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Desalination of Brackish Ground Waters and Produced Waters Using In-situ Precipitation

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ABSTRACT

The need for fresh water has increased exponentially during the last several decades due to the continuous growth of human population and industrial and agricultural activities. Yet existing resources are limited often because of their high salinity. This unfavorable situation requires the development of new, long-term strategies and alternative technologies for desalination of saline waters presently not being used to supply the population growth occurring in arid regions.

We have developed a novel environmentally friendly method for desalinating inland brackish waters. This process can be applied to either brackish ground water or produced waters (ie., coal-bed methane or oil and gas produced waters). Using a set of ion exchange and sorption materials, our process effectively removes anions and cations in separate steps. The ion exchange materials were chosen because of their specific selectivity for ions of interest, and for their ability to work in the temperature and pH regions necessary for cost and energy effectiveness.

For anion exchange, we have focused on hydrotalcite (HTC), a layered hydroxide similar to clay in structure. For cation exchange, we have developed an amorphous silica material that has enhanced cation (in particular Na^+) selectivity. In the case of produced waters with high concentrations of Ca^{2+}, a lime softening step is included.

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Executive Summary

Fresh water consumption has rapidly increased during the last several decades due to the increasing needs of industry and agriculture, and an exponentially growing human population. During this same time, the available natural fresh water supply remains limited - less than 0.5% of the Earth's water resources. This situation demands the development of long-term strategies and technologies for desalination of saline waters.

Over 90% of the existing industrial methods for water desalination are based on distillation and reverse osmosis technologies. In our project we applied an entirely new approach based exclusively on chemical processes. Our strategy was based on *in-situ* crystallization, ion exchange, and precipitation of inorganic phases able to sequester the major ionic constituents of brackish water. The goal of our project was to develop new (or modify known) inorganic phases, which are able to incorporate significant amounts of ions from saline waters. In our work we focused on three main types of materials:

- Anionic getters - materials that incorporate anions (Cl^-, SO_4^{2-}, CO_3^{2-})
- Cationic getters - materials that incorporate cations (Na^+, Mg^{2+}, Ca^{2+})
- Ionic getters - materials that could incorporate both anions and cations.

We present herein our desalination process that can be implemented inland, used as a pretreatment step for existing RO desalination processes, and is highly cost and energy efficient. Furthermore, it is also a process that minimizes and/or eliminates the problem of salt disposal and its associated environmental concerns; though solids-management costs of ion exchanges will be a factor.

Introduction

Background:

The great majority of the world's water is present in the oceans of the world and in saline ground water, inland seas, and ice formations. Of the earth's entire water supply, less than 0.5 % is directly suitable for human consumption, agricultural or industrial uses. [1]

To meet the global demand for freshwater, desalination of sea and brackish water will need to increase fourfold over the next 25 years. During the past 50 years, six desalination technologies have been pursued extensively: reverse osmosis (RO), distillation, pressure assisted evaporation, forward osmosis, electrodialysis, capacitive dionization. Yet the cost of desalting brackish water for consumption is still 2 to 3 times that of the typical publicly supplied water in municipal areas of the United States, while the cost of seawater desalination is still 3 to 5 times more than desalting brackish water. If breakthroughs are to be accomplished, then alternate strategies must be also pursued.

Brackish Water Desalination Focus Areas:

The majority of current desalination projects are focused on RO or distillation methods for seawater. [2-6, as examples of many different desalination patents] These methods are restricted to coastal water location for input of sea water (35,000 mg/L total dissolved solids (TDS)) and output of brackish water waste (<35,000 mg/L TDS). Using the Santa Barbara, CA RO plant and the proposed Tampa Bay, FL and Alamagordo, NM RO plants as models, the costs are still envisioned as high (in fact, the costs were prohibitively high in Santa Barbara and the plant was decommissioned in 1992 after only 3 weeks of initial test service). All methods require enormous amounts of energy input for the desalination methods (30% of cost) plus water and waste (30%) pumping. Furthermore, capital equipment (30%) and maintenance contribute a great deal to the cost. The result is an approximate water cost value of $1300-$2200 per acre-foot water produced. [7]

A different, yet equally important, efficient, inland desalination process is associated with the demineralization (and desalting) of produced waters from oil and natural gas wells. Currently, produced water needs to be either treated on-site prior to permitted dumping or trucked off site to a licensed dumping area. Either way is costly and energy inefficient. What is needed is a desalination process that would allow for the conservation of scarce water and maintain cost efficiency. In particular, treatment of produced water for rangeland or agricultural applications is appealing for many coal bed methane (CBM) areas. Treatment of produced water would turn a perceived environmental liability into an asset.

There are great economic drivers to convert produced brackish water into usable/potable water. Initial economic analyses have been performed for the desalination of waters from Lea County (NM) oil and gas fields and the San Juan Basin area (NM and CO). In Lea County, producers are required to dispose of 1 million barrels/day of oilfield brine. Producers are required to pay approximately $0.35/barrel to dispose of the brackish produced water and yet need 10,000 barrel/day for production needs. [8] In the San Juan Basin, CBM-produced water disposal is very expensive. Current costs average about $150K/day and could double as more CBM wells are developed and produced. The disposal costs remain high in part due to the lack of a developed water treatment infrastructure. This could be remedied if a water treatment facility or process were developed that was easily installed and cost effective. [9]

Our desalination process can be implemented inland, it can be used as a pretreatment step for existing RO desalination processes, and is highly cost and energy efficient. Furthermore, it is also a process that minimizes and/or eliminates the problem of salt disposal and its associated environmental concerns; though solids-management costs of ion exchanges will be a factor.

We present our patent-pending process [10] for the energy and cost efficient, in-situ ion exchange water treatment system. Energy and costs savings would result from: (1) the use of current city water treatment plants, with modifications; (2) the elimination of costly reverse osmosis pumping and membranes; (3) no brine product pumping/storage; (4) the ability to sell/use crystallized precipitates (building materials or infill); (5) the application inland to brine/brackish groundwater; (6) pre-treatment process for reverse osmosis.

In-situ Ion Exchangers for desalination:
Brackish water, either groundwater or produced water, can be viewed as a collection of various solvated anions and cations. What we have achieved with our process is the ability to use various low cost oxides that have a preference to select the ions commonly found in brackish water. This is done with minimal extra energy due to the high selectivity of the ion exchange materials. Furthermore, because the ion exchangers are comprised of durable inorganic oxides (as opposed to resins, such as organic polymers), they are very stable over a large pH range. Overall, the favorable kinetics of ion exchange allow for rapid and easily implemented desalination of the brackish water, resulting in potable water.

For bench scale testing, we developed a simulant solution that closely approximated brackish water concentrations found in the Tularosa Basin of New Mexico [11]. The “best” test solution was labeled Solution C. (See Table 1 for details.) We also tested our process on actual produced waters provided by Aztec Drilling of Farmington, NM. These waters had high concentrations of sodium and carbonate ions, a TDS of approximately 11,000ppm and a pH of 8.4. (See table 1)

The **anionic getter** we have developed, provides significant anionic sequestration from brackish waters. We have synthesized *Hydrotalcites* (HTCs) with general formula $[Mg_6Al_2(OH)_{16}]^{2+}[A]^{-}_{2}\bullet nH_2O$ where A = Cl^-, Br^-, I^-, NO_3^-, CO_3^{2-} and SO_4^{2-}. The synthesis of these materials is based on inexpensive starting chemicals, which react at room temperature and precipitate relatively rapidly. The HTC is activated (involving the collapse of the structure) by calcination at 550°C. After calcination and immersion in saline water, the material recovers its initial structure. In the course of water treatment, each mole of regenerated HTC incorporates two anionic equivalents from the salt solution. Our experiments showed that the activated HTCs have an average anionic incorporation capacity of 2.5 mEq/g, measured with $Na_2(SO_4)$.

Once a bulk amount of HTC is synthesized, it can be either disposed, or reused in a cyclic process. This method also allows for cost reduction - some of the side products of the synthesis and regeneration of HTCs could be either sold (NH_4NO_3) or used in the next steps of the technological process (HCl, H_2SO_4, HNO_3).

The **cationic getter** we have developed is an amorphous silica, which provides significant cationic sequestration from brackish waters. It is nominally related to an aluminosilicate named Permutite, with general formula Si_3AlO_9. We can add various amounts of elements to the framework (ie., Al; thereby incorporating a net negative charge) to tailor the ion exchange ability; depending on the dopant amount, the ion exchange capacity is between 1.7- 2.7 mEq/g, measured with NaOH.

Other cation getters have been synthesized and tested as replacements for permutite. They include zirconium phosphate and minerals such as illite, bentonite, and synthetic montmorillonite. Though their ion exchange capacities and efficiency values of exchange are less than the permutite, they could all be used as substitutes if local availability warranted.

Table 1: Ion Exchange Capacity Information from Solution C

Solution C (ppm): Ca^{2+} 40, Mg^{2+} 26, Na^{+} 665, Cl^{-} 496, SO_4^{2-} 575, CO_3^{2-} 420
pH 8.15
total X^{+} =731 ppm, total A^{-} = 1491 ppm, TDS = 2222 ppm, $\approx$ 32 mEq/l

Anion Getter	HTC: 0.95 mEq/g	η = 29.7 L/kg
Cation Getter(s)*	$Zr(HPO_4)_2\bullet H_2O$: 1.77 mEq/g	η = 55.3 L/kg
	Illite: 0.27 mEq/g	η = 8.4 L/kg
	Bentonite: 0.13 mEq/g	η = 4.1 L/kg
	Synthetic MON: 0.36 mEq/g	η = 11.3 L/kg
	Permutite (15% Al): 2.25 mEq/g	η = 70.3 L/kg

** = Exchange capacity values using post-Anion Exchanged Solution C*
η = "efficiency" value: exchange capacities of how many liters of sol C can be treated with 1 kg ion exchanger

Our new process achieves the desalination of brackish water to potable or disposable (permit-free) water by providing a process that uses a flow-through, column or settling tank systems similar to those found in municipal treatment plants. The preferred method of water treatment is first to flow the brackish water through a column containing an anion remover such as hydrotalcite, which removes monovalent ions such as chloride and nitrate, as well as divalent anions such as sulfate, and replaces them with hydroxide ion (OH^{-}). The water is then introduced into a column containing a cation exchanger, such as permutite that has been pretreated with acid. This column removes cations such as sodium, calcium, and magnesium, and replaces them with hydrogen (H^{+}) ions. The resultant water is potable, with a total dissolved solids concentration (TDS) less than 100 ppm and a pH of 5-8 (see figure 1). Note, the scheme can be reversed, where water is treated through the cation getter first, then the anion getter.

Initial cost analyses were performed by our Sandia colleagues Jim Miller and Lindsey Evans, using the Bureau of Reclamation's Water Treatment Estimation Routine (WaTER). [12] The study was based upon the treatment of Brackish water similar to Tularosa Basin composition, evaluation period of 20 years, and at a 5MGD plant capacity operating at 95% availability. The study did not include manufacturing costs of separations media, or brine water and waste disposal costs. This is also a study in which a direct comparison is made between a developmental process (in-situ) and an established process (RO) in which cost savings have already been realized due to extensive pilot-sized plant testing. This study also assumed 100% regeneration of ion exchange materials, though experiments show inability to recover ion exchange capacity with regeneration.

Cost Analysis:

The cost analysis results showed that our *in-situ* ion exchange process (named DESAL in the report) is comparable to existing RO technology (RO: \$1.16/kgal of treated water; *In-situ*/DESAL: \$2.34/kgal of treated water). We believe inclusion of inland waste costs will bring down the cost difference between our process and traditional desalination processes, like RO. Despite the cost difference, the proposed desalination process is an attractive technology for the disposal of produced waters.

Example Desalination Processes

Several desalination process sequences are possible using cation/anion getters for desalinating water. The best process cycle for a given application depends on several factors, such as the chemistry (particularly carbonate hardness) of the input water, and the desired chemistry of the output water.

Produced Water:

For example, lime softening can be used to pre-treat the brackish water to remove carbonate hardness (see table 2), which precipitates as $CaCO_3$. An equal amount of calcium/magnesium/barium hardness expressed as equivalents coprecipitates with the carbonate. The treated water then flows through the cation exchange column, followed by the anion remover column. This pre-treatment process considerably decreases the demand for cation/anion getter materials. In a separate process the water is lime softened, but the permutite is exchanged with Na^+ rather than H^+. The water is treated until the columns are saturated with divalent ions such as Ca, Mg and SO_4. If the brackish water contains a substantial amount of Na relative to Ca/Mg/Ba then a relatively small amount of permutite could pre-treat a large quantity of water prior to RO desalination. This might be done if the process is intended as a pre-treatment for RO desalination, to prevent scaling and extend the membrane life. In another process the cation exchange column is loaded with NH_4^+ rather than H^+. This might be done if the product water is intended for crop watering or rangeland reclamation.

An example process that incorporates lime softening was used to treat a sample of coal bed methane (CBM)-produced water with a TDS of 12,000 ppm in which the principal ions were Na^+, Cl^-, and HCO_3^-. Ca^{2+}, Ba^{2+}, and SO_4^{2-} were present as minor constituents at concentrations <100 ppm, and thus carbonate hardness was in excess. The water was mixed with calcium hydroxide powder in a tank that was stirred for 10 minutes, and then allowed to settle. The water was decanted and eluted through a column containing activated hydrotalcite. The eluent was then treated in a similar fashion using a column packed with acid-exchanged permutite. The final TDS of the water, as determined by conductivity measurement, was 600 ppm.

Brackish Water (Simulant):

A second example uses water where the Ca/Mg hardness is associated with chloride or sulfate rather than carbonate. In this case lime softening is not practical. A synthetic brackish water simulant (Sandia Solution Water C) containing 665 ppm Na^+, 40 ppm Ca^{2+}, 26 ppm Mg^{2+}, 496 ppm Cl^-, 420 ppm CO_3^{2-}, and 575 SO_4^{2-}. The test water was eluted first through HTC, and then through permutite. The resulting water had a TDS of 25 ppm, as measured by conductivity. (Figure 1)

In these flow-through processes, solids are incorporated into the column or tank media (i.e., the lime, cation exchanger and anion remover) and purified water exits. The resultant water is potable, with a total dissolved solids concentration (TDS) less than 600 ppm and a pH of 5-8. The column media (see figure 2; cation exchanger and anion remover) are inexpensive and can be regenerated or disposed. The cation exchanger can be regenerated by treating with acid or ammonium salt. The anion remover can be regenerated by calcination at moderate temperature. Alternatively, the used column media can be used as landfill, soil amendment, or raw material for cement production. Because the process is passive, the cost of energy for forced permeation, heating and pumping is eliminated. In addition, brackish water waste is eliminated, leading to environmental savings. The leach-free solids produced are retrieved and used as building materials or landfill. This process eliminates salt product disposal and membrane costs. Only material costs remain, resulting in a decrease over current method desalination costs.

Conclusion

The present invention has far reaching impact. The United States will greatly benefit because of the immediate availability of vast reserves of brackish inland water sources at minimized energy. There is great potential to turn a perceived environmental liability, hydrocarbon produced water, into useable fresh water. The present invention requires minimal to no extra energy input for salt and mineral removal. The novelty of the present invention is that it is a bulk process, much like current flocculation processes for cleaning city water and therefore can be incorporated into existing water treatment facilities with minor modifications (to account for increased solids production and difficulty in separation of ion exchange materials). Furthermore, salt and brackish water side-products would be non-existent in this process. The salt removal process of the present invention results in inert "dirt-like" products that are not caustic to the environment and have other applications and/or sales potentials.

Energy and cost savings result from (1) the use of current city water treatment plants, with modifications; (2) the elimination of costly reverse osmosis pumping and membranes replacement/upkeep; (3) no brine product pumping/storage; (4) the ability to sell/use crystallized precipitates (building materials or infill); (5) the application inland to brine/brackish groundwater; (6) pre-treatment process for reverse osmosis; (7) low capital requirements; (8) is field deployable in remote areas; and (9) can be efficiently operated at low plant capacities (< 1000 gal/day).

Table 2: Produced Water Flow-Diagram

- Brackish water was obtained from the San Juan Basin, Farmington, NM with composition:
  - TDS~11,000 ppm, pH = 8.4
  - Ca^{2+} 22 ppm
  - Mg^{2+} 17 ppm
  - Na+ 4500 ppm
  - Cl^- 2200 ppm
  - SO_4^{2-} <1 ppm
  - HCO_3^- 8300 ppm

- *Lime softening* reduced TDS, ~ 8,000 ppm, pH was increased to 12.4

↓

- Putting the water through *cation exchange* column, TDS ~ 2,600 ppm,
  pH = 2.9

↓

- Putting water through the *anion exchange* column, TDS ~ 600 ppm, pH increased to 5.0

↓

- Various combinations have benefit for rangeland and industrial needs

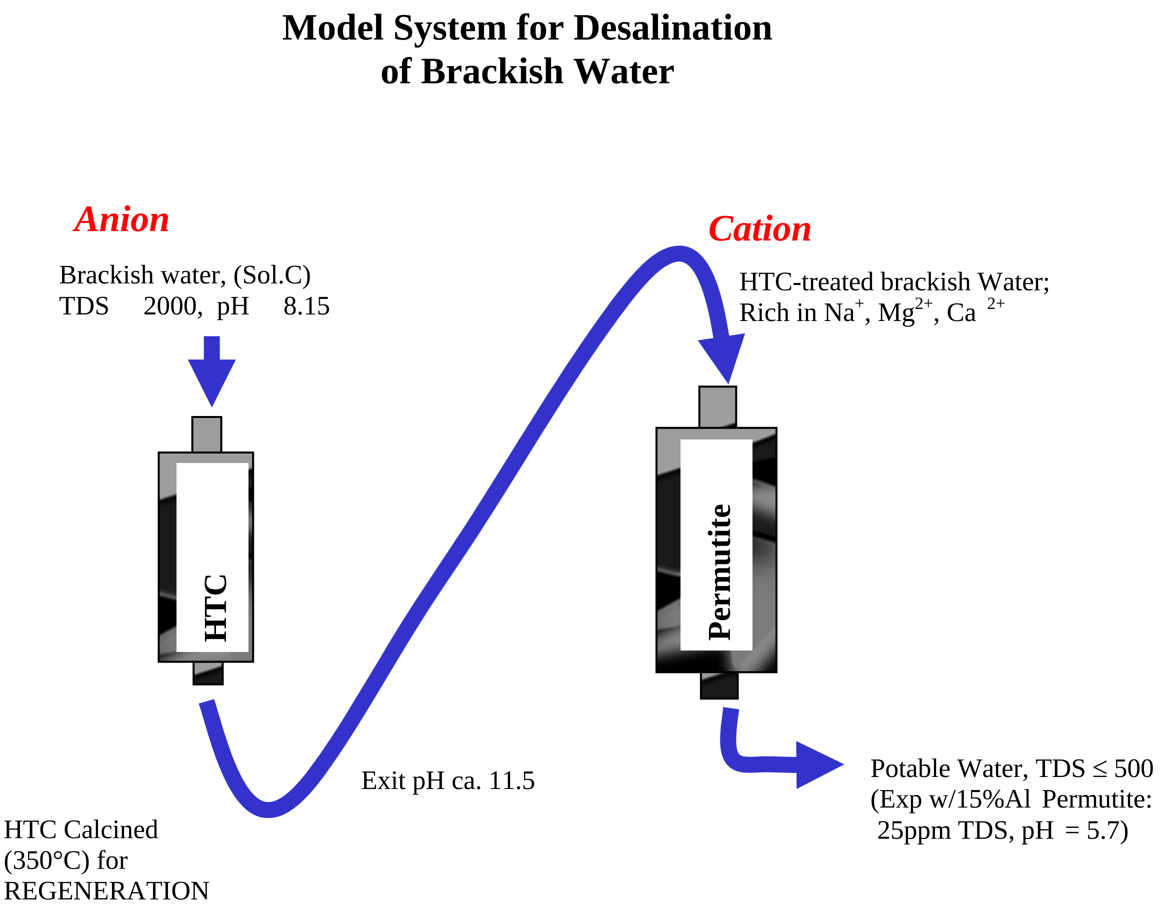

Figure 1. Test Apparatus on Sandia Solution Water C

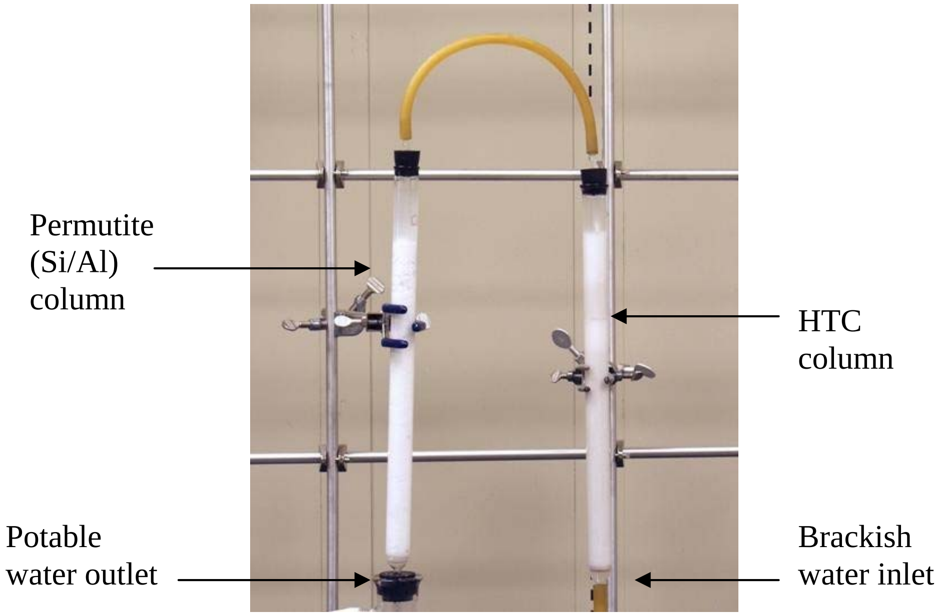

Figure 2: In-lab Column Testing

Acknowledgments

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