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# Treatment of Saline Irrigation Water Using a Sulfate-Reducing Bioreactor Coupled with an Iron-Based Desalination Reactor

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**Abstract:** Recent advances in alternative water desalination technologies have become increasingly common, due in part to expanding water scarcity and the ability to deliver usable water without the high energy cost and advanced infrastructure required of traditional desalination technologies such as reverse osmosis (RO). One such emerging technology is iron-based desalination or the use of nano- (or micron-sized) metals (principally iron) to desalinate water. In this study, iron-based desalination was coupled with passive sulfate reduction technology (SRB) to partially treat saline irrigation water similar in composition to that encountered in the San Joaquin Valley, California, USA. Water scarcity, especially in the southwestern United States, is driving an effort to identify and use less expensive but effective desalination methods to allow the use of saline groundwater, seawater, and impounded saline agricultural drainage and runoff for crop growth. The system described here used a synthetic water mimicking a typical saline irrigation water; this was then routed through a sulfate-reducing bioreactor to remove the sulfate prior to entry into an N-ZVM reactor for removal of Na and Cl. Sulfate at high concentrations can inhibit Na and Cl removal in N-ZVM reactors. The results showed that the sulfate was reduced from 2500 mg/L to less than 250 mg/L in the bioreactor, which allowed the N-ZVM to reduce the Na and Cl by 50%. This allowed the conductivity to decrease from 9.2 mS to about 5 mS. Synthetic irrigation water without sulfate removal was only desalinated by about 10%. The observed change in conductivity, sodium, and chloride content allowed the discharged water to be used for irrigation of many field crops and some vegetables. This paper provides reactor development, manufacture, and performance information including recommendations for continued performance increases.

**Keywords:** sulfate reducing bioreactor; nano iron; zero valent metals; saline irrigation water; desalination; passive water treatment; salinity; anaerobic sulfate reduction

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## 1. Introduction

Recent advances in alternative water desalination technologies have become increasingly common, due in part to expanding water scarcity and the ability to deliver usable water without the high energy cost and advanced infrastructure required of traditional reverse osmosis (RO) and other active treatment technologies. Carbon-based nanotubes, microbial desalination, natural zeolite desalination [1], solar distillation, removal via algal growth and harvesting, eutectic separation [2], desalination through electric field application [3,4], and iron-based desalination [5,6], US Patent 10919784B2 are but a few of the emerging technologies that can provide usable water without expensive equipment and with much lower energy costs. While not all of these technologies can produce drinking water, they can treat water sufficiently for irrigation and industrial use, thus lowering the pressure on potable water use.

With population growth and climate change applying additional pressures on precious freshwater resources, new methods of desalinating water must be developed. The nano zero valent metal (N-ZVM) reactor approach is a new process for desalinating water (removing Na and Cl primarily) using carbon modified nano-sized (20 nm to 200 nanometers) and/or micron-sized zero-valent metals, principally Fe, Al, and Cu, and occasionally Mg. This

method of desalination can be accomplished using near-zero to very little external energy. Certain details associated with the process are described in US Patent, US-10919784B2.

Metallic-based desalination is novel and may have wide applications, including: (1) treating saline water for irrigation use by lowering electrical conductivity to levels tolerable by different crop types, (2) desalinating aquifers by placing the reactive media in wells that are spaced to cover a large area of influence, (3) desalinating water where infrastructure is lacking due of its mobile characteristics, low energy input, and simple design, (4) desalinating frac water, oil field flowback, and produced water, since the media performance is concentration-dependent, (5) serving as an upfront (upstream) salt reduction system for RO plant efficiency improvement and/or a brine treatment process, when coupled with RO and IX systems, and (6) directly desalinating seawater.

The iron-based desalination approach is novel due to other process characteristics as well. While the method is somewhat kinetically sluggish compared to membrane and resin methods, it typically does not require any pretreatment of the water prior to desalination. The only constituent that appears to negatively affect the performance of the iron-based method is water with high sulfate concentrations. In this case, a passive bioreactor could be used to eliminate the sulfate prior to desalination, as in this study. The iron-based desalination does not produce brine. Instead, the salt is tied up in corrosion products that form a solid during treatment and salt removal.

The N-ZVM media also removes many other constituents in the water during desalination either directly or indirectly, including nitrate/nitrite, calcium, magnesium, bicarbonate, various metals (zinc, lead, chromium, copper), metalloids (arsenic, selenium, borate), and even chlorinated solvents.

The initial discovery that N-ZVM could remove significant quantities of Na and Cl was reported by [7]. Since that time other important publications describing improved desalination using N-ZVM as well as possible mechanism of N-ZVM desalination have been described by [8–10]. These publications served to identify properties of N-ZVM that facilitate removal of Na and Cl; describe different formulations of N-ZVM that could remove Na and Cl; explore the effect of particle size on rates of desalination; identify the effect of initial salt content on rates of desalination; and explore desalination outcomes at different Eh/pH regimes, pressures, temperatures, and water chemistry constituents. Different reactor configurations and uses of the technology were also explored.

As mentioned previously, iron-based, N-ZVM desalination systems can be used for seawater desalination and treatment of saline irrigation water and other saline-rich waters. However, with persistent and worsening drought conditions, sea level rise, and coastal intrusion of salt water into groundwater, the need for usable irrigation water in many parts of the world is becoming a problem of paramount importance. In southern California, USA alone an estimated 250,000 acres of land have gone out of production due to salt accumulation, while another 1.5 million is considered impaired (communication from the Daniel Cozad Central Valley Salinity Coalition). A technology that is inexpensive, does not require high energy input, and is easily mobilized and deployed could allow treatment of these saline irrigation return waters and local but saline groundwaters, thus easing the pressure on other water resources. While it has been shown that these N-ZVM treatment plants can remove Na, Cl, and a host of metals, nitrate/nitrite, and other chemicals, they do not appreciably lower the sulfate content of the water; hence, producing usable water from saline irrigation water in many parts of the western USA, all of which contain appreciable sulfate, could be a serious impediment to the ultimate application of the technology. This paper describes one means of overcoming the sulfate problem, coupling a sulfate-reducing bioreactor (SRB) with an iron-based desalination unit.

The objectives of this study were threefold:

1. Determine the compatibility of two (2) low-cost, low-energy-use water treatment systems for the demineralization of saline irrigation water.
2. Assess the overall chemical changes expected from each unit, and

3. Use the results of the study to improve the performance of the two-stage system for future pilot work.

## 2. Technology Description

What follows is a brief review of the system components and a description of the water used in the study.

### *2.1. Influent Water*

For this study, a chemical profile of a typical saline irrigation water was chosen. Irrigation water often has similar concentrations of chloride, sodium, and sulfate, in contrast to seawater which has much higher levels of sodium (Na) (10,000 mg/L) and chloride (Cl) (15,000 mg/L) compared to sulfate (2000 to 3000 mg/L). Seawater can be largely desalinated without first removing the sulfate. If saline irrigation water contains appreciable sulfate, it must be reduced before the Na and Cl can be removed, as the presence of sulfate is thought to alter the reaction sequence responsible for Na and Cl removal using the N-ZVM reactor [8].

The paper provided by [11] lists the chemical composition of common irrigation well water from the San Joaquin Valley in California, USA and was used as a guide in making synthetic irrigation water for this study. This water is similar to those described by [12,13].

### *2.2. The Sulfate-Reducing Bacteria Reactor (SRB)*

Sulfate-reducing bioreactors (SRBs), like the iron-based desalination unit, are inexpensive and can be operated in an almost completely passive manner [14]. There are other faster methods of removing sulfate, such as precipitation with calcium hydroxide, barium salts, or lime plus powdered aluminum metal, but these methods have high chemical costs and produce high volumes of sludge that require intensive management. The SRB is a simple unit to construct and only requires a carbon source to drive the bacterial reactions. In addition, the effluent typical of SRBs fits well with the operational parameters of N-ZVM desalination plants: circum-neutrality to alkaline pH and modest alkalinity (<250 mg/L).

Bioreactors have been used in recent years to treat oil field waters, primarily acid mine drainage (AMD) [15–21]. These anaerobic reactors utilize sulfate-reducing bacteria (SRB) to (1) reduce sulfate to sulfide, (2) precipitate divalent heavy metals to sulfide solids, and (3) produce alkalinity in proportion to carbon utilization by the microbial population. High-metal concentrations are removed as sulfides, carbonates or oxides, while acidity decreases and pH increases [22–25]. Many of the bioreactors are constructed using a flow-through design wherein water flows through the treatment media, which also serves as the carbon source. Carbon media typically utilized include mushroom compost, manure, and wood chips [21,26], though other efforts have explored the use of liquid carbon sources [26–29]. Reactors with a solid carbon media source are usually very effective initially but can lose effectiveness over time due to consumption of easily utilized carbon, significant changes in hydraulic conductivity, and sludge accumulation in the reactors. The primary purpose of these reactors has typically been acidity and metal removal; sulfate reduction is used as a mechanism to create enough sulfide to treat the metals and generate alkalinity.

In this work, sulfate reduction was the main concern, and design was tailored to optimize sulfate reduction rates. Instead of flow-through organic media, the carbon source, ethanol, was fed continuously into the reactor as a source of chemical oxygen demand (COD) to achieve reduction. Ethanol theoretically produces 2.09 mg COD/mg ethanol [19]. The reactors were also filled with media, as described below, needed for bacterial support.

The basic microbial processes are well known and include the following generalized reactions.

For sulfate and carbon, utilization by the sulfate-reducing bacteria produced sulfide (dissolved and as a gas) and alkalinity as shown in Reaction (1). The reaction shown is an

overall representation of several microbial processes and chemical pathways. The sulfide produced was partially deprotonated and solubilized based on ambient pH.

$$SO_4^{2-}{}_{(aq)} + 2CH_2O_{(aq)} \rightarrow H_2S_{(g)} + 2HCO_3^{-}{}_{(aq)} \quad (1)$$

Any divalent metals (such as zinc, copper, iron, or lead) in the water reacted with the sulfide and precipitated as sulfide solids:

$$HS^{-}{}_{(aq)} + M^{2+}{}_{(aq)} \rightarrow MS_{(s)} + H^{+}{}_{(aq)} \quad (2)$$

Excess sulfide off-gassed or formed elemental sulfur:

$$2HS^{-}{}_{(aq)} + O_{2(aq)} \rightarrow 2S^{o}{}_{(s)} + 2OH^{-}{}_{(aq)} \quad (3)$$

and/or converted back to sulfate in high $O_2$ waters:

$$2HS^{-}{}_{(aq)} + 4O_{2(aq)} \rightarrow 2SO_4^{2-}{}_{(aq)} + 2H^{+}{}_{(aq)} \quad (4)$$

### *2.3. The Nano Zero Valent Metal (N-ZVM) Reactor*

Overall, the iron-based desalination process used in this study was simple (Figure 1):

- In this study, a single desalination reactor was used. In other pilots, to improve performance and throughput, multiple tanks in series or parallel or both can be used. If multiple reactors were to be used, they were placed in close proximity to allow the saline water to transfer from one tank to the next via gravity, the number determined by the desired level of desalination.
- Compressed air was injected at the bottom of each tank to provide an air flow of about 0.5 to 2 L/min depending on tank size and water volume. This induces air bubbles which rise to the top of the tanks.
- At the same time as air was injected at the bottom, the modified nano-media as a slurry was injected through the top of the tank to produce a counterflow effect and allow the nano particles to interact with the rising air bubbles.
- Once in place, the desalination of the water in the tank began.
- The reaction lowered the salinity and conductivity of the water until a baseline level was reached.
- The system did not produce brine as a waste. Instead, it produced a small amount of solid waste consisting of salt-intruded metal hydroxides.

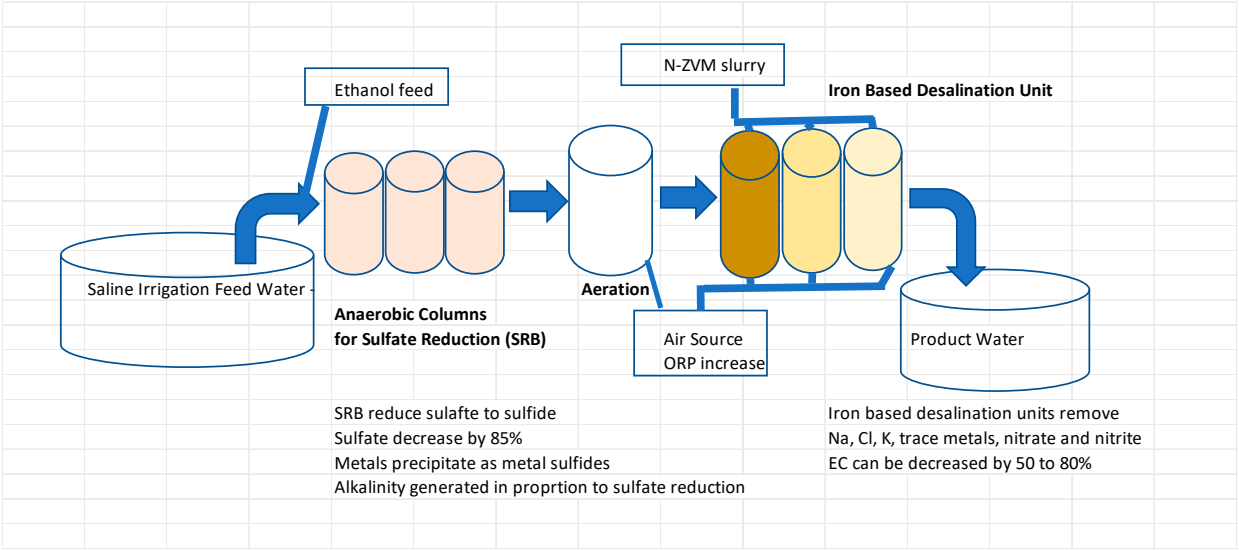



**Figure 1.** General schematic of the proposed system for saline irrigation water treatment.

The actual chemical process associated with the desalination method is not completely understood but does include a surface area affect and a catalytic mechanism associated with certain corrosion products that occur when metallic iron (and other metals) is placed in saline water under oxic or anoxic conditions. Much of the history and background on N-ZVM salt removal and the possible mechanisms can be found in [8].

## 3. Design, Construction, and Operation

The design considerations for the system were derived primarily from past studies, literature sources, and private communications with several other researchers in this field. These are summarized below. For the SRB:

- The SRB reactors were run in flow-through mode to continuously empty into a collection tank which when full was batch-treated by the N-ZVM reactor. Biologically mediated sulfate reduction is slow compared to desalination and would require more reactors to allow flow through both components of the system.
- The pilot test relies on SRB for sulfate reduction, while the N-ZVM reactor removes Na and Cl after the sulfate is reduced.
- The carbon source for the SRB was a liquid alcohol (ethanol) source fed at the influent to the reactors. The ethanol solution also contained 10% of a calcium lactate solution for suppression of the bicarbonate produced by the SRB reactors.
- Saline water was pumped from a set of 250 L plastic containers via a peristaltic pump.
- Water flowed from the first reactor in an up-flow manner, then to the second and third SRB reactors in series. Once complete, the effluent from the SRB part of the system was collected in a 200 L plastic tank where it was used to batch-feed the N-ZVM reactor.
- Each SRB reactor contained 1 sampling point on the effluent port between the reactors.

Overall, the SRB process included:

- Three 55 L SRB reactors, each with 40 L of void volume.
- Each SRB reactor was approximately 30.5 cm diameter and 91 cm tall.
- Each reactor contained 3 cm of rock above the inlet piping at the bottom, followed by 6 to 8 cm of vegetable compost and 70 to 80 cm of plastic fluidized media.
- Three pumps were used, one to deliver raw synthetic saline irrigation water to the SRB, a smaller peristaltic pump connected to the main raw water feed line to allow carbon dosing of the raw water, and a third to batch-feed sulfate-free water to the N-ZVM reactor.
- Carbon dosing was set to achieve a COD-to-sulfate ratio of 1 to 1.5 using ethanol with 10% calcium lactate added to suppress carbonate increases produced from the microbial metabolism of added carbon substrate.
- While it is possible to achieve significant sulfate reduction in less than 36 h, a 48 h retention time was used to maximize the sulfate reduction [14].
- The flow rate through the system based on this hydraulic retention time (HRT) was 2.5 L/h.
- A startup period where each of the 3 SRB cells was inoculated with 5 mL of anerobic sludge obtained from the King County Municipal Water Treatment Plant, Washington State, USA. Approximately 3 weeks were required for the system to begin the sulfate reduction, usually characterized by an oxidation reduction potential (ORP) of −350 to −400 mv.

Effluent water from the SRB system was directed to a feed tank for the 130 L N-ZVM reactor with dimensions of 30.5 cm diameter by 183 cm height. This reactor had an airline connected to the bottom of the reactor and an internal diffuser that bubbled air up through the reactor at an external flow rate of 0.5 to 1 L of air/min. The air flow was controlled by an air compressor or medium-sized aquarium air pump. A small reservoir (2 L) containing the N-ZVM slurry allowed delivery of the N-ZVM slurry to the top of the reactor to provide a dose predetermined (approximately 10 mL of slurry containing 2 to 5 g of solid N-ZVM) to achieve at least 60% Na and Cl removal over a 2 h time period. The slurry was composed

similarly to that described in US Patent 10919784B2. This amount of slurry resulted in a range of salt removal of 160 to 192 g of NaCl per g of added N-ZVM. The N-ZVM used in the study was purchased from Honwu Nanometer, Guangzhou, China. The material was shipped as a wet cake in a sealed plastic bag with a nitrogen gas blanket. The average particle diameter was 50 nm. The nanoparticles were blended with aluminum and copper metal powder and then treated with organic mixtures to cap and retard the rapid oxidation. Many experimental runs were also accomplished successfully using polyphenol/iron salt mixtures, but not in this particular study. Several runs were also accomplished, placing the slurry in an open-ended cannister securely held within the reactor body as described in US Patent 10919784B2.

Since the SRB portion of the system was the rate-limiting step, the N-ZVM reactor was run in batches. Once the SRB effluent tank reached about 120 L, it was pumped to the N-ZVM reactor using a small transfer pump. After 2 h of treatment, the N-ZVM-treated water was conveyed to a holding tank to settle the reaction products prior to discharge. Overall, the general conceptual system used to demineralize the water is depicted in Figure 1.

## 4. Sampling and Analysis Methods

*Operation of System Components*

Once the system was started, the following samples were collected:

At the SRB reactors, an influent raw water sample was collected for the determination of sulfate, pH, ORP, and electrical conductivity (EC). During the operation, the samples were collected on the effluent side of the SRB every 48 h (the HRT) and also analyzed for sulfate, pH, ORP, and EC.

The water collected from the SRB cells was tested before entry into the N-ZVM reactor. The 120 L sample introduced to the NZVI reactor occurred every 48 h, as it took two days to produce sufficient effluent to fill the ZVI reactor. These analyses included sulfate, sulfide, chloride, EC, pH, and ORP. Once the reactor was started, the samples were collected at the end of each 2 h run for the same analyses.

An additional four runs were also performed to demonstrate the effect sulfate has on suppressing Na and Cl removal via the N-ZVM reactor. In these cases, synthetic water was directed directly to the N-ZVM reactor without routing through the SRB sulfate removal cells.

Methods of Analysis included:

Sulfate—turbidimetric method using a Hach 900 portable spectrophotometer. Quality control samples for assessing accuracy and precision of sulfate measurements were prepared from a stock sulfate solution of 1000 mg/L purchased from Hanna Instruments. Otherwise, the manufacturer's instructions for use were followed.

Chloride was determined with ISE methodology using an Oakton combination chloride ion-specific electrode and meter. The chloride standards were prepared from a stock 10,000 mg/L Cl solution prepared and purchased from Cole-Parmer. The standards ranged from 100 mg/L Cl to 1000 mg/L to 10,000 mg/L.

EC was determined using a HANNA Instruments HI6321 benchtop EC meter and EC cell with a range from 0.001 uS/cm to 1000 mS/cm.

pH was determined using a Hanna HI9900.3 combination, a portable solid-state pH/ORP/Temperature electrode, and a meter.

COD was determined using Hach DRB200 digital reactor COD test equipment.

Prior to measurement, all the probes and glassware were rinsed thoroughly with deionized water. The glassware was acid-washed at the end of each day and the probes set in standard storage solutions. Calibration was carried out at the beginning of each run and then again after the next set of samples was collected. The error associated with the chemical measurements was generally 10% or less. This was determined primarily from multiple measurements for accuracy and precision using standard solutions. The EC, pH, and ORP measurements appeared to be consistent, but both could drift with time. The drift in either direction could be due to ongoing chemical reactions, so to minimize the effect,

the probes were kept very clean and changed monthly to keep the electrode response rapid relative to the drift rate. Chloride determination was the most difficult to perform due to rapid electrode fouling in certain slurry combinations, which on occasion would increase the rate of error to almost 20%. Three methods assisted in obtaining more reliable chloride data: (1) filtering the samples prior to determination (0.2 micron nylon filter), letting the solutions settle after collection for 2 h, and (2) keeping a duplicate Cl electrode in the discharge vessel to collect continuous data much like an inline measurement configuration.

## 5. Results

The water used in the study was made from a mixture of halite (NaCL) salt and magnesium sulfate salts mixed with tap water to achieve the following water composition. For comparison, the well water used for irrigation in the Thellier [11] studies also shown in Table 1.

**Table 1.** Chemical composition of feed water used in study.

| Anaylte | This Study | Irrigation Well Water (San Joaquin Valley, CA) after Thellier [11] |
|---|---|---|
| Cl (mg/L) | 2100 | 1643 |
| Na (mg/L) | 1342 | 1219 |
| $SO_4$ (mg/L) | 2500 | 4116 |
| pH (standard units) | 7.2 | 7.5 |
| Electrical Conductivity (EC in mS) | 9.3 | 7.96 |

The primary difference between the samples consisted of the sulfate content and the resulting EC. The test water used in the study had a lower sulfate content (2500 mg/L compared to 4100 mg/L) in the reported saline well irrigation water. Our test water also had a slightly higher EC (9.3 mS) compared to about 8 mS in the Thellier [11] study. In both cases the sulfate was higher than either the sodium or chloride in the water, which fulfilled the main objective.

Prior to initiation, the SRB reactors were run for 5 weeks during and after inoculation to determine when peak sulfate reduction occurred. When sufficient sulfate reduction occurred (>85%), the treatment process was started (Figure 2).

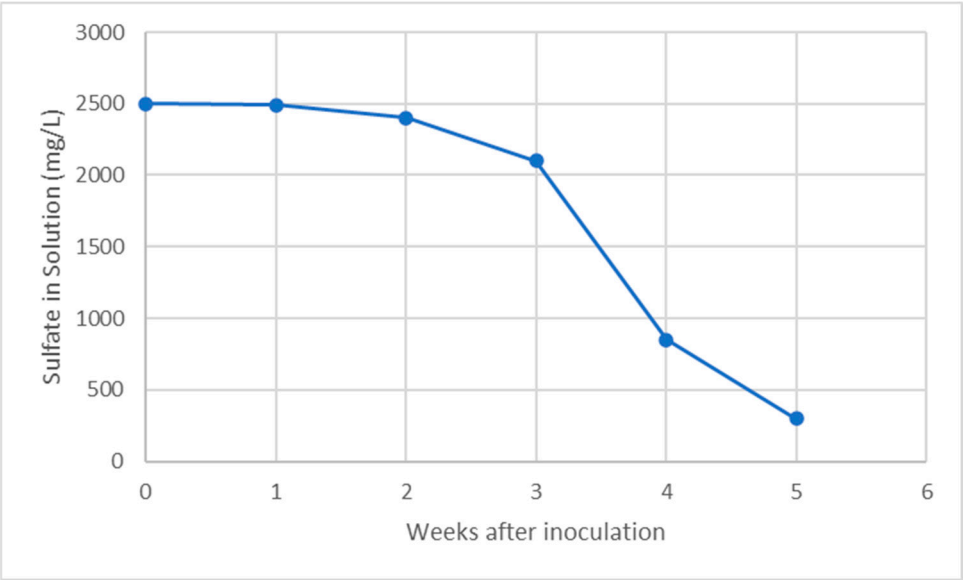



**Figure 2.** SRB reactor startup and inoculation period.

As depicted in the figure, sulfate reduction began at week 3 and then declined substantially from an initial concentration of near 2500 mg/L to under 500 mg/L. At this time, the reactor was allowed to continuously operate. Discharge from the SRB cells was collected for introduction to the N-ZVM reactor. The ORP on the effluent side of the SRB at week 3 was approximately −370 mv and declined to −440 mv by week 5. This range of ORP values is commonly used to guide the startup of SRB reactors [14].

Once the SRB cells were started, it took 48 h of operation for the SRB to produce sufficient water to fill the N-ZVI system. Table 2 displays the effluent from the SRB and the effluent from the NZVI reactor for the entire 14 run time frame (roughly 28 days).

**Table 2.** SRB and N-ZVM discharge data.

| Run # | SRB Effluent $SO_4$ (mg/L) | SRB Effluent EC (mS) | N-ZVM Effluent EC (mS) | N-ZVM Effluent Cl (mg/L) |
|---|---|---|---|---|
| 1 | 420 | 9.3 | 5.5 | 1210 |
| 2 | 305 | 9.1 | 5.2 | 1100 |
| 3 | 200 | 9.4 | 5.1 | 1050 |
| 4 | 180 | 9.2 | 5.4 | 1050 |
| 5 | 190 | 9 | 5.2 | 1200 |
| 6 | 220 | 8.9 | 4.9 | 1000 |
| 7 | 200 | 9.1 | 4.8 | 950 |
| 8 | 220 | 9.0 | 4.7 | 900 |
| 9 | 150 | 9.1 | 4.8 | 990 |
| 10 | 180 | 9.1 | 4.9 | 1050 |
| 11 | 2450 | 8.9 | 8.3 | 1745 |
| 12 | 2500 | 9.0 | 8.1 | 1710 |
| 13 | 2300 | 9.1 | 8.2 | 1735 |
| 14 | 2400 | 9.0 | 8.1 | 1755 |

There are a number of interesting observations in the effluent data:

Firstly, the SRB effluent sulfate continued to decrease during the run sequence. The sulfate at startup was just under 500 mg/L but dropped to about 200 mg/L at run 3 and remained close to this value for the duration of the study.

Secondly, the expected SRB effluent EC did not appreciably change, since sulfate reduction typically results in an increase in bicarbonate (and sulfide) concentrations from the biological carbon metabolism, offsetting the reductions in sulfate. The bicarbonate concentration was dampened somewhat by the addition of calcium as calcium lactate, but this was not really clear from the effluent data. In addition, the presence of soluble, charged organic species from the lactate and the layer of compost producing charged organic species in the reactor cells may have contributed to the observed conductivity readings.

The N-ZVM reactor was able to reduce the conductivity from about 9 mS to between 5.5 and 4.7 mS or roughly 47% on average, a substantial drop in the salt content of the water. This was validated by the change in chloride concentrations, which decreased from 2100 mg/L on the influent side to consistently near 1000 mg/L on the effluent side. Assuming the Cl and Na are removed in a normal molar relationship, the sodium would have decreased from 1342 mg/L to about 600 to 700 mg/L. Given the decrease in Na and Cl observed in the effluent, other dissolved constituents such as magnesium, bicarbonate, and organic acids would have contributed to a higher observed EC than that predicted from the Na and Cl alone. Future studies with the reactor will account for all the major dissolved chemical species.

Test runs 11 through 14 demonstrate the N-ZVM reactor performance without first removing the sulfate. In these cases, the conductivity only decreased from 9.0 to only 8.2 or decreased by only 9% compared to about 50% with the sulfate first removed.

## 6. Discussion

The pairing of an SRB reactor with an N-ZVM reactor produced a substantial decrease (near 50%) in salt content. The water produced from the treatment system at an EC of 5 would have a total dissolved solids content of around 2500 to 3000 mg/L, which is likely considered a usable water for many crop types [9].

This type of system for agricultural use is promising due its low material and construction cost and very simple operational parameters. The system used in this study cost less than $350 USD, with half the cost being for pumps and aerators. The materials can be sourced locally, and the waste from the system is highly manageable. For example, the SRB reactors upon decommissioning simply dry out, and the biomat decomposes completely, leaving only the plastic media behind, which can be reused or recycled. The N-ZVI system does not produce a brine but only a thin layer of iron/aluminum hydroxide reaction products containing imbedded halite compounds at the bottom of the settling tank. If the N-ZVM media is contained within a canister in the reactor, then the only real waste is the used canister.

Improvements to both components of the system will include expansion of the SRB footprint to produce effluent at a rate that matches the operational rate of the N-ZVM reactor. Expanding the SRB half of the system to include 10 to 12, 2 $m^3$ HDPE reactors, a continuous source of sulfate-low water can be fed to the desalination unit at 0.03 $m^3$/min or about 40 $m^3$/day. Multiple units would increase the capacity further. In this study, a 48 h retention time was used on the SRB side of the system, but this could be shortened to 24 h and perhaps even 12 h. This would reduce the SRB footprint and allow much faster processing of water. Finally, it is worth comparing the use of lime or lime plus aluminum powder as a means of rapidly reducing the sulfate instead of biological sulfate reduction, if the resulting gypsum sludge could be recycled back into agricultural use. The study also did not consider how much sulfate reduction had to occur to allow desalination to occur. If only 50% sulfate reduction was required, then the system capacity increases substantially. The next steps include identifying the optimal sulfate/chloride ratio required for substantial (50 to 80%) desalination of the product irrigation water.

The SRB-N-ZVM reactor is already being expanded (Figure 3). The aluminum SRB reactor depicted contains six separate SRB cells, each with a 0.3 $m^3$ capacity. This will be used to test different HRTs and sulfate removal targets. The desalination unit will also be further tested to increase efficiency and throughput and to reduce the salt content by 75 to 80% rather than 50% as in this study. The new pilot system will also be controlled via a programmable logic controller (PLC) such that influent flow rate, air pressure, and flow are remotely controllable. The device is fitted with pH, ORP, and EC meters on the influent and effluent side of the pilot. Continued improvements in this technology will make it attractive as a mobile source for desalination of irrigation water, irrigation drainage water, and seawater.



**Figure 3.** SRB portion of N-ZVM pilot plant under construction.

## 7. Conclusions

A sulfate-reducing bacteria reactor was coupled with a nanometal (N-ZVM) reactor to determine if the two systems could effectively remove sulfate and NaCl from a synthetic irrigation water modeled on the saline irrigation water in the San Joaquin Valley, California, USA. Past studies and various patents have demonstrated that zero valent metals, especially iron, could effectively remove Na and Cl (and other chemicals) from water. However, the zero valent metals do not substantially reduce sulfate in water. In waters with high Na and Cl contents relative to sulfate, such as seawater, this may not be a significant problem. It is a problem in arid regions where gypsiferous soils or evapoconcentration of irrigation water lead to high soluble sulfate levels equal to or exceeding Na and Cl concentrations. Wide application of the N-ZVM process will depend on a means of inexpensively removing sulfate.

The results of the study suggest that the two systems are compatible and can be expected to reduce salinity by as much as 50%, which could allow reuse of the saline irrigation water without having to blend it with potable water; this is often the preferred practice in parts of California and other regions of the arid western US.

The study is not without its limitations. For example, the SRB part of the system can be quite slow, with typical hydraulic residence times of 48 h to achieve 75% or more sulfate reduction. A viable system will have to maximize the number of anaerobic cells to continually feed the N-ZVM reactor. The carbon feed used to drive the microbial reaction will have to be examined to ensure it is cost-effective, readily available, and most importantly, easily metabolized by the bacteria. The N-ZVM reactor can be improved by treating the water using reactors in a series, such that far more than 50% of the Na and Cl can be removed.

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**Conflicts of Interest:** The author declares no conflict of interest.

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