

| Parameter | unit | raw water | standard |
|---|---|---|---|
| Fe | mg/L | 3.1 | < 0.1 |
| Mn | mg/L | 0.1 | < 0.04 |
| Ca | mg/L | 76 | < 40 |
| $HCO_3$ | mg/L | 235 | > 73 |
| T.H. | mMol/L | 2.4 | < 1.5 |
| TDS | mg/L | 634 | < 500 |

Table 1 shows that TDS and hardness exceed the standards, but are not in a different order of magnitude. Pellet softening can achieve a total hardness of 1.0 mMol/l at this water quality, which is less than required. This allowed the application of split treatment: two thirds of the flow are softened deeper than necessary and one third bypasses the softening reactors. The required hardness is achieved by mixing the two flows.

The advantage of this set-up is that it reduces the demand of lime, because the dose for carbon dioxide removal and the overdose for achieving a residual super saturation as a driving force for the reaction are only required for the softened partial flow. In addition to this the carbon dioxide from the bypass flow neutralizes part of the super saturation in the softened flow, which reduces the consumption of carbon dioxide. The resulting process design is presented in figure 2.

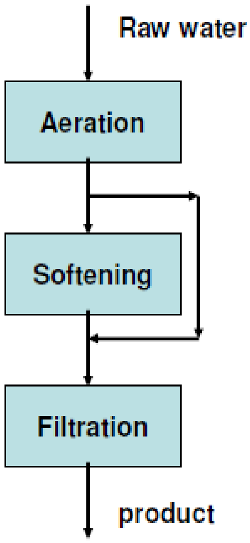


*Figure 2: Block diagram of the Neerabup GWTP process*

QASIM PROJECT SAUDI ARABIA

An early project where pellet softening was applied as pretreatment before RO in inland desalination was 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 m3/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, De Moel et al. 1985.

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 figure 3.

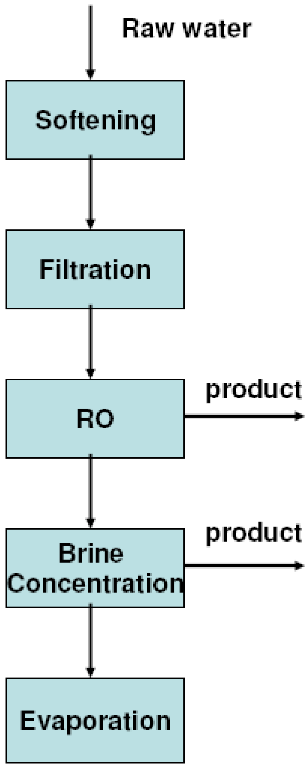


*Figure 3: Block diagram of the process in the Qasim desalination plants*

The first plant of the project 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 was 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.

## WRF 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.
- 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 Water Research Foundation (WRF; formerly 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, Bond et al. 2007.

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 figure 4.

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).

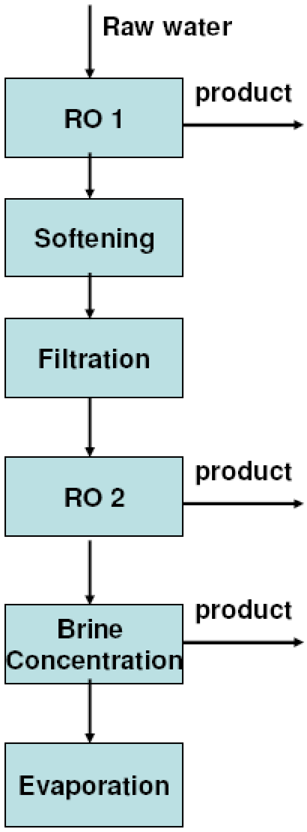


*Figure 4: Block diagram of the process studied in the WRF project*

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 to 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 hours 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 to 60 percent of those for thermal desalination followed by an evaporation pond. Energy requirements were estimated to be approximately 70 percent less.

ARLINGTON DESALTER EXPANSION

One of the first plants that will be constructed using the insights that were obtained in the WRF project described above is the expansion of the Arlington desalter.

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 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%.

Construction of the full scale plant was planned for 2009, but has been delayed as a result of the economic crisis.

## CONCLUSIONS

Pellet reactor softening is a valuable tool that can assist in the development towards zero liquid desalination. Depending on the raw water quality this can be either as stand alone process or as pretreatment for a primary or secondary RO.


## ACKNOWLEDGEMENTS

The authors would like to thank Peter Spencer and Adriana Zemunovic of the Water Corporation and for their contributions to the paper.


## REFERENCES


Dijk, J.C. van and Wilms, D.A. 1991. J Water SRT-Aqua Vol. 40, No. 5 pp263-280

Haan, A.B. de and Bosch H. 2007. Fundamentals of Industrial Separations, 2nd edition pp 8-13 to 8-19

Schagen, K.M. van. 2009. Model-Based Control of Drinking-Water Treatment Plants, p 12

Moel, P.J. de, Gier R.F.M. de and Onderdelinden, G. 1985. Design of the 50,000 $m^3$/d treatment plants for Qasim S.A.; Desalination of brackish water at 99% recovery; Second World Congress on Desalination and Water Reuse

Bond, R. and Veerapaneni, S. 2007. Zero Liquid Discharge for Inland Desalination.