



Article Partial Desalination of Saline Groundwater, including Flowback Water, to Produce Irrigation Water

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Abstract: Globally, more than 50 million ha of arable land is irrigated with saline water. The majority of this saline irrigation water is derived from saline groundwater. Global irrigation requirements may increase from 270 million ha in 2014 to about 750 million ha by 2050 as the global population increases to 9.1 billion people. The majority of this additional irrigation water is likely to come from saline groundwater sources. Desalination of irrigation water increases crop yield. A combination of high water volume requirements and low crop yields requires that, for widespread usage, the desalinated irrigation water product will require a delivery price of <USD 0.5 m³. This study considers five passive desalination routes (n-Fe⁰; n-Fe₃O₄; Fe⁰:Fe(b)@C⁰ polymer; n-Fe⁰:Fe(b) polymer; n-Fe(b) polymer) that may potentially achieve this goal: A common desalination mechanism is identified for the Fe^{0} :Fe(b)@ C^{0} polymer; n-Fe⁰:Fe(b) polymer; and n-Fe(b) polymer routes. The analysis establishes that the n-Fe(b) polymer route may be able to achieve (with a reaction time of 1 h) an 80% to 90% desalination of saline groundwater or flowback water (12.3 g NaCl L^{-1} ; EC = 17.6 dSm⁻¹), to form partially desalinated irrigation water (1.2 to 2.4 g NaCl L^{-1} ; EC = 2 to 3.4 dSm⁻¹) with an associated reduction in the sodium adsorption ratio (SAR) from 125 to between 1.2 and 2.5, for a potential material (n-Fe(b) polymer) treatment cost of $\langle USD 0.01 m^{-3}$, after considering polymer reuse and recycle, but excluding all other plant and other operating costs. The examples demonstrate that the polymers can be used to create: (i) a desalinated stationary hydrodynamic plume, containing 47,123 m³ water (1 to 2.5 g NaCl L⁻¹), within 157,080 m³ porous rock forming a confined, saline aquifer (18.59 g NaCl L^{-1}), to act as a reservoir of desalinated water (96 m³ d⁻¹) for irrigation, with the potential to produce >960 m³ d⁻¹ as required; (ii) a desalinated, perched, stationary, shallow groundwater mound, located above the regional water table, containing >200 m³ of desalinated water.

Keywords: saline groundwater; saline irrigation; flowback water; desalination; zero valent iron desalination; metal polymer desalination; groundwater mound; stationary hydrodynamic plume

1. Introduction

Global cropland comprises about 1724.08 million ha, of which about 403 million ha were irrigated during 2019 [1]. Water used for irrigation falls into two categories: (i) rainfall-derived water, which is termed green water [1]; and (ii) surface water + groundwater-derived water, which is termed blue water [1]. Globally, about 72.5% of cropland is rain fed, receiving about 8325.12 km³ a⁻¹ [1], The remaining 27.5% of global cropland is irrigated with blue water, about 1299.19 km³ a⁻¹ [1]. Blue water represents >87% of global consumptive water usage [1]. This consumption is currently split as follows: Asia 72.6% [1]; Africa 6.4% [1]; Europe 7.2% [1]; North America 10.8% [1]; Oceania 0.5% [1]; and South America 2.5% [1]. Total water consumption due to irrigation is 1131.04 km³ a⁻¹, of which 910.83 km³ a⁻¹ is used for crop irrigation [1].

One billion ha of land are adversely affected by salinization, including more than 20% of irrigated land (>80.6 million ha) [2]. Soil is considered to be saline when its electrical conductivity (EC) exceeds 4 dSm^{-1} (4 mScm^{-1}) [2]. This equates to a pore-water salinity of about 2–2.6 g NaCl L⁻¹. Globally, about 21,368 million ha of salinized land has been identified as being potentially suitable for irrigation using saline or desalinated water [2].

Groundwater irrigation reduces overall global poverty but can increase socioeconomic vulnerability, particularly in arid and semi-arid regions [3].

Groundwater forms a primary buffer for anthropogenic domestic use, industrial use, municipal use, and agricultural use. In 2014, around 270 million ha of arable land was irrigated, of which about 89 million ha was irrigated directly from groundwater [4]. This irrigation requirement has been forecast to rise to >750 million ha by 2050, to assist in meeting the required increase in global food supply, as the global population rises from its current level of around 8 billion to a forecast level of around 9.1–9.9 billion by 2050 [4]. The bulk of the water required to meet the increased irrigation requirement is likely to be obtained from saline groundwater. Saline irrigation (water EC = 0.6 to 15.7 dSm⁻¹) reduces crop yields when compared with freshwater irrigation [5–7].

Once aquifer groundwater (or groundwater extracted from shale gas or shale oil wells (flowback water)) is used for irrigation, the associated overland flow and shallow groundwater flow are not returned to the primary originating aquifer. This can result in the depletion of the primary aquifer. Crop irrigation currently provides a low return on investment. While replacing saline irrigation water with desalinated water increases crop yields and the total crop sale value, the total return on investment decreases as the cost of the desalinated water increases [4,6,7].

The predicted increase in global irrigated land area between 2014 and 2050 implies that global consumptive water usage will rise from its current level of about 63% of current global water usage to more than 175% of current global water usage. The majority of this projected increase in water demand (14,300 km³ a⁻¹) is likely to be from saline groundwater.

1.1. Saline Groundwater Sources

Five types of saline groundwater are potentially available to meet this expected increase in water demand. They are: (i) aquifer groundwater abstracted from a borehole, this includes both fossil saline water [8–11] and groundwater, which is actively recharged by precipitation and riparian interactions [12–15]; (ii) associated water produced as a by-product of mining [16–18] or hydrocarbon production [19–21]; (iii) geothermal water produced as a by-product of geothermal energy extraction [22–24]; (iv), flowback water associated with oil shale and gas shale hydrocarbon extraction activities [25–27]; and (v) aquifer water in areas where the aquifer is subject to seawater incursion [28–30]. Additionally, in some areas, saline water may be available from tidally influenced riparian water [31] and saline lakes [32]. In many areas, prolonged irrigation has led to the salinization of both groundwater [33] and downstream lakes [34].

1.2. Desalination Solutions

A number of possible desalination solutions can be constructed for this saline groundwater, which are designed to create an increase in crop yield and an increase in the return on investment for the agricultural holder through the use of partially desalinated groundwater for irrigation. Desalination processes can use a physical process or a chemical process.

Conventional pressure-based desalination systems (e.g., reverse osmosis), thermalbased systems, and electrocoagulation systems can all produce an almost pure (desalinated) water product, but the removed Na⁺ and Cl⁻ ions are retained in a larger volume of waste (reject) brine, which requires disposal.

These systems are energy intensive and typically consume 3 to 6 m³ of water for each 1 m³ of product water. The residue is discharged as a waste brine. Conventional systems typically produce desalinated water for a cost of >USD 3 m⁻³, and for most agricultural crops, the increased revenue associated with the increased yield resulting from the use of purchased desalinated water is more than offset by the costs associated with purchasing desalinated water.

Since 2008, the patent and academic literature (Figure 1) has identified that passive (chemical) approaches (termed ZVI (zero valent iron) desalination) based on the use of Fe^{0} , Fe^{n+} , or $Fe_xO_vH_z$ polymers (e.g., akageneite, green rust), Fe(a) polymers, Fe(b) polymers,

Fe(c) polymers, or Fe-organic polymers could be used to partially desalinate water [4,6,7]. These studies have indicated that it may be possible to create solutions where the provision of partially desalinated water could cost between USD 0.1 and 3 m⁻³. These processes do not produce a reject brine waste product and can be operated without an external energy source. They may therefore create a situation that increases crop yields, increases the agricultural unit's return on investment, and reduces the overall amount of water required to irrigate a specific acreage.



Figure 1. ZVI desalination approaches considered in this study. The n-Fe⁰ and n-Fe₃O₄ routes are addressed in Appendix D. The Fe⁰:Fe(b)@C⁰ polymer routes are addressed in Appendix A, the n-Fe⁰:Fe(b) polymer routes are addressed in Section 3. The n-Fe(b) sol-gel polymer routes are addressed in Sections 4 and 5. The Fe⁰:Fe(b)@urea and SiO₂@Fe(b)@urea polymers are addressed in references [4,7]. Patterns associated with ZVI desalination are summarized in Appendix B.

1.3. ZVI Desalination Considerations

This study considers how five different unsupported ZVI desalination approaches (n-Fe⁰; n-Fe₃O₄; Fe⁰:Fe(b)@C⁰ polymer; n-Fe⁰:Fe(b) polymer; n-Fe(b) polymer (Figure 1)) could be adapted to produce partially desalinated water from saline groundwater or saline flowback water, which may be suitable for irrigation. Two other supported ZVI desalination polymer approaches (Fe⁰:Fe(b)@Urea [4] and SiO₂@Fe(b)@Urea [7]) have been trialed at commercial scale and are not addressed further in this study. They are designed to catalytically convert Fe ions in the water into scavenging polymers (Fe(b,c)), which remove the NaCl from the water [7].

Commercial operation of the five different unsupported desalination approaches will require the use of a number of different reactor trains operating in parallel. The n-Fe(b)—Sol Gel polymers (Figure 1) are designed to be used in a multi-train reactor, which either involves a batch flow process or a continuous flow process. The polymer examples provided in this study are based on batch flow results.

Subsequent, ongoing commercial-scale experiments (utilizing the data from this study) are based on the design concept of a multi-tubular, transport line (moving bed) [35,36] reactor. The commercial-scale test reactors have a tube length of between 3 and 12 m and an outer diameter (O.D.) of 0.0423 m. Each tube has been trialed (in vertical, horizontal, and inclined orientations) at a continuous flow rate of up to 0.2 m³ h⁻¹ (4.3 m³ d⁻¹). A tube bundle of 100 tubes ((0.45 m × 0.45 m + baffle space) × 3 to 12 m length) will be

expected to process >400 m³ d⁻¹. Commercial-scale reactors will be constructed using ABS (Acrylonitrile-butadiene-styrene) tubing (3 to 6 m lengths, 0.04–0.2 m O.D.; Class C, E, or T; BS5391; rated to 0.9 MPa and -40 °C to 70 °C) with ABS solvent weld joints and ABS pipe, flange, and valve fittings.

1.4. Production of Irrigation Quality Water

In many agricultural areas, freshwater aquifers are either reserved for domestic use or, when used for irrigation, have become depleted. In these areas, the primary remaining irrigation water source is saline groundwater. This has five impacts on agricultural land. They are: (i) the soil becomes progressively salinized; (ii) the crop yield ($t ha^{-1}$); (iii) the range of crop varieties that can be grown decreases progressively as the water salinity and soil salinization increase; (iv) the crop value may decrease, particularly with tomatoes, vegetables, and fruit, due to discoloration, skin thickening, and taste changes; (v) reduction in land value due to the reduced economic return from the land. In some cases, the land is rendered valueless and is abandoned, either as a direct result of salinization associated with saline irrigation or due to freshwater aquifer depletion (in areas where the saline aquifer is too saline to be considered an economic irrigation water source).

Irrigation is a major cause of groundwater depletion in many freshwater aquifers. This depletion results in (i) salinization of the soils, accompanied in some areas with a gradual deepening of both the salinization zone and the upper shallow perched (or regional) water table; (ii) a requirement to use saline water from saline groundwater aquifers for irrigation; (iii) a gradual salinization of freshwater aquifers in coastal areas due to seawater incursion. The salinization of this irrigation water, and irrigated soils, associated with agricultural intensification, results in an eventual reduction in agricultural economic activity within the area.

Most agricultural holdings are limited in size and do not have sufficient spare land to accommodate large scale tanks or impoundments ($1000-60,000 \text{ m}^3$) to accommodate the amount of irrigation water required for a few days' irrigation. Irrigation requirements typically fall in the range of 1000 to 10,000 ha⁻¹.

The alternative to surface storage (with associated land sterilization) is to either store the desalinated water in a perched shallow groundwater mound or in a stationary hydrodynamic plume within a confined aquifer, located under the ground surface of the agricultural holding. This is the approach considered in this study.

This approach requires the construction of either a stationary hydrodynamic plume within a confined (or unconfined) saline aquifer or a perched shallow groundwater mound in salinized soil. This process desalinates both the salinized soil and aquifer contained within the groundwater mound or stationary plume. This creates a reservoir of mobile desalinated water that can be abstracted as required for irrigation.

A hydrodynamic stationary plume, or perched groundwater mound, is created using a combination of infiltration and abstraction wells, where water is continuously abstracted, desalinated, and reinfiltrated (Figure 2). The hydrodynamic concepts were originally developed in the hydrocarbon industry to both search for hydrodynamically trapped hydrocarbon accumulations and enhance the proportion of mobile hydrocarbon recovered from aquifers.

The results from this study could be used to actively desalinate and reverse the impact of seawater incursion into the groundwater associated with freshwater aquifers.

1.5. Desalination Decision

The decision as to whether to use a batch of desalinated water for irrigation is complex (Figure 2). Once the ZVI desalination technology has been selected and the stationary hydrodynamic plume or perched groundwater mound has been created (Figure 2), the abstracted desalinated water is then checked to determine:

- The expected crop yield and value following the use of the water;
- The expected costs associated with using the water,



• Whether the water complies with local regulations in terms of its chemistry and water quality indicators. Most global regulators have standards that have to be complied with.

Figure 2. The desalination concept evaluated by this study. An aquifer or soil is used to provide temporary (or permanent) storage for the desalinated water. Blue arrow = saline water source; Green arrow = desalination processing; Brown arrow = decision criterion; Purple arrow = regulatory water quality indicators; Red arrow = water returned for further processing. Patterns associated with ZVI desalination are provided in Appendix B; Regulatory water quality indicators are summarized in Appendix C; The formation and operation of a hydrodynamic stationary plume are addressed in Appendix D; The formation and operation of a perched groundwater mound are addressed in Appendix D.

2. Terminology, Materials and Methods

2.1. ZVI Terminology, Groundwater Salinity Indices and Patent Terminology

2.1.1. ZVI Definition

The term ZVI is used in this study as a generic basket term to include Fe^0 , Fe_xO_y , FeOOH, $Fe_xO_yH_z$, Fe inorganic polymers, and Fe-organic polymers. The term Fe^0 is used in this study to refer to native iron metal. The suffix "n-"denotes a nano-sized-particle, typically between 10 and 100 nm. The suffix "m-"denotes a micron-sized-particle, typically between 1 and 100 microns.

2.1.2. Patent Terminology

Patents are referred to in the text by their patent number. The prefixes used are US = US patent; ES = Spanish patent; FR = French patent; GB = UK patent; TW = Taiwan patent; JP = Japanese patent; and CH = Chinese patent. The standard patent number end terminology is: Letter [A] = application; Letter [B] = awarded patent following examination.

2.1.3. Desalination Pattern Classification

A classification of the different patterns of changing salinity with time that have been observed over the last 14 years associated with ZVI desalination is provided in Appendix B.

2.1.4. Salinity Indices

The various molar geochemical indices, which are used to describe groundwater's suitability for irrigation water, are summarized in Appendix C. The Sodium Adsorption Ratio (SAR) is the most widely used. ZVI desalination reduces the various indices by reducing the amount of Na⁺ and Cl⁻ ions in the irrigation (product) water. The sol-gel approaches (Figure 1) may also decrease the various indices by increasing the availability of Ca²⁺ ions in the irrigation (product) water.

2.2. Assessment of Crop Yield Resulting from the Use of Partially Desalinated Irrigation Water

Desalinated (or partially desalinated) irrigation water, when used in place of saline irrigation water, results in an increase in crop yield, a decrease in soil salinization, a decrease in soil waterlogging, and it may result in an increase in crop quality [4,6,7]. The exact yield increase resulting from desalination is a function of crop type, farming practice, soil conditions, crop variety, and climatic conditions.

Yield Increase Assessment Methodology

A simple, easy-to-use screening method for assessing the relative increase in crop yield resulting from the use of partially desalinated irrigation is provided in references [4,7]. The final example in this study takes feed water with a salinity of 12.3 g NaCl L⁻¹; EC = 17.6 dSm⁻¹ to form partially desalinated irrigation water (1.2 to 2.4 g NaCl L⁻¹; EC = 2 to 3.4 dSm⁻¹). This was accompanied by an associated reduction in the sodium adsorption ratio (SAR) from 125 to between 1.2 and 2.5.

The method described in Reference [7] indicates that if this saline (flowback or groundwater-sourced) water (12.3 g L⁻¹) was used for irrigation, then only a few crops may provide a meaningful crop yield (e.g., sugar beet and wheat [7]). Reducing the irrigation water salinity to 1.5 g L⁻¹ would be expected [7] to increase sugar beet yields by 236% and wheat yields by 414%. It would also allow the area to be used (subject to soil conditions and climate) to grow the majority of crops that can be grown in an area receiving freshwater irrigation [7].

Reducing irrigation water salinity will therefore have benefits associated with:

- Increased crop yield and increased gross revenue;
- Increased choice of crops which can be grown on a holding; and
- Increased agricultural land value.

2.3. Polymer Terminology

2.3.1. Initial Polymer Product

Feⁿ⁺ ions in the presence of Na⁺, OH⁻, and Cl⁻ ions initially produce dimers with edge-shaped and corner-shaped octahedral sites [37]. After a short period (about 1 h), distinct trimers are associated with these sites, and coalescence of the trimmers results in the formation of β -FeOOH type polymers [37]. The rate of formation is a function of the NaOH:Feⁿ⁺ ratio (*r*) in the water at the reaction onset [37]. For *r* > 1.5, the hydrated polymers are stable and have a similar structure to β -FeOOH [37].

 β -FeOOH type polymers are formed when Fe³⁺ ions are mixed with Cl⁻ ions and one or more of OH⁻ ions, HCO₃⁻ ions, and CO₃²⁻ ions [JP2018020920A; JP2018030748A]. The manufacturing process can require an increase in pH [US20120315479A1]. Individual β -FeOOH type crystallites have a width of 15–18 nm and a length of 100–200 nm [US20120315479A1]. β -FeOOH type polymers can incorporate Mn and Ca ions [US8313653B2].

2.3.2. Polymer Characterization

The characterization of the polymeric desalination catalyst, produced from n-Fe⁰ and Feⁿ⁺ ions, in terms of detailed chemical analyses and detailed morphology, is outside of the scope of this study.

The following polymer terminology is used [38–40]. M = metal. M(a), Fe(a), Ca(a), Zn(a) = mononuclear hydroxyl complexes, e.g., HZnOH²⁺, HCaOH²⁺, HFeOH²⁺, HFeOH³⁺, Fe³⁺, Fe(OH)²⁺, Fe(OH)₂⁺, Fe(OH)₃, Fe(OH)₄⁻ (Fe₂(OH)₂⁴⁺ and Fe₃(OH)₄⁵⁺), some small polymers, and instantaneous reaction products. M(b) = polynuclear hydroxyl complexes with medium and high molecular masses, e.g., Fe(OH)₂⁴⁺; Fe(O₂H₆)³⁺; Fe₃(OH)₄⁵⁺; Fe₅(OH)₉⁶⁺, etc. M(c) = larger polymer or colloidal species, which include inert macromolecular coagulation of the forms M(OH)_x and MOOH. In practice, most metal polymers are a mixture of M(a) + M(b) + M(c). [@] signifies physical adsorption on a surface [7]; [:] signifies chemical adsorption on a surface [7].

2.4. ZVI Desalination Measurement

ZVI desalination is observed by comparing the feed water and product water using one or more of the following instruments and methods:

- Electrical conductivity (EC, mScm⁻¹, dSm⁻¹);
- Ion Selective Electrodes (ISE) for Na⁺ ions and Cl⁻ ions;
- Evaporation of product and feed waters to produce a residual measurable product;
- Ion chromatography and spectroscopy to identify Na⁺ and Cl⁻ ions;
- Flame emission photometry to identify Na⁺ ions
- Chemical titration to identify Cl⁻ ions;

The most common tool used globally to measure salinity is the EC. In this study, the primary tools used to measure salinity are Na⁺ ISE and Cl⁻ ISE. Confirmation or corroboration of the ISE results is provided by both EC and evaporation analyses.

2.4.1. Desalination Assessment

Desalination (D_s) , as a fraction of the feed concentration, is determined as:

$$D_s = 1 - (C_{t=n}/C_{t=0}), \tag{1}$$

 $C_{t=n}$ = ion concentration in the product water at time t = n; $C_{t=0}$ = ion concentration in the feed water at time t = 0.

2.4.2. Relationship between EC and Salinity

EC varies with water salinity but is also influenced by the conductivity of other ion components in the water, where [41]:

NaCl, g L⁻¹ =
$$F$$
 (EC), (2)

F = a constant. F is commonly stated [41] as being in the range of 0.50 to 0.55 for NaCl determination in most EC meter instruction booklets. Chemical tables [42] suggest that the actual relationship between F and EC in pure saline water is:

$$F = 0.001967(EC) + 0.605453,$$
(3)

Each ion present in the water provides a contribution to EC [42]. It follows that if two components are present and the desalination process only removes one component, then the resultant product EC at time t = n, will be determined as:

$$EC_{t=n} = EC_{t=0} - EC$$
 attributable to removed NaCl, (4)

Consequently, the amount of desalination indicated by an ISE can be higher than desalination measured by an EC when significant concentrations of other ions are present. Most water contains a multiplicity of ion components. Each component has its own value of *F*.

The other principal dissolved components in saline water are: Na₂SO₄ (F = 0.9732EC [42]), KCl (F = 0.6646EC [42]), CaCl₂ (F = 0.6677EC [42]), Na₂CO₃ (F = 0.878EC [42]), MgSO₄ (F = 1.4416EC [42]), and MgCl₃ (F = 0.6296EC [42]). Organic acids, when present, have high values of F. For example: HCOOH (F = 5.0576EC [42]), CH₃COOH (F = 21.56EC [42]), H₂C₂O₄ (F = 0.5184EC [42]), and H₃C(OH)(COO)₃ (F = 5.5856EC [42]). Organic species, when present, have a disproportionate impact on the EC. Sulphates, when present in significant quantities, can increase F into the range of 0.9 to 1.7 [42]. Carbonates, when present in significant quantities, can increase F into the range of 0.8 to 1.0 [42]. Hydroxides, when present in significant quantities, can reduce F into the range of 0.2 to 0.5 [42].

Since most water is composite, the EC is normally used to define total dissolved solids (TDS) [41], where TDS, g $L^{-1} = F(EC)$. In the absence of any compositional data, *F* is commonly set at 0.55 to determine TDS [41]. In most saline water, the concentration of NaCl may represent >95% of the dissolved solids. In these circumstances, the EC becomes a proxy indicator of salinity.

The addition of Fe⁰ to acidic water results in the release of Feⁿ⁺ ions [43,44]. This release is accompanied by an increase in the EC, which can mask any decline in Na⁺ ion and Cl⁻ ion concentrations [44]. Consequently, the preferred instrument for salinity measurement in this study is an ISE.

Detailed analyses of TDS (20–292 g L^{-1}) in groundwater brines [45] have established that the relationship between TDS and EC for a saline water body typically follows a polynomial function, where:

$$\Gamma DS = a(EC)^4 + b(EC)^3 + c(EC)^2 + d(EC) + e,$$
(5)

a to e = polynomial constants that are specific to a water body. In pure sodium chloride solution, the relationship is considered to be exponential [45]:

$$\Gamma DS = a e^{b(EC)}, \tag{6}$$

a and b are exponential constants. The relative concentrations of monovalent and divalent ions in the water have a significant impact on EC [45]. Brine EC, for a specific TDS, decreases as the ratio of monovalent: divalent ions in the water decreases [45].

2.4.3. Significance of Fe⁰ Dissolution to Feⁿ⁺ ions

The dissolution of Fe^0 to form Fe^{n+} ions and associated polymers can be a zero-order reaction [46]. A zero-order reaction is described [6,7] by regression equations of the form:

$$C_{t=n}/C_{t=0} = k_{\text{dissolution}} \times t + [b], \tag{7}$$

$$C_{t=n} = k_{\text{dissolution}} \times t + [C_{t=0}], \tag{8}$$

where $C_{t=n} = \text{Fe}^0$ concentration at time t = n; $C_{t=0} = \text{initial Fe}^0$ concentration; t = reaction time; [b] = a constant; $k_{\text{dissolution}} = \text{the Fe}^0$ dissolution rate constant, for the reaction: $\text{Fe}^0 = \text{Fe}^{n+} + \text{ne}^-$; $C_{t=n}/C_{t=0} = \text{normalized}$, or fractional proportion of the original Fe⁰ charge left at time t = n.

2.4.4. Uncoated Fe⁰

Uncoated Fe⁰ (Figure 3) will dissolve (rust) rapidly in water [44,46]. The rate of dissolution is a function of the water composition, temperature, particle size, and particle shape. The zero-order kinetic data [46] for uncoated steel wool dissolution (unadjusted for coating retardation) provides a reasonable indication of the dissolution rates, which might be expected for uncoated n-Fe⁰ (Figure 3).



Figure 3. Indicative rates of polymer (rust) formation from uncoated Fe⁰ placed in water. (a) $C_{t=n}/C_{t=0}$ versus time; (b) Weight of polymer produced/weight of Fe⁰ at time t = 0, versus time. Blue line = 1st quartile; red line = median expectation; green line = 3rd quartile.; (c) Pourbaix Diagram for Fe: Red dots = Product water Reactor 1; Blue dots = Product water Reactor 2; Brown dot = feed water; (d) Pourbaix Diagram for Fe + Hydrogen; (e) Pourbaix diagram for Fe, Hydrogen, OH⁻, H₂O₂ and O₂. Brown arrows indicate reaction direction in the presence of Fe⁰. (f) Corrosion of iron: Red = Fe⁰; Yellow = Fe²⁺, Fe(OH)⁺, Fe(OH)₂; Green = green rust; Brown = Fe(OH)²⁺, Fe(OH)²⁺, Fe(OH)₃; Purple stripe = layered FeOOH, Fe(OH)₃; Orange Diagonal Stripe = Adsorbed oxyhydroxides; Black Diagonal Stripe = Coating.

Uncoated n-Fe⁰ is expected to have a rate of dissolution (and Fe(a,b,c) polymer formation), which is greater than that associated with the median value and perhaps greater than the 3rd quartile (Figure 3). Therefore, if polymer formation (Figure 1) is associated with NaCl removal [4,6,7], then uncoated n-Fe⁰, or functionalized n-Fe⁰ may be required in order to achieve an economic desalination rate.

Figure 3c provides the Eh and pH of a continuous flow of water over 77 days through two fixed bed tubular (0.04 m O.D.) reactors. Reactor 1 contained 0.5 kg m-Fe⁰ (0.02 to 0.08 mm, flow rate, $Q_A = 0.9 \text{ L h}^{-1}$). Reactor 2 contained 0.4 kg Fe⁰ (>1 mm, $Q_A = 8 \text{ L h}^{-1}$).

In both examples, the average product water Eh dropped and the pH increased relative to the feed water.

The bulk of the product water associated with the Fe⁰ (Reactor 2) remained in the Fe²⁺ stability zone [45–50] at around the Fe(b) polymer:Fe²⁺ redox fence, indicating that a net dissolution of Fe⁰ was expected and that only part of the dissolved Fe⁰ would be converted to polymer. Oxygenated flow lines and tanks associated with this water are coated with orange Fe(c) polymers (Fe(OH)₃, FeOOH). The bulk of the product water associated with the m-Fe⁰ (Reactor 1) remained in the Fe(b) polymer stability zone [47–52]. No dissolved Fe²⁼ ions were detected in the product water. In each example (Figure 2d), the product water was in Hydrogen Stability Zone 0 [52,53], indicating oxygenated conditions. It has been established that: (i) combining Fe⁰ with Al⁰ in saline water can move the metal bed into Hydrogen Stability Zone 2 [52,53]; (ii) decreasing the Fe⁰ particle size increases the pH of the product water. The pH shift moves the water into the H₂O₂ stability zone [52,54] (Figure 2e). This potentially allows Fenton remediation reactions to occur [55].

2.4.5. Coated Fe^0

Coated n-Fe⁰ (Figure 3f) is expected to have a rate of dissolution and polymer formation that is substantially less than that associated with the 1st quartile (Figure 1). Therefore, if polymer formation is associated with NaCl removal [4,6,7], coated n-Fe⁰ will form a slow-reacting, useful evaluation tool to allow the desalination pattern to be monitored. In this study, it is used to determine if NaCl removal by coated n-Fe⁰ can be described as a zero-order reaction or a first-order reaction.

Coatings can take a number of forms and are placed on the nanoparticles for a number of different reasons. The principal reasons are: (i) to make the particles air stable, and to inhibit oxidation (e.g., TW201504159A; US10329179B2); This coating can be Fe₃O₄ (magnetite (US10329179B2)); activated carbon (e.g., US11103854B2; CN109305684B); tetraethyl orthosilicate (TEOS (US20130058724A1)); ethyl triethoxysilane (ETES (US20130058724A1)); (ii) to prevent the particles from corroding, when placed in water; (iii) add functional sites to the particle surface to aid selectivity and ion removal; (iv) control the dispersibility of nanoparticles to prevent clumping (e.g., US7635236B2). Coated n-Fe⁰ is commonly termed stabilized zero-valent iron nanoparticles. Detailed discussion of Fe⁰ coating approaches, coating types, and functionalized Fe⁰ is outside the scope of this study.

2.5. Desalination Mechanism

The ZVI desalination mechanism is unknown [7]. A number of different hypotheses have been developed. The desalination models used in the 2008/20015 patents (Figure 1) are different from those currently being developed for polymers. Each model will be addressed in this study. The current working model [7] for desalination using polymers is that:

- Fe⁰ surfaces corrode to form $Fe_xO_yH_z$ species and release Feⁿ⁺ ions [56];
- The Feⁿ⁺ ions and Fe_xO_yH_z species interact with the water to form entrained polymer monomers (Fe(a), or Fe(b) or Fe(c)) [4,6,7,56];
- The polymer monomers aggregate to form fluid-filled entrained colloidal spheres [7,39];
- The spheres actively adsorb Na⁺ and Cl⁻ ions from the water and sequester them within the colloidal structures [6,7,56]. This process creates a zero-order pattern of ion removal [57,58] in Fe⁰:Fe(b)@C⁰ polymer desalination pellets [6,7,59], where:

$$C_{t=n} = k_{ob}s \ t_r + C_t = 0, \tag{9}$$

where k_{obs} = observed rate constant; t_r = reaction time. A first-order pattern of ion removal [57,58] is associated with n-Fe⁰, and both supported and unsupported sol-gel metal polymers [59], where:

$$Ln[C_{t=n}] = k_{obs} t_r + Ln[C_t = 0],$$
(10)

• The colloidal structure breaks down to produce an amorphous polymer containing dead end porosity, which can include fluids contained within the former colloidal structure [6,59].

This study investigates this morphological desalination model further using n-Fe⁰:Fe(b) and n-Fe(b) polymers (Figure 1).

2.6. Desalination Pattern

The main ion removal patterns observed over the last 14 years are summarized in Appendix B. Each segment of the decline pattern can be defined in terms of a reaction of a specific order [59]. The reason why a decline pattern is not a simple zero, first, second, or higher order reaction [57,58] is unknown. The reason why a specific pattern develops is unknown. The common pattern is composite.

In most instances:

- A plot of ion concentration at time t = n ($C_{t=n}$) versus reaction time, t_r , or a plot of $Ln(C_{t=n})$ versus t_r , will equate to a straight line for each time segment, where $C_{t=n}$ either declines with time, or increases with time, indicating that the reaction is zero-order, or pseudo-zero order, or first-order, or pseudo-first order [6,7,59,60].
- A plot of $Ln(C_{t=n}/C_{t=0})$ versus t_r , can be described using a trendline regression equation [7,59], e.g.,:
 - Power function observed [7,59]

$$Ln(C_{t=n}/C_{t=0}) = [a] [t_r][b],$$
(11)

• Linear function observed [7]

$$Ln(C_{t=n}/C_{t=0}) = [a] [t_r] + [b], \qquad (12)$$

• Logarithmic function observed [7]

$$Ln(C_{t=n}/C_{t=0}) = [a] Ln([t_r]) + [b],$$
(13)

• Exponential function observed [7]

$$Ln(C_{t=n}/C_{t=0}) = [a] e([tr])[b],$$
(14)

where [a] and [b] are regression constants. $[t_r]$ = time. In this study, the sol-gel, n-Fe(b) polymers remove N^{a+} and Cl⁻ ions using a power function.

2.7. Statistical Methodology Used

The measured data was collated and processed in accordance with the methodology defined by the British Standards Institute [61]. Regression trend lines and associated statistics were calculated in MS Excel 2019. The Monte Carlo analyses were undertaken in MS Excel using the @Rand() random number generator function to generate values between 0 and 1. The polynomial equations, linear equations, and power equations were generated using the Trendline function in MS Excel.

The coefficient of determination, R^2 , is the square of the Pearson Correlation Coefficient (PCC). By definition, R^2 falls within the range 1 and 0, and PCC falls between +1 and -1 [62,63]. The following interpretations are made [62,63]:

- PCC = 0.9 to 1.0 (R^2 = 0.81 to 1.00): Interpretation = very strong correlation
- PCC = 0.7 to 0.89 (R^2 = 0.49 to 0.79): Interpretation = strong correlation
- PCC = 0.4 to 0.69 (R^2 = 0.16 to 0.47): Interpretation = moderate correlation
- PCC = 0.1 to 0.39 (R^2 = 0.01 to 0.15): Interpretation = weak correlation
- PCC = 0.0 to 0.10 (R^2 = 0.00 to 0.01): Interpretation = negligible correlation

2.8. Data

The data generated by this study is provided in the text tables and figures.

- 2.9. Measurement Equipment
 - The instruments used were:
- ORP (oxidation reduction potential) meter (HM Digital) calibrated at ORP = 200 mV; Measured ORP (oxidation reduction potential) values are converted to Eh, mV as: Eh, mV = -65.667pH + 744.67 + ORP (mV), using a quinhydrone calibration at pH = 4 and pH = 7.
- pH meter (HM Digital) calibrated at pH = 4.01; 7.0; 10.0.
- EC (electrical conductivity) meter (HM Digital meter calibrated at EC = 1.431 mScm^{-1}).
- Cl⁻ ISE (Ion Selective Electrode); Bante Cl⁻ ISE, EDT Flow Plus Combination Cl⁻ ISE; Cole Parmer Cl⁻ ISE attached to a Bante 931 Ion meter. Calibration was undertaken using 0.001, 0.01, 0.1, and 1.0 M NaCl calibration solutions.
- Na⁺ ISE (Ion Selective Electrode); Bante Na ISE, Sciquip Na ISE, Cole Parmer Na ISE attached to a Bante 931 Ion Meter. Calibration was undertaken using 0.001, 0.01, 0.1, and 1.0 M NaCl calibration solutions.
- Temperature measurements, were made using a temperature probe, attached to a Bante 931 Ion Meter.

2.10. Reactor Size Used

The standard reactor size used was 1 L for n-Fe⁰ studies and 2.3 L for polymer studies. The reactor was operated as a static flow, static diffusion, and batch reactor. Operating pressure = atmospheric. Operating temperature = external environment temperature. This varies with the time of year and the time of day. At the site location, the operating temperature range was between 0 °C and 25 °C.

2.11. Materials Used

The saline water used was either seawater extracted from the North Sea at Blackness Castle, Firth of Forth, Scotland, or fresh water containing dissolved halite. The halite was purchased from Wickes Ltd., Perth, Scotland, UK.

The [FeSO₄ [H₂O]₇], MgCO₃, CaO, K₂CO₃, MnO₂, ZnO, urea, and tartaric acid powders, together with the formic acid used in this study were purchased from a variety of UK-based commercial agricultural and chemical suppliers.

2.12. Hydrology of a Stationary Plume

The desalination results are used to reconstruct the salinity of a saline aquifer by creating a stationary hydrodynamic plume within the aquifer. The hydrological and hydrodynamic equations and modeled examples are provided in Appendix D.

2.13. Past ZVI Desalination Processes

The ZVI desalination processes, n-Fe⁰; n-Fe₃O₄, and Fe⁰:Fe(b)@C⁰ are addressed in Appendix A. This analysis provides the technical background to the analysis of n-Fe⁰:Fe(a,b,c) and n-Fe(a,b,c) polymers undertaken in this study.

3. n-Fe⁰:Fe(a,b,c) Polymers

The analysis (Appendix A) of the existing n-Fe⁰ desalination route (Figure 1) indicated the presence of substantial technical and economic barriers, which need to be addressed prior to being able to economically utilize n-Fe⁰ to produce partially desalinated irrigation water from saline groundwater. Placement of n-Fe⁰ in water will result in the formation of n-Fe⁰:Fe(a,b,c) polymers and Fe(a,b,c) polymers [6,7,59]. In saline water, the dominant polymers are hydrated variations of the minerals green rust chloride and akageneite. Conventional ZVI water remediation theory does not consider that these polymers are active in the water remediation process; instead, it assumes that the n-Fe⁰ acts as an electron donor to effect remediation [64]. The polymer shell (Figure 3f) is commonly ignored or considered not to be involved in the remediation process [64]. This study considers that the polymer shell plays an active part in the desalination process [4,6,7].

This study reconfigures the conventional n-Fe⁰ desalination model and process (Appendix A) from a general circular process (Figure 4) of desalination followed by magnetic recovery, followed by reprocessing and regeneration, followed by reuse with makeup as appropriate, to a general circular process (Figure 4) of desalination, followed by gravity separation, followed by washing and separation, followed by reuse of the recovered iron polymers.



Figure 4. Summary of the desalination of groundwater using n-Fe⁰ to produce partially desalinated irrigation water.

This section considers desalination using a modified version of the conventional n-Fe⁰ desalination process (Figure 4). The conventional model assumes that the functionalized sites are located on the n-Fe⁰ surface (Appendix A). In this study, it is assumed that the functionalized sites are located on the n-Fe polymer surfaces (Appendix A).

3.1. Functionalized Fe-Polymer Colloids

The functionalized, entrained, and corroding n-Fe⁰ particle aggregates by a form of snowball accretion to form agglomerated, colloidal nodules, constructed from n-Fe polymers. A typical example is provided in Figure 5a. Each of these nodules forms and grows by the accretion of fluid-filled colloidal spheres of n-Fe⁰:Fe(a,b,c) (Figure 5b). In the example illustrated in Figure 5, the average colloid sphere outer diameter was 0.0031 mm (3.1 microns); inner diameter was 0.002 mm; (outer volume = 1.56×10^{-8} mm³; inner (fluid) volume = 4.19×10^{-9} mm³; n-Fe⁰:Fe(a,b,c) rim volume = 1.14×10^{-8} mm³; n-Fe⁰:Fe(a,b,c) rim thickness = 0.00055 mm; sphere porosity = 26.8%).



Figure 5. Functionalized n-Fe⁰:Fe(a,b,c) polymer agglomerates: (a), Settled agglomerated, hydrated, colloidal nodules produced by n-Fe⁰ (50 nm diameter) in saline water after 2000 h. Transmitted light. Field of view = 0.266 mm. Agglomerate size: Average = 0.037 mm; standard deviation = 0.01014; 1st quartile = 0.027 mm; median = 0.0377 mm; 3rd quartile = 0.044 mm; (b) agglomerated colloidal, hydrated nodule produced by n-Fe⁰ (50 nm diameter) in saline water (after 2000 h). Nodule size = 0.0498 mm × 0.0459 mm. The nodule grows by the accretion of hydrated colloidal spheres (about 0.003 mm in diameter) around its periphery. Transmitted light. Field of view = 0.05 mm.

3.2. Possible Ion Transport Model

If the m-Fe⁰:Fe(a,b,c)@C⁰ polymers [6] extract ions from one water surface and then transport the ions through the polymer to another water or fluid surface (e.g., Appendix D), then the fluid volumes within the fluid-filled colloid spheres (dead-end pores (Figure 5b)), may act as sinks for ion removal [59].

3.3. Fe:Fe(a,b,c) Polymer Spheres

If the n-Fe⁰ is placed in freshwater, it forms amorphous, flocculate aggregates (Figure 6a). In saline water, initially, the n-Fe⁰ aggregates to form hydrogen + water-filled n -Fe⁰:Fe(a,b,c) polymer spheres (Figure 6b), where within the sphere:

$$H_2O = OH^- + H^+ = OH^{\bullet} + 0.5H_2,$$
 (15)

This set of reactions results in a charged internal surface at the fluid-polymer interface, e.g.,

$$2[n-Fe^{0}:Fe(a,b,c)] + H_{2}O = [n-Fe^{0}:Fe(a,b,c)@OH^{-}] + [n-Fe^{0}:Fe(a,b,c)@H^{+}],$$
(16)

$$[n-Fe^{0}:Fe(a,b,c)] + H_{2}O = [n-Fe^{0}:Fe(a,b,c)@OH^{\bullet}] + H_{2(gas)},$$
(17)

3.4. Colloidal Spheres

The initial n-Fe⁰:Fe(b) colloidal spheres have a strong optical refraction contrast between the fluid in the spheres, the water body, and the sphere rim (Figure 6b). This is due to the presence of hydrogen within the spheres. Spheres, where the microscope optics are focused on the sphere center, have a doughnut-like appearance, as the sphere walls above the core are effectively transparent. There is a weak positive statistical trend between sphere diameter and the diameter of the encapsulated fluid core (Figure 7a).



Figure 6. Colloidal nodules produced by n-Fe⁰. (a) fresh water. Agglomerated, hydrated, amorphous colloidal nodules produced by n-Fe⁰ (50 nm diameter) in fresh water after 2 h. Transmitted light. Field of view = 0.057 mm. (b) Gas (hydrogen) and water filled, entrained, hydrated colloidal spheres produced by Fe₃O₄ coated n-Fe⁰ (50 nm diameter) in saline water after 2 h. Some of the spheres are starting to agglomerate. Transmitted light. Field of view = 0.04 mm. The relative refractive indices are: Hydrogen = 1.000132; water = 1.333; NaCl = 1.55; β -FeOOH = 2.365. The doughnut structures indicate the presence of a major refractive index contrast between a low refractive index core and a higher refractive index in the doughnut rim. (c), Agglomerated colloidal nodules produced by n-Fe⁰ (50 nm diameter) in saline water (1.5 g L⁻¹) after 4000 h. The cellular spheres are filled with minerals adsorbed from the water. Transmitted light. Field of view = 0.127 mm.

3.5. Colloidal Sphere Diameter

For any specific sphere diameter, there is a wide range of internal fluid core diameters (Figure 7a). There is a positive linear relationship (Figure 7b) between sphere diameter and the thickness of the polymer rim surrounding the internal fluid core. There is a very weakly positive relationship between the sphere diameter and the volume of the internal fluid core (Figure 7c). This probably results from the formation of hydrogen, as the conversion of 1 mole of water to hydrogen will create an increase from 18 cm³ to 11,200 cm³.

3.6. Fluid Core Volume of the Spheres

Each observed doubling in the volume of the internal fluid core could be explained if 0.16% of the water in the fluid core (before the volume increase) was converted to hydrogen. This interpretation indicates that the principal control on the volume of the fluid core is the formation of hydrogen. Hydrogen gas generation by the n-Fe⁰ is therefore essential to increase the volume of dead-end porosity (Figure 7c) and the dead-end porosity as a proportion of total sphere volume (Figure 7d). It will also increase sphere buoyancy and sphere mobility, allowing spheres to aggregate and grow by accretion.



Figure 7. Colloidal spheres produced by n-Fe⁰ (50 nm in diameter) in saline water. Blue = after 2 h; Red = after 4000 h (**a**) Outer diameter versus diameter of the fluid core; (**b**) outer diameter versus the wall thickness of the sphere; (**c**) sphere diameter versus volume of the fluid core; (**d**) sphere diameter versus total (percentage) fluid volume as a function of the sphere volume.

3.7. Change in Sphere Rim Thickness with Time

Analysis of entrained n-Fe⁰:Fe(a,b,c) polymers (Figure 6c) following extraction from saline water after 4000 h established (Figure 6c) that the entrained particles comprised thin-walled spheres containing solid minerals (NaCl, CaCl₂, NaHCO₃, CaCO₃, and NaOH) adsorbed from the water.

If the spheres produced after 2 h (Figure 7b) are compared with those present after 4000 h (Figure 6c), the following observations can be made:

- For a sphere with a specific outer diameter, the inner diameter of the fluid sphere increases with time (Figure 7a);
- The average sphere outer diameter and the sphere size range increase with time (Figure 7a);
- The average sphere wall thickness, when formed, shows a distinct positive correlation between outer diameter and wall thickness (Figure 7b); as time increases, the wall thickness observed for a specific outer diameter decreases relative to the initial regression trend line (Figure 7b);
- Increasing reaction time results in an increase in the internal fluid volume of the spheres and a positive correlation developing between internal fluid volume and sphere size (Figure 7c);
- After about 2 h, the typical sphere has a fluid volume of <10% (Figure 7d); this fluid volume (as a proportion of the sphere volume) can increase to >70% as the sphere grows (Figure 7d).
- After 4000 h, the spheres appear to be completely mineralized (Figure 6c).

3.8. Model for Desalination by the Polymer Spheres

Comparison of the removal of NaCl from the feed water (Figure 8a–c) with the sphere morphology (Figure 7) suggests that desalination occurs in a number of phases:

- The initial functionalization of the n-Fe⁰ is associated with a pH shift into the range 8.5 to 11, and a decrease in Eh (Figure 8d–f);
- The trend of decreasing salinity continues while the pH remains in the range of 9 to 11, and the Eh is below 0 mV (Figure 8d–f);
- The cessation of salinity removal is associated with a decrease in pH into the range of 7 to 9, combined with an increase in Eh (Figure 8d–f).
- The removal of NaCl occurs in the redox (Eh:pH) regime, where the dominant Fe oxidation number is 3 (Figure 8d–f). This redox regime is consistent with desalination being associated with nFe⁰:n-Fe(a,b,c) polymers.

This analysis indicates that in saline water, the dominant method of ion removal may be in metal polymer colloidal spheres.

3.9. Reuse of n-Fe⁰

If the conventional n-Fe⁰ model is correct (Appendix D), the presence of corrosion products on the recovered n-Fe⁰ will result, if the recovered n-Fe⁰ is reused, in the amount of observed desalination progressively decreasing with time, as the corroding n-Fe⁰ becomes covered in Fe polymers.

This hypothesis was tested using gravity separation to recover a batch of n-Fe⁰ following use (Figure 8b). The recovered n-Fe⁰ + Fe polymers were not magnetic. This indicated that the bulk of the initial magnetic n-Fe⁰ charge had corroded to form polymers during the desalination process.

The recovered n-Fe⁰ was reused (Figure 8c). This reused n-Fe⁰ resulted in a lower increase in pH and a lower decrease in Eh during the desalination phase (Figure 8g,h). The redox regime (Figure 8i) is consistent with desalination being associated with n-Fe⁰:n-Fe(a,b,c) polymers. The reused n-Fe⁰ (Figure 8c) displayed a higher level of ion removal than its initial n-Fe⁰ application (Figure 8b). This observation is not consistent with the conventional n-Fe⁰ desalination model. It suggests that the main ion removal agent is not n-Fe⁰ but instead the Fe-polymer corrosion products that formed on its surface.

The desalination examples illustrated in Figure 8 are too slow to be considered viable options for the desalination of groundwater, or flowback water, to produce irrigation water by a single pass, batch processing, but they do illustrate the key points associated with desalination.

The key redox points are:

- Desalination is associated with a pH within the range of 8 to 11;
- Desalination is associated with an Eh of <500 mV.

The key operating points are:

• All n-Fe⁰, m-Fe⁰ particles and Fe-polymers change the Eh and pH of water flowing through them. The degree of change decreases with increasing throughput and increasing space velocity (*SV*), where:

$$SV, m^3 t^{-1} h^{-1} = J/W,$$
 (18)

J = water flow rate through the reactor, m³ h⁻¹; W = weight of n-Fe⁰ or m-Fe⁰ in the reactor.

3.10. Creating a Viable Desalination Process from the Experimental Results

The practical and economic key to being able to use n-ZVI to desalinate aquifer groundwater, or flowback water, is the ability to rapidly remove Na⁺ and Cl⁻ ions from the water. Preferably with a contact time of <1 h, combined with the ability to reuse the n-ZVI.



Figure 8. Examples of n-Fe⁰ (50 nm, 25 g L⁻¹ Fe₃O₄ coated) desalination ($C_{t=n}/C_{t=0}$) versus time. (a) 1.5 g NaCl L⁻¹ feed water (25 g L⁻¹); (b), 8.89 g NaCl L⁻¹ feed water (3 g L⁻¹); (c), 7.43 g L⁻¹ feed water (Resused n-Fe⁰, 3 g L⁻¹); (d) 1.5 g NaCl L⁻¹ feed water versus pH; (e), 1.5 g NaCl L⁻¹ feed water versus Eh, mV; (f) 1.5 g NaCl L⁻¹ feed water, pH versus Eh, mV; (g) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV; (i) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV; (i) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV; (i) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV; (i) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV; (i) 7.43 g NaCl L⁻¹ feed water, pH versus Eh, mV.

3.10.1. Uncoated n-Fe⁰

Uncoated n-Fe⁰ is pyrophoric in the air. It can generate a temperature of 620–820 °C in less than 1 s if exposed to air [65,66]. n-Fe⁰ will dissolve to form Feⁿ⁺ ions in acidic water [4,52]. In alkali water, it develops an OH⁻ coating on its surface [4,52]. In acidic waters, it can develop a Cl⁻ coating on its surface [67–69]. In alkali waters, the Cl⁻ tends to be concentrated within intra-particle porosity associated with the OH⁻ ions (e.g., within green rust and akageneite precipitates) [69]:

$$Fe^{0} + OH^{-} = [Fe^{3+}@OH^{-}]_{n},$$
 (19)

$$Fe^{0} + Cl^{-} = [Fe^{3+}@Cl^{-}]_{n}$$
 (20)

$$Fe^{0} + H_{2}O + Cl^{-} = [[Fe^{3+}@OH^{-}]@[H+Cl^{-}]]_{n},$$
 (21)

The subscript [n] is used to signify that the product is a metal polymer. The initially functionalized surface comprises a mixture of OH⁻ sites and Fe⁺ sites.

3.10.2. Coated n-Fe⁰

Iron losses due to dissolution will be reduced if the particles are coated with anionic sites or cationic sites. The particles could be coated with cationic polyethylenimine (PEI) or anionic poly(ethylene glycol) of anionic poly(acrylic acid) (PAA-EG), or another ionic species (e.g., Figure 9) [70,71]. This has five benefits:

- it acts as a protection of the particle from corrosion;
- it allows the removed Na⁺ ions and Cl⁻ ions to be recovered;
- it allows the nanoparticles to be reused;
- it can allow the nanoparticles to be stable in air, thereby improving safe handling; and
- it can prevent the annealing and cementation of the particles.



Figure 9. Conceptual model for a functionalized n-Fe⁰ particle.

This approach will allow any functionalized nanoparticle to replace $n-Fe^0$ in a desalination process. Coatings can be relatively simple and quick to add to a particle. For example, polyethylenimine (PEI) is a water-soluble cationic polymer that can be coated onto $n-Fe^0$ or $Fe_xO_yH_z$ polymers [71,72]. This results in each polymer chain being positively charged by amino and imino groups [72]. There will be some solubility loss of PEI into the product water during desalination from the $n-Fe^0$ or polymer.

A variety of coating approaches for PEI are available. A simple approach, described in reference [72], is to mix (in a weight ratio) 1 part PEI to 100 parts n-Fe⁰/polymer to 600 parts water to 10 parts H_2O_2 . After about 1 h, the particles are recovered and washed in deionized water. They are then available for use.

3.10.3. Formation of β -FeOOH and Green Rust Chloride Polymer Spheres

Bare n-Fe⁰ will form, in saline water, an outer coating of β -FeOOH (akageneite) polymers or green rust chloride (Fe(OH)_nCl_y) polymers, commonly termed Fe(a) or Fe(b) or Fe(c) polymers.

The akageneite reacts with saline water as follows:

$\beta - FeOOH + H_2O + Na^+ + Cl^- = [\beta - FeOOH @[H^+ + Cl^-]_{Internal Adsorption}]@[Na^+ + OH^-]_{external surface adsorption}$ (22)

This creates an oxyhydroxide, which contains H⁺ ions and Cl⁻ ions within its internal tunnel structure [73–76] and Na⁺ ions and OH⁻ ions around its periphery. It is an effective adsorber of both anionic and cationic species from water. Compact, β -FeOOH, with 100% occupancy of the internal tunnel sites, has a structure of the form: [\equiv (OH) Cl⁻ (HO) \equiv], where the akageneite can be defined as: [β -FeOOH[HCl]_{0.256}], i.e., 1 g Fe removes 0.16 g Cl⁻. Hydrated β -FeOOH, takes the form [β -FeOOH, [H₂O]_n]. This structure allows the hydrated β -FeOOH to absorb more than 1 mole of NaCl for each mole of β -FeOOH. A schematic of the initial particle structuring is shown in Figure 10.



Figure 10. Initial n-Fe⁰ oxidation to provide a hydrated polymer coating.

3.10.4. Sphere Growth

The particle flocculates are composed of grains with the structure shown in Figure 10. These flocculates grow by accretion around a particle nucleus (e.g., Figure 11), with a gradual conversion of the n-Fe⁰ core to β -FeOOH (Figure 11). At this point, the structure starts to consolidate with a gradual migration of the β -FeOOH core to the margins and the replacement of the core by both H₂O and H₂ (Figure 11). The fluid-filled sphere grows by accretion, capturing [β -Fe₂(OH)₃]⁺, Fe(OH)ⁿ⁺, and FeOH²⁺] ions. Ion accretion may be expected to increase the thickness of the β -FeOOH rim (Figure 11) as the sphere expands in size. This does not happen (Figure 8b); instead, the rim thickness remains constant or slightly decreases as the particle expands (Figure 8b), and the main expansion of the particle size is associated with an increase in the internal fluid volume (Figure 8c,d). Accreted ions are used to expand the size of the polymer rim.

These observations update and modify the earlier observational models for Fe-polymer colloidal sphere formation documented in references [56,59]. Hollow, self-assembly colloidal spheres, constructed from nanocrystallites/particles, are sometimes termed "superballs" [77].

Hollow β -FeOOH polymer spheres have previously been formulated in experiments, where 0.202 g Fe(NO₃)₃·9H₂O + 0.08 g urea + 0.5 mL 1-n-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF₄]) + 25 mL deionized water were mixed by magnetic stirring at a temperature of 160 °C for a period of 5 to 20 min [78]. The sphere forms from the aggregation of lath-shaped β -FeOOH particles. Dissolution of the laths in within the core, accompanied by migration of the dissolved ions and recrystallization on the outer margins of the laths, may create a hollow core using a form of Otswald ripening [78].



Figure 11. Evolution of an initial flocculate particle in saline water to form a water or gas-filled sphere coated in β -FeOOH. Red = n-Fe0; blue = water; orange = β -FeOOH. This can include: [β -Fe₂(OH)₃]⁺; Blue arrow indicates the direction of evolutionary change.

3.10.5. Relationship between Sphere Rim Volume, Fluid Volume and Hydration Shell

The data in Figure 12a indicates that a particle with a rim volume of 10 microns³ will have a fluid core after 2 h of about 0.3 microns³. This increases to >10 micron³ after 4000 h. This analysis indicates that 1 cm³ of β -FeOOH polymer, weighing about 4.25 g, containing 2.8 g Fe, has the potential to directly hold by physical adsorption up to 1.2 g NaCl + 2.14 g NaCl in its core + NaCl in its outer hydration shells. Figure 12b indicates that a 250 nm hydration shell contains more than 3 times the rim volume. It is therefore possible for a charge of n-Fe⁰ to remove more than its own weight, as NaCl adsorbed around a β -FeOOH polymer within the hydration shell.



Figure 12. Evolution of an initial flocculate particle between 2 h after placement in water and 4000 h after placement in water. Data set: Figure 11; (a) rim volume versus fluid volume in the particle core; blue = after 2 h; red = after 4000 h; (b) hydration shell volume versus rim volume after 4000 h; blue = hydration shell thickness of 0.25 microns; red = hydration shell thickness of 0.5 microns; green = hydration shell thickness of 1 micron; purple = hydration shell thickness of 2 microns.

NaCl can be recovered from a β -FeOOH polymer by simply washing the polymer with deionized water to recover the adsorbed chlorides and sodium [76]. This allows the β -FeOOH polymer to be returned to the reactor for reuse as a desalination agent. An example process flow diagram showing how the n-Fe⁰: n- β -FeOOH polymer or n-Fe⁰:Fe(b) polymer may be commercialized to process saline groundwater or saline flowback water into partially desalinated irrigation water is shown in Figure 13.



Figure 13. Process flow diagram for the partial desalination of irrigation water or flowback water using $n-Fe^0$ or a β -FeOOH polymer.

The key process requirements are:

- a tank, reservoir, or impoundment to hold the saline groundwater or saline flowback water;
- A reactor that receives water from the tank or impoundment plus a charge of [n-Fe⁰ + n-Fe⁰:Fe polymer + n-Fe polymer];
- A gravity separation unit that recovers the [n-Fe⁰ + n-Fe⁰:Fe polymer + n-Fe polymer] and then discharges a product water (partially desalinated irrigation water). Optionally, part of the product water may be recycled;
- The recovered [n-Fe⁰ + n-Fe⁰:Fe polymer + n-Fe polymer] is recycled, with or without additional processing to remove the adsorbed Na⁺ and Cl⁻ ions.

This process flow (Figure 13) is relatively simple and robust. It also has a relatively low construction and operating cost. It could easily be constructed on an agricultural unit to convert saline groundwater or saline flowback water held in a tank or impoundment into partially desalinated water.

3.11. Desalination Modeling Associated with n-Fe⁰ or a β -FeOOH Polymer or a Fe(b) Polymer

The primary purpose of the ZVI desalination analyses in this study is to determine how much polymer is required to achieve a specific desalination outcome, the time frame required to achieve the desired outcome, and the reactor size required. This study was designed to understand, for a reactor operating at atmospheric pressure (0.1 MPa) at a temperature in the range of 273 to 298 K, the expected reaction kinetics. This, in turn, defined the required catalyst volume and the required reactor dimensions. This study has also considered the catalyst's design life and its activity with time (Figure 14). This information is required before the economic viability of the studied desalination routes can be considered.

3.11.1. Example Viability Assessment of the n-Fe⁰:Fe(b) Polymer

An experiment utilizing 25 g L⁻¹ of fresh, Fe₃O₄-coated n-Fe⁰ reduced the water salinity by 15% during the first reaction hour (Figure 8a). The main decline in salinity (Figure 8a) occurred later. The observed relationship (Figure 8a) between Ln($C_{t=n}/C_{t=0}$) versus time, after a reaction time of 100 h (Figure 8a), approximates to:

$$(C_{t=n}/C_{t=0}) = e^{-0.0116} [a]^{-0.3128},$$
(23)

[a] = water residence time in the reactor, days. $C_{t=n}$ = water salinity at time [a]; $C_{t=0}$ = initial water salinity. This relationship will differ with the water source and the type of n-Fe⁰ used, but it provides the kinetic data required to size a reactor (Figure 14).



Figure 14. Flow diagram showing the various catalyst parameters considered in this study.

Example Reactor Size Assessment

If a reactor (Figure 13) is to produce 100 m³ d⁻¹ of partially desalinated water using n-Fe⁰ or n-Fe polymer, then, from Figure 8:

- The feed water equates to $4.17 \text{ m}^3 \text{ h}^{-1}$;
- The n-Fe⁰ feed equates to 104.25 kg h^{-1} (25 g L⁻¹);
- The required desalination in the initial hour is $15\% (C_{t=1h}/C_{t=0} = 0.85)$;
- The required reactor volume is 4.17 m³.
- 1. Example Reactor Specification

A suitable reactor (medium density polyethylene, or MDPE) tank (Figures 13 and 14) has dimensions of 2.6 m in diameter; 1.3 m height; 0.14 t of weight; 5 m³ of capacity, 0.62 m access hatch, with ball valve level control, level monitors, and lifting lugs. A typical FOB cost is <USD 1500 (www.directwatertanks.co.uk, accessed on 18 October 2022).

2. Example Reactor Operation: Without Recycle

If the reactor is operated without recycle, and with a residence time, t_r , in the reactor of 1 h, then the expected value of $(C_{t=n}/C_{t=0})$, from Figure 8, without recycle is about 0.85. The presence, and use, of a recycle loop (Figure 13) will require either the feedwater inflow rate to be decreased or the reactor size to be increased.

3. Example Reactor Operation: With Recycle

Recycling 90% of the product water (Figure 13) will require the reactor tank capacity to be increased to about 45 m³. This will require the compact MDPE reactor (Figure 13) to be replaced with a galvanized steel reactor with the following dimensions: 4.6 m diameter; 3.04 m height; capacity 50 m³; EPPM (ethylene propylene diene monomer) liner; 10 cm diameter inlet and outlet pipes; steel cover. A typical FOB, pre-siteworks cost; the pre-installation cost is <USD 5000 (www.directwatertanks.co.uk, accessed on 18 October 2022).

4. Example Reactor Operation: With Recycle—Economies of Scale

Increasing the reactor capacity to 500 m³ will require a galvanized steel reactor with dimensions: 12.9 m in diameter; 3.84 m in height; capacity of 500 m³; EPPM (ethylene propylene diene monomer) liner; 10 cm diameter inlet and outlet pipes; steel cover. A typical FOB, pre-siteworks cost; the pre-installation cost is <USD 25,000 (www.directwatertanks.co.uk, accessed on 18 October 2022).

This brief costing analysis indicates that substantial economies of scale may be available as the reactor capacity is increased, with <5-fold increase in I costs for each 10-fold increase in reactor capacity.

Assessing Expected Yield

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If 100% of the n-Fe⁰ + β -FeOOH polymer + n-Fe(b) polymer is recovered for recycling (Figure 13), and 90% of the product water is recycled (Figure 13), then:

$$\ln(C_{t=n}/C_{t=0})_{kinetic} = -[a] [a_s] [P_w],$$
(24)

 a_s = particle surface area, m² g⁻¹ = 20 m² g⁻¹ for 50 nm Fe⁰; P_w = particle concentration, g L⁻¹; [*a*] = normalized rate constant. In Figure 11, the following applies:

$$Ln(0.85) = -[a], \tag{25}$$

In a recycle reactor, where both water and ZVI are recycled (Figure 13), [a] and $[a_s]$ remain constant, but $[P_w]$ increases with time.

$$Ln(0.85) = -0.16252 = -[a] = [-0.00033],$$
(26)

This relationship indicates that at t = 1 h, when $P_w = 3$ g L⁻¹, $(C_{t=n}/C_{t=0}) = 0.98$. This is consistent with the observations in Figure 8b,c. This kinetic relationship indicates that if 100% of the n-Fe⁰ + β -FeOOH polymer is recovered for recycling, then P_w and $(C_{t=n}/C_{t=0})$ must increase with time while n-Fe⁰ is being added. There will be a loss of activity as some active sites will become blocked during the recycling and regeneration processes (Figure 14), where:

$$Ln(C_{t=n}/C_{t=0}) = ([a] [a_s] [P_w])/[d],$$
(27)

where [d] = site blocking constant where 1 < [d]. [d] will not be known prior to a pilot (or full-scale reactor train) being commissioned, as it is a function of how the feed water interacts with the n-Fe⁰ + β -FeOOH polymer. [d] may vary as a function of time spent in the reaction environment [t], e.g., $[d]^{[t]}$. This aging (Figure 14) may be modeled as:

$$(C_{t=n}/C_{t=0})_{\text{observed}} = [(C_{t=n}/C_{t=0})_{\text{kinetic}} [d]]^{[t]},$$
(28)

This model will result in $(C_{t=n}/C_{t=0})_{\text{observed}}$ initially declining with time before increasing. The n-Fe⁰ + β -FeOOH polymer will be replaced, when $(C_{t=n}/C_{t=0})_{\text{observed}}$ exceeds a critical value. The life expectancy of a n-Fe⁰ + β -FeOOH polymer in a recycle reactor is not known. This study has only tested a single recycling process.

Impact of Adsorption/Reaction Site Blocking on the Particles

The magnitude of [d] defines the particle life expectancy before either regeneration or replacement is required. The expected modeled operation (Figure 14) of the recycle reactor (Figure 13) for different values of [d] can be used to provide an indication of the expected desalination outcome using Fe₃O₄-coated n-Fe⁰. Bare (uncoated) n-Fe⁰ and other coatings on n-Fe⁰ will have different values for [a] and [d]. They may also have a different relationship between [d] and [t].

Example Reaction Time and Reactor Size

The reaction time (Figure 14) between the feed water entering the reactor and the product water leaving the separator (Figure 13) is assumed to be 1 h. $[R_r] = 0.9$; fresh n-Fe⁰ equates to 104.25 kg h⁻¹ for 10 h. No new n-Fe⁰ is added after the initial 10 h. In this model,



100% of the n-Fe⁰ is recycled. This equates to a target n-Fe⁰ + β -FeOOH polymer + n-Fe(b) polymer concentration in the recycle reactor (Figure 14) of around 225 g L⁻¹ (Figure 15a).

Figure 15. Modeled desalination outcomes for the reactor shown in Figure 13 with a n-Fe⁰ charge. $R_r = 90\%$; n-Fe⁰ is added at a rate of 25 g L⁻¹ for the first 10 h. All n-Fe⁰ within the reaction environment is recycled. (a) n-Fe⁰ (kg) provided to the reactor versus hours on line; (b) water volume being processed in the reactor versus time; (c) partially desalinated water production as a function of time; (d) n-Fe⁰, $P_w = 25$ g L⁻¹; expected value of $C_{t=n}/C_{t=0}$ versus hours on line for: [d] = 1: (e), n-Fe⁰, $P_w = 50$ g L⁻¹; expected value of $C_{t=n}/C_{t=0}$ versus hours on line for: [d] = 1: (f), n-Fe⁰, $P_w = 100$ g L⁻¹ expected value of $C_{t=n}/C_{t=0}$ versus hours on line for: [d] = 1.005: red; [d] = 1.01: purple; [d] = 1.02: green.

In this example, where $[R_r] = 0.9$, the process water volume within the reactor (Figures 13 and 14) stabilizes at about 41 m³ (Figure 15b). This stabilized volume (required reactor size) increases as $[R_r]$ increases above 0.9 but decreases as $[R_r]$ decreases below 0.9. The product water outflow rises to a stable output level, which equals the feed

water flow rate (Figure 15c). The time taken to reach this flow rate is a function of the recycle ratio. This stabilization time increases as $[R_r]$ increases.

Example Product Water Salinity

The product water salinity is a function of [*d*] (Figures 14 and 15d). Ideally, [*d*] = 1. In reality, [*d*] will be >1. The product water salinity reduces to a base level (Figure 15d). This base level is controlled by the amount of n-Fe⁰ + β -FeOOH polymer ($P_w = g L^{-1}$) within the recycle reactor. The total amount of desalination increases as P_w increases.

This kinetic modeling (Figure 14) indicates that $(C_{t=n}/C_{t=0})_{observed}$ is minimized (i.e., desalination is maximized) by maximizing [*a*] and minimizing [*d*]. The parameter [*d*] controls the economic life expectancy of the n-Fe⁰ + β -FeOOH polymer within the reactor (Figure 14) and the economic viability of the desalination process. The parameter [*a*] controls the minimum achievable value for $(C_{t=n}/C_{t=0})_{observed}$ (Figure 14).

The effectiveness of a β -FeOOH polymer decreases with decreasing water salinity and decreases with decreasing water pH. Initially, the n-Fe⁰ is used to increase the water's pH (Figure 8). Once the addition of fresh n-Fe⁰ to the reactor ceases (Figure 15a), the pH of the water retained in the reactor will gradually decrease (Figure 8), and [*d*] will increase (Figure 15d).

3.11.2. Significance of Increasing P_w

The modeling in Figure 15d demonstrated that operating the process (Figures 13 and 14) with recycle and an initial n-Fe⁰ charge of 25 g L⁻¹ (for 10 h) with 100% ZVI recycle thereafter, it may be possible to achieve $C_{t=n}/C_{t=0}$ of 80%, i.e., 20% desalination. Increasing P_w to 50 g L⁻¹ (for 10 h) allows $C_{t=n}/C_{t=0}$ to reduce to 61% (Figure 15e). Increasing P_w further to 100 g L⁻¹ (for 10 h) allows $C_{t=n}/C_{t=0}$ to reduce to 38% (Figure 15f), i.e., 62% desalination.

This analysis indicates that the economic viability of partial desalination (Figure 14) using n-Fe⁰:Fe(b) is a function of [*a*], [*d*] and P_w . [*a*] controls the amount of n-Fe⁰ required (P_w), to achieve a specific $C_{t=n}/C_{t=0}$ ratio. [*d*] controls the frequency of n-Fe⁰ replacement, and the decline in catalytic efficiency (Figure 14).

For example, if the maximum acceptable $C_{t=n}/C_{t=0}$ ratio was 0.5, Figure 15d would indicate the following replacement, or regeneration, intervals:

- d = 1.02, replacement is at 15-h intervals (processing 62 m³);
- d = 1.01, replacement is at 29-h intervals (processing 120 m³);
- d = 1.005, replacement is at 56-h intervals (processing 233 m³).

These parameters are specific to a specific batch and composition of n-Fe⁰, a specific water composition, a specific reactor process, and a specific mode of reactor operation. They may also vary with temperature. Replacing Fe₃O₄ coated n-Fe⁰ with uncoated n-Fe⁰ will increase [*a*], possibly by several orders of magnitude. This increase in [*a*] will be accompanied by an increase in [*d*], requiring more frequent replacement of the n-Fe⁰, but the increase in [*a*] may allow P_w to be reduced.

This analysis indicates that if the n-Fe⁰ recovery system is switched from magnetic separation to gravity separation, and if it is assumed that the primary agent for ion removal is n-Fe⁰:Fe polymers, then it may be possible to substantially reduce the cost of using n-Fe⁰ to produce partially desalinated irrigation water from groundwater.

4. Boosting Desalination Using Sol-Gel Polymers

The preceding analysis has indicated that n-Fe⁰ can be used to provide a source of β -FeOOH polymer, or Fe(a), Fe(b), and Fe(c) polymer in the water. The principal expenses associated with the process are: (i) the cost of n-Fe⁰; (ii) the large tank sizes associated with the slow reaction rates, and the requirement for a high recycle ratio.

This study has identified that the principal desalination agent may not be n-Fe⁰, but is instead a derivative polymer (Fe(a,b,c)). The formation of these derivative polymers allows the desalination reaction to proceed. These polymers have not been specifically identified, but the redox environment is consistent with the presence of akaganeite (β -

FeOOH polymer), other FeOOH polymers, and green rust ($Fe_xO_yH_z$) polymers. These polymers and associated ions can be formed directly from Fe⁰, e.g., [52],

$$Fe0 + H2O = HFeOHx+,$$
(29)

Increasing the rate at which n-Fe⁰ produces polymeric ions (e.g., $-[HFeOH^{*+}]^{n-}$) will increase the desalination rate and reduce the P_w required to achieve a specific desalination rate. Substituting Fe⁰ with Feⁿ⁺ may make it possible to manufacture n-[β -FeOOH polymer] or an equivalent polymer within the reactor, using a substantially smaller quantity of Fe.

Since the materials required to manufacture Feⁿ⁺ ions are perhaps two to four orders of magnitude cheaper to purchase than n-Fe⁰, are widely available, and are safer to handle than n-Fe⁰, it may be more effective to manufacture the Fe-polymers directly from dissolved ions within the reactor, using a sol-gel approach, rather than from n-Fe⁰.

This concept is summarized in Figure 16. This section investigates whether the sol-gel approach may provide a viable route that could allow saline groundwater to provide partially desalinated irrigation water for a cost of <USD 0.5 m⁻³.



Figure 16. Comparison of polymer desalination using a sol gel approach to polymer manufacture and n-Fe⁰ as the polymer source.

4.1. Reactor Process Flow

The initial n-Fe⁰ process flow assumed that Fe-polymers (iron corrosion products) formed no part of the desalination process (Appendix A). Desalination was undertaken by functionalized magnetic n-Fe⁰ (Appendix A). The experimental observations that iron polymers are directly associated with desalination [6] or catalyze desalination [4,7], provided the technical basis for the revisiting of this hypothesis. The experimental data in Figure 8b,c demonstrated that higher desalination rates occur in the reused non-magnetic n-Fe⁰:Fe(b) polymer.

This suggests that many of the operational issues associated with operating a reactor with functionalized magnetic n-Fe⁰ are over complications and that the process could be simplified by replacing the magnetic separators with a simple gravitational separator (Figure 13). This then allows the non-magnetic n-Fe⁰:Fe(b) polymer to be washed to recover bound NaCl prior to reuse (Figure 13). This process restructuring creates an obvious reduction in both processing costs and material requirements in desalinating saline groundwater to produce partially desalinated irrigation water, relative to the prior art (Appendix A).

The principal material cost in the revised n-Fe⁰:Fe(b) polymer desalination process is the cost of the n-Fe⁰. The revised n-Fe⁰:Fe(b) polymer model indicates that the sole

function of the n-Fe⁰ is to act as a generating source of Fe(b) polymers. This conclusion is consistent with the operating results of a catalytic pressure swing adsorption/desorption desalination reactor [7], which demonstrated that supported Fe(b) polymers could catalyze the formation of entrained hydrated Fe(b) polymers within the water body. These entrained polymers desalinated the water. A follow-up series of experiments [59] established that sol-gel polymers may have the potential to replace n-Fe⁰ and n-Fe⁰:Fe(b) polymers.

The key feature associated with n-[β -FeOOH polymer] formation associated with n-Fe⁰ is the increase in pH into the range of 8 to 11 (Figure 8). This is associated with the availability of Feⁿ⁺ ions, produced from the corrosion of n-Fe⁰. The sol-gel precipitates used in this study are designed to increase the product water's pH into the range of 9 to 13.

4.2. Increasing pH to Facilitate Sol-Gel Formation

Adding CaO (or a soluble carbonate) to water increases its pH. Therefore, addition to water of CaO (or another oxide (ZnO), or a soluble bicarbonate/carbonate) to saline water containing Feⁿ⁺ ions will result in the precipitation of β -FeOOH polymer, Fe polymers, and green rust polymers [59]. The addition of Feⁿ⁺ ions to water containing organic species, such as acids or polyphenols, will also result in the precipitation of n-Fe@organic polymer species [56,59]. The target Eh:pH regime for the sol-gel polymer formation is summarized in Figure 3.

4.3. Fe-Ca Polymer

Ion removal for both Cl⁻ and Na⁺ ions approximate to a relationship of the form [59]:

$$(C_{t=n}/C_{t=0}) = \exp(-(([a] [a_s]) [P_w])[t_r][b])(3600 t_r)), \tag{30}$$

where ([*a*] [a_s] [P_w]) and [*b*] are derived from a regression plot of $\text{Ln}(C_{t=n}/C_{t=0})$ versus residence time, [t_r], hours (Table 1). This sol-gel combination has an expected low level of Na⁺ removal (<5%) combined with 35–45% Cl⁻ ion removal after an hour. The expected relationships between ($C_{t=n}/C_{t=0}$) and t_r are provided in Figure 17. The amount of desalination increases with increasing P_w and decreases with t_r as [*d*] increases. The cationic nature of this polymer is consistent with the formation of a β -FeOOH polymer.

Table 1. Fe-Ca polymer; R^2 = Coefficient of determination; PCC = Pearson's Correlation Coefficient. All weights are g L⁻¹. Data Source: Table A5 reference [20]. Trial 1. 1.4 g FeSO₄ + 3.34 g CaO; feed water salinity (FW): = 14.38 g NaCl L⁻¹; Trial 2. 1.4 g FeSO₄ + 1.67 g CaO; FW = 15.27 g NaCl L⁻¹; Trial 3. 1.4 g FeSO₄ + 3.34 g CaO + 1.32 g urea; FW = 30.14 g Cl⁻ L⁻¹ + 18.38 g Na⁺ L⁻¹; Trial 4. 1 g FeSO₄ + 1.67 g CaO + 2.52 g MnO₂ + 1 cm³ formic acid; FW = 30.14 g Cl⁻ L⁻¹ + 18.38 g Na⁺ L⁻¹; Trial 5. 1 g FeSO₄ + 3.34 g CaO + 2.52 g MnO₂ + 1 cm³ formic acid; FW = 30.14 g Cl⁻ L⁻¹ + 18.38 g Na⁺ L⁻¹; Trial 6. 0.8 g FeSO₄ + 3.34 g CaO + 2.71 g ZnO + 0.94 g gallic acid; FW = 22.11 g Cl⁻ L⁻¹ + 14.33 g Na⁺ L⁻¹; Trial 7. 1.42 g FeSO₄ + 5.61 g ZnO; FW = 30.47 g Cl⁻ L⁻¹ + 10.3 g Na⁺ L⁻¹. Trial 8. 1.0 g FeSO₄ + 1.67 g CaO + 2.52 g MnO₂ + 2.96 g MgCO₃ + 1 cm³ formic acid; FW = 26.55 g Cl⁻ L⁻¹ + 14.33 g Na⁺ L⁻¹ Trial 9. 1 g FeSO₄ + 3.34 g CaO + 2.52 g MnO₂ + 2.96 g MgCO₃ + 1 cm³ formic acid; FW = 22.11 g Cl⁻ L⁻¹ + 14.33 g Na⁺ L⁻¹ Trial 9. 1 g FeSO₄ + 3.34 g CaO + 2.52 g MnO₂ + 2.96 g MgCO₃ + 1 cm³ formic acid; FW = 22.11 g Cl⁻ L⁻¹ + 14.33 g Na⁺ L⁻¹ Trial 9. 1 g FeSO₄ + 3.34 g CaO + 2.52 g MnO₂ + 2.52 g MnO₂ + 2.52 g MnO₂ + 1 cm³ formic acid; FW = 22.11 g Cl⁻ L⁻¹ + 14.33 g Na⁺ L⁻¹ Trial 9. 1 g FeSO₄ + 3.34 g CaO + 11.22 g ZnO + 0.9 g tartaric acid; FW = 23.22 g Cl⁻ L⁻¹ + 19.83 g Na⁺ L⁻¹.

		Cl ⁻				Na ⁺			
Polymer	Trial	[a]	[b]	R^2	PCC	[a]	[b]	R^2	PCC
Fe-Ca	1	0.000120540	-0.9842	0.999	1.000	0.0000851	-0.92801	0.997	0.998
	2	0.000168210	-0.9867	0.999	0.999	0.0000039	-1.61133	1.000	1.000
Fe-Ca-Urea	3	0.000278500	-0.9542	0.954	0.977	0.0001331	-1.01025	1.000	1.000
Fe-Ca-Mn-Formic Acid	4	0.000049800	-0.4236	0.918	0.958	0.0002348	-1.05551	0.842	0.918
	5	0.000135500	-0.7804	0.975	0.987	0.0002164	-0.88604	0.955	0.977
Fe-Ca-Zn-Gallic Acid	6	0.000020820	-0.5451	1.000	1.000	14.4647000	-0.00100	1.000	1.000
Fe-Zn	7	0.000027580	-1.1817	1.000	1.000	0.0000730	-0.86425	0.999	0.999
Fe-Ca-Mn-Mg-Formic Acid	8	0.000179580	-0.7637	0.990	0.995	0.0001411	-0.94756	0.996	0.998
Fe-Ca-Mn-Formic Acid	9	0.000031490	-0.4312	0.732	0.856	0.0001519	-0.92883	0.906	0.952
Fe-Ca-Zn- Tartaric Acid	10	0.000289940	-0.7276	0.963	0.981	0.0003781	-0.86185	0.988	0.994



Figure 17. Expected values of $C_{t=n}/C_{t=0}$ for different polymers, where C = salinity, versus time. [d] = 1: blue; [d] = 1.005: red; [d] = 1.01: purple; [d] = 1.02: green; [d] = 1.05: orange; Reactor Process flow: Figure 13. (**a**), Fe-Ca polymer, Table 1, Trial 1; dashed lines = 1.4 g FeSO₄ L⁻¹; solid lines = 2.8 g FeSO₄ L⁻¹. [R_r] = 0%. (**b**), Fe-Ca polymer Trial 2 (Table 1); dashed lines = 1.4 g FeSO₄ L⁻¹; solid lines = 7 g FeSO₄ L⁻¹. [R_r] = 0%. (**c**), Fe-Ca- urea polymer, Trial 3, Table 1; [R_r] = 0%. (**d**), Fe-Ca-Mn-Formic Acid polymer Trial 4 (Table 1); [R_r] = 90%; (**e**), Fe-Ca-Mn-formic acid polymer Trial 5 (Table 1); [R_r] = 90%; (**f**), Fe-Ca-Zn-gallic acid polymer Trial 6 (Table 1); dashed lines = 0.8 g FeSO₄ L⁻¹; solid lines = 8 g FeSO₄ L⁻¹. [R_r] = 90%. (**g**), Fe-Zn-urea polymer, Trial 7, Table 1; dashed lines = 1.42 g FeSO₄ L⁻¹; solid lines = 14.2 g FeSO₄ L⁻¹; [R_r] = 90%; (**h**), Fe-Ca-Mn-Mg-formic acid polymer; Trial 8, Table 1; [R_r] = 90%; (**i**), Fe-Ca-Mn-K-formic acid polymer; Trial 9, Table 1; [R_r] = 90%; (**j**), Fe-Ca-Zn-tartaric acid polymer. Trial 10, Table 1; [R_r] = 90%.

4.4. Fe-Ca-Urea Polymer

Replacing n-Fe⁰ with a Fe-Ca-urea and sol-gel combination (Table 1) indicates an expected 38% Na⁺ removal combined with a 63% Cl⁻ ion removal after an hour. Replacing the 25 g of n-Fe⁰ L⁻¹ with this polymer (1.4 g FeSO₄ L⁻¹) in the recycle reactor increases the polymer's life (Figure 17c) when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d). The addition of urea adds both cationic and anionic sites to the polymer.

4.5. Fe-Ca-Mn-Formic Acid Polymer

Replacing n-Fe⁰ with a Fe-Ca-Mn-Formic acid sol gel combination (Table 1) indicates an expected 54–58% Na⁺ removal combined with a 17–39% Cl⁻ ion removal after an hour. Replacing the 25 g of n-Fe⁰ L⁻¹ with this polymer (1 g FeSO₄ L⁻¹) in the recycle reactor increases the polymer's life (Figure 17d,e), when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d).

4.6. Fe-Ca-Zn-Galic Acid Polymer

Replacing n-Fe⁰ with a Fe-Ca-Zn-gallic acid sol-gel combination (Table 1) indicates an expected 0% Na⁺ removal combined with a 7% Cl⁻ ion removal after an hour. Increasing the amount of FeSO₄ from 0.8 g L⁻¹ to 8 g L⁻¹ increases, after 1 h, the Na⁺ removal to 1% and the Cl⁻ removal to 52%. Replacing the 25 g of n-Fe⁰ L⁻¹ with this polymer (8 g FeSO₄ L⁻¹) in the recycle reactor increases the polymer life (Figure 17f), when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d). This polymer initially preferentially removes Cl⁻ ions before removing Na⁺ ions. This is consistent with the initial Fe@gallic acid polymer being dominated by cationic sites.

4.7. Fe-Zn Polymer

Replacing n-Fe⁰ with a Fe-Zn sol gel combination (Table 1) indicates an expected 23% Na⁺ removal combined with a 9% Cl⁻ ion removal after an hour. Increasing the amount of FeSO₄ from 1.42 g L⁻¹ to 14.2 g L⁻¹ increases, after 1 h, the Na⁺ removal to 92% and the Cl⁻ removal to 62%. Replacing the 25 g n-Fe⁰ L⁻¹ with this polymer (14.2 g of FeSO₄ L⁻¹) in the recycle reactor increases the polymer's life (Figure 17g), when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d). This polymer contains a higher proportion of anionic sites relative to cationic sites.

4.8. Fe-Ca-Mn-Mg-Formic Acid Polymer

Replacing n-Fe⁰ with a Fe-Ca-Mn-Mg-formic acid sol gel combination (Table 1) indicates an expected 40% Na⁺ removal combined with a 48% Cl⁻ ion removal after an hour. Replacing the 25 g of n-Fe⁰ L⁻¹ with this polymer in the recycle reactor increases the polymer's life (Figure 17h), when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d). This polymer has a similar proportion of cationic and anionic sites.

4.9. Fe-Ca-Mn-K-Formic Acid Polymer

Replacing n-Fe⁰ with a Fe-Ca-Mn-K-formic sol gel combination (Table 1) indicates an expected 75% Na⁺ removal combined with a 65% Cl⁻ ion removal after an hour. Replacing the 25 g n-Fe⁰ L⁻¹ with this polymer in the recycle reactor increases the polymer's life (Figure 17i), when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d).

4.10. Fe-Ca-Zn-Tartaric Acid Polymer

Replacing n-Fe⁰ with a Fe-Ca-Zn-tartaric acid sol gel combination (Table 1) indicates an expected 74% Na⁺ removal combined with a 64% Cl⁻ ion removal after an hour. Replacing the 25 g n-Fe⁰ L⁻¹ with this polymer in the recycle reactor increases the polymer's life (Figure 17j) when compared to the n-Fe⁰ + β -FeOOH polymer (Figure 15d). This polymer contains a similar proportion of cationic and anionic sites.

5. Expected Desalination

The amount of desalination that could be achieved in a recycle reactor (Figure 13), for a specific R_r , is a function of the average P_w , and [*d*] (Figure 14). Any commercial application of this technology for the treatment of groundwater will require the following criteria (Figure 2) to be met:

- The technology should be able to partially desalinate the irrigation water;
- The pH of the irrigation water and composition of the residual polymers and ions in the water should not adversely affect either the plant (crop) growth or the soil structure;
- The technology should improve the standard measures used by the regulatory agricultural authorities to assess the suitability of water for irrigation;
- The amount of desalination achieved should be sufficient to induce an increase in crop yield (t ha⁻¹), without inducing a decrease in crop value (USD t⁻¹);
- Application of the partially desalinated irrigation water should decrease soil salinization and should not contribute to soil salinization. Increasing soil salinization is associated with decreasing agricultural land values (USD ha⁻¹);
- The cost of providing the partially desalinated irrigation water should be less than the increased net revenue resulting from increased crop yields associated with using the water;
- The regulatory authorities provide approval for the use of the appropriate desalination
 polymer, provide approval for irrigation overland flow to enter the local riparian
 environment, and provide approval for the resultant soil throughflow to enter both
 the shallow groundwater environment and the local riparian environment, through
 field drainage to ditches and streams, etc.

5.1. Environmental Impact

The use of n-Fe⁰ in treating groundwater within aquifers is subject to regulation in many countries. The use of most chemicals for application to the soil, where there is a risk that the chemicals could either reach groundwater or the riparian environment or potentially interfere with potable water supplies, is also subject to regulation in many countries.

In this study, the polymer ingredients were selected from widely available agricultural chemicals. This was to reduce the risk that the chemicals associated with the partially desalinated water would have an adverse impact on plant growth and also to reduce the risk that the regulatory authorities would place impractical requirements on their use to create partially desalinated irrigation water from saline groundwater.

All the chemicals used to form the polymers are used as fertilizers for some agricultural applications: ZnO [79]; CaO [80,81]; MnO₂ [82,83]; Fe_SO₄ [84,85]; MgCO₃ [86,87]; K_2CO_3 [88]; formic acid [89]; tartaric acid [90]; and urea [91,92]. Therefore, excess quantities of these components in the desalinated water are likely to assist crop growth.

5.2. Indicative Costs

If the polymer ingredients for a reactor charge cost USD *y*, then:

Cost (USD m⁻³) =
$$(y \times t_n/10)/(t_n P_r)$$
 (31)

 t_n = number of hours (h) of processing using a single polymer charge; P_r = partially desalinated water production rate, m³ h⁻¹. The choice of polymer, and t_n is a function of the feed water composition, required level of desalination. Example polymer costs are provided in Table 2.

These two example polymers provide an example of the material cost. For the purposes of this study, an of example saline flowback water from the Marcellus Shale (Table 3) is used to illustrate the possible outcomes associated with using the Fe-Ca-Urea polymer (Polymer B, Table 2). The data source for this water composition is [59]. The target salinity (Figure 14) is between 1 and 2 g NaCl L⁻¹.

Table 2. Example costs. Material costs are FOB, USD t⁻¹, Source—(www.alibaba.com, accessed on 5 October 2022); Polymer A = 2.0 g FeSO₄ L⁻¹ + 3.34 g CaO L⁻¹ + 11.22 g ZnO L⁻¹ + 0.9 g Tartaric Acid L⁻¹; Polymer B = 1.4 g FeSO₄ L⁻¹ + 3.34 g CaO L⁻¹ + 1.32 g Urea L⁻¹. Polymer A and B ingredient costs (FOB) are USD m⁻³ processed (without polymer recycle).

	FeSO ₄	CaO	ZnO	Tartaric Acid	Urea	Polymer A	Polymer B
Low	80	60	2900	1500	15	34.25	0.33
High	150	120	3200	30,000	150	63.60	0.81

Table 3. Example flowback water composition from a shale gas well, USA (Marcellus Shale). All measurements are in g L⁻¹. EC1 = EC when F = 0.55; EC2 = EC when F = 0.7. EC units = dSm⁻¹ (mScm⁻¹); FeSO₄ data is excluded from the compositional analysis and the EC calculations. EC and SAR calculations assume that the Ca remains in solution and is not incorporated in the Fe(a,b,c) polymers. Incorporation of Ca in the polymers will result in a lower EC and a higher SAR.

	Ca	K	Mg	Na	C1	HCO ₃	SO_4	NaCl	SAR	EC1	EC2
Example Well	0.1633	0.0327	0.0262	4.659	7.64	1.036	0.0656	12.3	125.94	24.77	19.46
0% Desalination	2.5490	0.0327	0.0262	4.659	7.64	1.036	0.0656	12.3	35.58	29.11	22.87
20% Desalination	2.5490	0.0327	0.0262	3.727	6.11	1.036	0.0656	9.8	28.47	24.63	19.36
50% Desalination	2.5490	0.0327	0.0262	2.330	3.82	1.036	0.0656	6.1	17.79	17.93	14.08
80% Desalination	2.5490	0.0327	0.0262	0.932	1.53	1.036	0.0656	2.5	7.12	11.22	8.81
100% Desalination	2.5490	0.0327	0.0262	0.000	0.00	1.036	0.0656	0.0	0.00	6.74	5.30

5.3. Regulatory Indices

Regulatory consent procedures and requirements vary between countries. Regulatory consent (Figure 2) to use desalinated irrigation water commonly requires that the irrigation water comply with regulation-defined criteria and compositional indices. Examples of appropriate compositional indices are provided in Appendix C. The most widely considered regulatory criteria for the characterization of irrigation water (apart from electrical conductivity (EC)) is the sodium adsorption ratio (SAR) [41] (Appendix C). The exact values of SAR that are acceptable to a regulatory authority vary globally. The Fe@Ca polymers decrease Na⁺ while increasing Ca²⁺. This has the effect (Appendix C) of reducing SAR as the salinity decreases (Table 3). FAO guidelines recommend regulatory restrictions on irrigation water use when EC > 3 dSm⁻¹ and SAR >3.0. The analysis in Table 3 indicates that the product water EC will be >3 unless measures are adopted to remove Fe-Ca polymers following processing. Their removal from the product water in a gravitational separator (Figure 13) will allow the product water to potentially have EC < 3 dSm⁻¹ and SAR < 3.0.

5.4. Example Fe-Ca-Urea Polymer Analysis

The Fe-Ca-urea polymer's effectiveness is a function of P_w and [d] (Figure 18). The data in Table 3, indicates that the required $C_{t=n}/C_{t=0}$ should be <16%, to achieve a salinity of <2 g L⁻¹. Modeling (Figure 18) using the data set in Table 2 indicates that this criterion is met, when P_w includes >5.6 g FeSO₄ L⁻¹ (Figure 18d).

Increasing the level of Ca²⁺ ions will assist in reducing the SAR value (Appendix C) into the range 1.83 to 3.67, if the salinity can be reduced into the range of 1.2 to 2.5 g L⁻¹ (Table 4). The modeled data indicates (Figure 18) that this may occur if P_w includes >5.6 g FeSO₄ L⁻¹ (Figure 18d).



Figure 18. Fe@Ca@urea polymer product water salinity versus hours on line (t_r). Assumptions. Process flow: Figure 13; $R_r = 90\%$; 100% of the polymer recovered from the product water is returned to the reactor. t_r = time between entering the reactor and leaving the separator. [d] = 1: blue; [d] = 1.005: red; [d] = 1.01: purple; [d] = 1.02: green; [d] = 1.05: orange; (a), $P_w = 1.4$ g FeSO₄ L⁻¹ + 3.34 g CaO L⁻¹ + 1.32 g urea L⁻¹; (b), $P_w = 2.8$ g FeSO₄ L⁻¹ + 6.68 g CaO L⁻¹ + 2.64 g urea L⁻¹; (c), $P_w = 4.2$ g FeSO₄ L⁻¹ + 10.02 g CaO L⁻¹ + 3.96 g urea L⁻¹; (d), $P_w = 5.6$ g FeSO₄ L⁻¹ + 13.36 g CaO L⁻¹ + 5.28 g Urea L⁻¹.

Table 4. Example flowback water composition from a shale gas well, USA (Marcellus Shale), where P_w includes >5.6 g FeSO₄ L⁻¹. All measurements are in g L⁻¹. EC1 = EC, when F = 0.55; EC2 = EC, when F = 0.7. EC units = dSm⁻¹ (mScm⁻¹); FeSO₄ data is excluded from the compositional analysis. Product water composition entering the gravitational separator.

	Ca	К	Mg	Na	C1	HCO ₃	SO_4	NaCl	SAR	EC1	EC2
Example Well	0.1633	0.0327	0.0262	4.659	7.64	1.036	0.0656	12.3	125.94	24.77	19.46
0% Desalination	9.7062	0.0327	0.0262	4.659	7.64	1.036	0.0656	12.3	18.35	42.12	33.09
20% Desalination	9.7062	0.0327	0.0262	3.727	6.11	1.036	0.0656	9.8	14.68	37.65	29.58
50% Desalination	9.7062	0.0327	0.0262	2.330	3.82	1.036	0.0656	6.1	9.17	30.94	24.31
80% Desalination	9.7062	0.0327	0.0262	0.932	1.53	1.036	0.0656	2.5	3.67	24.23	19.04
90% Desalination	9.7062	0.0327	0.0262	0.466	0.76	1.036	0.0656	1.2	1.83	21.99	17.28
100% Desalination	9.7062	0.0327	0.0262	0.000	0.00	1.036	0.0656	0.0	0.00	19.76	15.52

The efficiency of the gravitational separator will define both the SAR value and the EC of the product water. Table 4 indicates the expected water compositions without removal of the polymer precipitate from the water. Removal of the polymer precipitate will reduce the product irrigation water's EC and SAR.

Example Impact of Polymer Recycle on Product Water Composition

If the reactor (Figure 13) is filled with 4.17 m³ of saline water plus 22.96 kg FeSO₄ + 54.78 kg CaO + 21.65 kg urea (Figure 18d, Table 4), and the reactors' (Figures 13 and 14) operating conditions are:

- Feed water flow rate = $4.17 \text{ m}^3 \text{ h}^{-1}$;
- Product water flow rate = $4.17 \text{ m}^3 \text{ h}^{-1}$;
- $R_r = 0\%$ for product water; $R_r = 100\%$ for polymer recovered from the separator;
- Reactor volume = 4.17 m³, including flowlines to the separator (Figure 17).
- $t_r = 1 \text{ h};$
- [*d*] is between 1.005 and 1.01.

Then, the expected product water salinity will be <2 g NaCl L⁻¹ for between 90 h ([*d*]= 1.01) and 185 h ([*d*]= 1.005), i.e., a single catalyst (sol-gel polymer) charge costing about USD 3.33 will process between 375 and 770 m³ (Figure 19a,b). Reactivation of the polymer is achieved by washing it in fresh water. This reduces the net polymer cost for the water processing to between USD 0.0044 and 0.0088 m⁻³.



Figure 19. Fe@Ca@urea polymer: Flowback water analysis. $R_r = 0\%$; $P_w = 5.6$ g FeSO₄ L⁻¹ + 13.36 g CaO L⁻¹ + 5.28 g urea L⁻¹; (**a**) product water NaCl g L⁻¹ versus time without polymer replacement. [d] = 1.005: red; [d] = 1.01: purple; green dashed line = maximum acceptable salinity; orange arrow = point at which the polymer needs to be replaced or recharged for [d] = 1.01; blue arrow = point at which the polymer needs to be replaced or recharged for [d] = 1.005; (**b**) product water NaCl g L⁻¹ versus time with periodic polymer replacement. Feed water contains 12.3 g L⁻¹; Water duration in the reaction environment = 1 h.

6. Application to Groundwater Management

The discussion and analysis in Sections 3–5 have focused on:

- Reaction kinetics (Figure 14) considering:
 - Polymer Type
 - Supported: n-Fe⁰:Fe(b);
 - Unsupported: n-Fe(b);
 - Static diffusion operating conditions;
 - Pressure of 0.1 MPa and temperature of 273–298 K;
 - Different P_w ;
 - Different activity dieback relationships;
- Reactor Operation (Figure 13) considering:
 - desalination with no product water recycled to the reactor;
 - desalination with product water recycled to the reactor;
 - desalination with polymer recycled to the reactor.

This analysis has established that the polymer desalination process may provide a technically viable solution for the provision of irrigation water from groundwater or flowback water. This product water will either be placed in storage for later use or be used as it is produced. Storage can be:

 Above ground in tanks or impoundments. This is the conventional approach. The typical irrigation requirement is 1000–10,000 m³ ha⁻¹ a⁻¹. An agricultural holding of 100 ha, would require surface-based storage (e.g., 3 m deep) covering 33,000–330,000 m² (3.3 to 33 ha). This large land take for desalinated water storage may be both physically and economically impractical.

• In the subsurface, contained within hydrodynamic mounds or plumes. The latter approach allows the reactor (Figure 13) to be used to desalinate part of an aquifer or soil body (Figures 2 and 20).



Figure 20. A flow diagram summarizing the decision process used in this study to reconstruct a hydrodynamic stationary groundwater plume or a perched stationary groundwater mound.

The desalinated water created using this process (Figure 2) can be used to reconstruct the groundwater in three areas: (i) the creation of stationary hydrodynamic plumes of desalinated water within saline aquifers; (ii) the creation of shallow pressured mounds (containing desalinated water) within salinized impermeable soils; and (iii) the prevention, stabilization, and reversal of seawater intrusion within an aquifer. The decision process flow used to achieve this is summarized in Figure 20. A more detailed analysis of this process, which demonstrates the potential applications of the polymers for sub-surface storage and for desalinating aquifers and soils, is provided in Appendix D.

7. Commerciality

ZVI desalination technology is at various stages of commerciality. Desalination processes based on n-Fe⁰ have undergone pre-commercial (commercial scale) trials (since 2014) in the USA, tackling waste saline water associated with hydrocarbon extraction and mine waters. The desalination processes based on Fe⁰:Fe(b)@urea polymers and SiO₂@Fe(b)@urea polymers [4,7] have undergone pre-commercial (commercial scale) trials in the UK (since 2015).

This study has focused on a static diffusion and batch flow analysis in order to determine whether this polymer process may provide an alternative route to commerciality. Batch flow trials can be used to design both batch flow reactors and continuous flow reactors. Historically, multi-tubular reactor design and commerciality decisions have normally focused on the performance of a single commercial-scale tube.

The kinetic results (Table 2) established that the catalyst's effectiveness increases with residence time within the reactor. It had previously been established [93] that the coagulation rate to form polymeric agglomerates increases as:

- The turbulence within the reaction environment increases; and
- The pH in the turbulent environment increased.

The increase in rate constant resulting from a combination of a pH increase and turbulence can be several orders of magnitude [93].

The majority of polymeric catalysts examined in Table 2 resulted in the pH of the product water being higher than the pH of the feed water. n-Fe@Ca@gallic acid polymers (e.g., Trial 6, Table 2; Figure 17f) operate by first reducing the pH (due to the presence of gallic acid and SO_4^{2-} ions). The pH then slowly rises as the CaO gradually forms Ca(OH)₂. The final pH of the product water can be the same as or similar to the pH of the feed water. An example analysis, processing 240 L of seawater, is shown in Figure 21. This analysis (Figure 21d), when compared with the 2.3 L kinetic data (Figure 17f), indicates that in the 240 L reactor, [*d*] >1.01.



Figure 21. Example batch flow analysis for a n-Fe@Ca@Zn@gallic acid polymer, polymer composition: Trial 6, Table 2. Feedwater = seawater (15.83 g Cl⁻ L⁻¹; 10.27 g Na⁺ L⁻¹). Reactor size = 240 L. (**a**), =pH versus Eh; (**b**) pH versus proportion of ions removed; (**c**) = Eh versus proportion of ion removed; (**d**) cumulative reaction time, hours, versus proportion of the ions removed; blue dot = feed water; In (**b**–**d**) the red dots are Cl⁻ ions; the green dots are Na⁺ ions.

An initial program of pre-commercial (commercial scale) desalination trials using these polymers, based on a multi-tubular, transport line reactor design, has been commenced. Preliminary results using n-Fe@Ca@Zn@gallic acid polymers at a continuous flow rate of 24 L h⁻¹, through a 3 m long, 0.042 m O.D. uni-tubular reactor (reaction time = 3.14 min) have achieved an average Cl⁻ removal of 63% and an average Na⁺ ion removal of 38%, from feed water with an average salinity of 11.68 g L⁻¹ (feed water pH = 9.1; product water pH = 10.3; polymer composition: Table 2: Trial 6; continuous run time = 10 h). These observations (when compared with Figure 21) confirm that an increase in the desalination rate constant can be achieved in a transport line reactor from a combination of a rapid pH increase and a turbulent reaction environment, and that the associated increase in the rate constant can be several orders of magnitude when compared with a batch flow example (Figures 17f and 21).

The formation of stationary hydrodynamic plumes and groundwater mounds has been demonstrated in both aquifers and soils (Appendix D). The future field groundwater tests, which adopt the process decision flow shown in Figures 2 and 20, are contingent on the results of both commercial-scale polymer trials and the identification of suitable application areas.

8. Conclusions

Five different groups of ZVI-based partial desalination routes have been compared (n- Fe^0 ; n- Fe_3O_4 ; Fe^0 :Fe(b)@C⁰; n-Fe:Fe(b); n-Fe(b)). These have been subdivided into two basic processing groups based on the mechanism for recovering the ZVI from the product water prior to recycling. These are:

- Magnetic separation route (n-Fe⁰; n-Fe₃O₄);
- Gravitational separation route (Fe⁰:Fe(b)@C⁰; n-Fe:Fe(b), n-Fe(b)).

The analysis concludes that the only potentially economically viable routes (to produce desalinated water for irrigation) involve gravity separation and recycling. The screening analysis indicated that a n-Fe(b) polymer constructed using FeSO₄ + CaO + urea may provide a processing route that could result in 80–90% ion removal in a static diffusion batch flow environment within a 1-h processing time. The examples demonstrate that this route may potentially allow both saline groundwater and flowback water to be desalinated to form partially desalinated irrigation water for a cost of less than USD 0.5 m⁻³.

Batch flow scaleup from a 2.3 L reactor to a 240 L reactor processing seawater using an n-Fe(b)@Ca@Zn@gallic acid polymers demonstrated that:

- The kinetic desalination results from a 2.3 L reactor operation are effectively replicated in a 240 L reactor, indicating that it may be reasonable to expect that the desalination results from a 240 L reactor will be replicated in a 24 m³ reactor;
- The site blocking constant [*d*] was increased to between 1.01 and 1.015, relative to the 2.3 L reactor;
- Desalination increases as pH increases and Eh decreases.

This information indicated that it may be possible to substantially increase the rate constant by switching to a transport line reactor, processing 24 L h^{-1} tube⁻¹ over 10 h. This reactor incorporated a rapid pH shift combined with a turbulent environment. This was demonstrated to reduce the time taken to achieve an average Cl⁻ removal of 63% and an average Na⁺ ion removal of 38% (average 50.5% desalination) from between 23 h (2.3 L reactor) and 120 h (240 L reactor) to 3.14 min. The operation in a transport line reactor reduced [*d*] to below the normalized value of [1] in the 2.3 L reactor.

These observations suggest that static diffusion reactor scale-up results in an increase in [d], while switching from a static diffusion reactor to a transport line reactor results in a substantial decrease in [d].

A combination of hydrodynamic and adsorption/catalytic modeling has established that a commercial-scale reactor scale-up could be used to desalinate part of a confined or unconfined aquifer containing saline groundwater (18.58 g L⁻¹), where the targeted desalination reduces the aquifer salinity to between 1 and 2.5 g L⁻¹. This analysis indicates that:

- It is technically feasible to use existing saline aquifers to store desalinated water in hydrodynamic stationary plumes, and it will be possible to abstract this water for irrigation use when required.
- This concept could be used to reverse or contain seawater incursion into an aquifer.
- It will be possible to create perched hydrodynamic stationary mounds in some soils, which could be used to desalinate the soil and/or store desalinated water within the mounds for future use as irrigation water.
- This study has highlighted five areas for future investigation:
- The formation of colloids and micron-sized hollow polymer agglomerates and their role in desalination;
- The ability of n-polymers to catalytically remove Na+ and Cl- ions, their selectivity, and associated kinetic controls;
- Scalability and statistical repeatability analysis of desalination observations;
- Influence of reactor type and reactor operating conditions on the desalination outcome;

• Field demonstration of the creation and stability of desalinated hydrodynamic stationary plumes in saline aquifers and desalinated perched hydrodynamic groundwater mounds in saline soil as potential reservoirs and sources of desalinated water.

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Appendix A. Magnetic Zero Valent Iron Desalination and Fe⁰:Fe(b)@C⁰ Polymers

Zero valent iron (n-Fe⁰) desalination has been operated using a number of different reactor types [4,39,59,94]. This section considers patented processes associated with using n-Fe⁰, n-Fe₃O₄ and Fe₀:Fe₆b)@C⁰ polymers (Figure 1) and their applicability to produce partially desalinated irrigation water from saline groundwater.

Appendix A.1. Magnetic n-Fe⁰ Desalination: Spanish Patent ES2598032

Spanish Patent ES2598032B1 (2015) was the first patent, which was solely designed to specifically desalinate water using magnetic n-Fe⁰ (Figure A1). It is assumed that the presence of n-Fe⁰ will increase the water's pH to between 8 and 10. In this pH range, the n-Fe⁰ surfaces will become charged (functionalized) due to the presence of OH⁻ ions and H⁺ ions, i.e.,

$$2Fe^{0} + H_{2}O = Fe^{0}@OH^{-} + Fe^{0}@H^{+},$$
(A1)

In saline water, this will result in:

$$2Fe^{0} + H_{2}O + Na^{+} + Cl^{-} = [Fe^{0}@OH^{-}]@Na^{+} + [Fe^{0}@H^{+}]@Cl^{-},$$
 (A2)

This state will only last for a short time (t_x) before the Fe⁰ physically reacts with the OH⁻ ions to form n-Fe(a,b,c) polymers [6,7,56]. t_x can be increased by using coatings on the surface of the Fe⁰ (e.g., PVP (Polyvinylpyrrolidone)). The patent specification recommends a contact time, t_x , of 10 min. The patent specifies that the Fe⁰:brine mixture is moved from a mixing vessel to a vessel containing a removable rotating magnet. The magnet will remove n-Fe⁰ + [Fe⁰@OH⁻]@Na⁺ + [Fe⁰@H⁺]@Cl⁻ to leave a desalinated or partially desalinated water product. The process flow diagram required to produce partially desalinated water from groundwater using this process is summarized in Figure A1.



Figure A1. Interpretation of the ZVI desalinator described in patent ES2598032B1, showing how it may be operated to allow for a continuous water feed (of seawater or saline groundwater) producing fresh water (potable) quality irrigation water with a batch removal of n-Fe⁰ + NaCl. This reactor requires a Desalination Pattern 1 (Appendix B) outcome to operate. A stirred reactor is used to maximize particle disaggregation.

Appendix A.1.1. Removal Potential of a Functionalized n-Fe⁰ Particle

Equations (A1) and (A2) indicate that the Na⁺ and Cl⁻ ion removal potential of spherical n-Fe⁰ is a function of its surface area. A spherical 50 nm-diameter (25 nm radius (r)) n-Fe⁰ particle will have a surface area, calculated as:

Surface Area =
$$4 \pi r^2$$
, (A3)

This equation implies that a 50 nm n-Fe⁰ particle has a surface area of 7854 nm² and weighs about 2.89×10^{-16} g. Each particle will contain about 5.19×10^{-18} moles of Fe⁰. The key ions associated with Equations (A1) and (A2) have ionic radii of OH⁻ = 0.137 nm; Cl⁻ = 0.181 nm; Na⁺ = 0.139 nm [42,57]. This indicates that each n-Fe⁰ particle has the potential to be functionalized with >7854 [OH⁻ + H⁺] sites. It follows that each particle, if fully functionalized, has the potential to remove 7854 Na⁺ + Cl⁻ ions. A fully functionalized collection of n-Fe⁰ particles will have the potential to remove 0.000044 moles of NaCl/n-Fe⁰ particle.

The instantaneous (Pattern 1 (Appendix B)) removal of NaCl is therefore a function of the degree of functionalization, f_u , (Equations (A1) and (A2)), associated with a batch of n-Fe⁰. Uncoated n-Fe⁰ is normally produced under reducing conditions (i.e., in the presence of one or more of H₂, CO, NH₃, CH₄, and C_xH_y). It is normally transported under a reducing gas blanket or an inert gas blanket. When the n-Fe⁰ is placed in alkali water (pH = 7 to 9), a portion of the potential sites will react to form Fe(OH)₂, Fe(OH)₃ and FeOOH. These sites are not available for functionalization (Equations (A1) and (A2)). Therefore, f_u will always be less than the maximum potential of 7854 sites. The average proportion of functionalized sites (per particle), which are not oxidized, can increase as the concentration of n-Fe⁰ in the water increases.

This analysis indicates that the effectiveness of n-Fe⁰ can be enhanced if the saline groundwater or flowback water is deoxygenized prior to entry into the n-Fe⁰ environment. There are a number of ways this can be achieved. The principal preparation approaches for the feed groundwater are:

- Approach 1: Saturation of the water in a bubble column reactor with a reducing gas [6] selected from H₂, CO, CH₄, and NH₃. This approach is not practical in most agricultural environments.
- Approach 2: Saturation of the water with hydrogen in a diffusion reactor containing one or more of Fe⁰ + Al⁰ + Cu⁰ [56];
- Approach 3: Saturation of water in a bubble column reactor using hydrogen generated from the reaction of ferrosilicon, or silicon, with NaOH [e.g., GB147519A; GB191111640A; GB191109623A]

$$2NaOH + Si^0 + H_2O = Na_2SiO_3 + 2H_2,$$
 (A4)

• Approach 4: Saturation of water in a bubble column reactor using hydrogen generated from the reaction of native iron, a perchlorate, and slaked (hydrated) lime, e.g., [GB191109623A]

$$5Fe + KClO_3 + 4Ca(OH)_2 = Fe_2O_3 + Fe_3O_4 + 4CaO + KCl + 4H_2,$$
(A5)

Approach 3 is probably the lowest-cost option available to produce hydrogen, to deoxygenate the feed groundwater. The benefit of saturating the feed groundwater with hydrogen is that it has the potential to reduce the amount of n-Fe⁰ required (g L⁻¹) to achieve a specific level of desalination by one or two orders of magnitude by maximizing the value of f_u .

The recovered $n-Fe^0 + Na^+$ ions $+ Cl^-$ ions will need to be separated prior to the residual $n-Fe^0$ being returned to the reactor. The separation and regeneration approach used in ES2598032B1 is not defined. The high reactivity of $n-Fe^0$ will require the Eh of the

water containing the recovered n-Fe⁰ to be processed in redox Hydrogen Stability Zone 2, as defined in reference [53].

$$[Fe^{0}@OH^{-}]@Na^{+} + [Fe^{0}@H^{+}]@Cl^{-} = 2Fe^{0} + NaOH + HCl,$$
(A6)

This purification/regeneration approach is costly. It may be more cost effective to discard the recovered n-Fe⁰ and use a processing strategy that only uses new n-Fe⁰ and no recycled, or regenerated, n-Fe⁰.

Appendix A.1.2. Economic Viability

The economic viability of this process is a function of the n-Fe⁰ replacement interval. If the n-Fe⁰ costs USD 10,000 t⁻¹, and if 25 g of magnetic n-Fe⁰ L⁻¹ are required, then the processing of a single volume of 1 m³ water will have a nominal cost of USD 250 m⁻³. If the n-Fe⁰ can be used 100 times without requiring makeup, then the nominal cost will reduce to USD 2.5 m⁻³. To be economically viable for the provision of partially desalinated irrigation water, a single n-Fe⁰ may have to be reusable over 1000 cycles.

Based on a cost of USD 10,000 t⁻¹, the relationship between n-Fe⁰ charge g L⁻¹ is

- $25 \text{ g n-Fe}^0 \text{ L}^{-1} = \text{USD } 250 \text{ m}^{-3}$
- $2.5 \text{ g n-Fe}^0 \text{ L}^{-1} = \text{USD } 25 \text{ m}^{-3}$
- $0.25 \text{ g n-Fe}^0 \text{ L}^{-1} = \text{USD } 2.5 \text{ m}^{-3}$
- $0.025 \text{ b n-Fe}^0 \text{ L}^{-1} = \text{USD } 0.25 \text{ m}^{-3}.$

The target desalination cost for partially desalinated water is $\langle USD 0.5 \text{ m}^{-3}$. Nanoiron cost varies with the supplier and quantity purchased. n-Fe⁰, 15–20 nm particle size, spherical, carbonyl-derived, sourced from China, has a price (FOB) of USD 50,000 to USD 250,000 t⁻¹ (www.alibaba.com, accessed on 16 October 2022).

The ion removal rate constant increases with decreasing particle size, increasing particle concentration, and increasing f_u . The economic viability of the process using n-Fe⁰ to produce partially desalinated irrigation water is a function of the ion removal rate constant, particle cost, and the economic feasibility of regenerating and reusing used n-Fe⁰.

Appendix A.1.3. Corrosion Analysis

The corrosion analysis in Figure 3a,b indicates that after 10 min, the $C_{t=n}/C_{t=0}$ ratio for uncoated Fe⁰ may fall within the range of 0.96 to 0.985 (1st to 3rd quartile range) from an initial value of 1.0. The weight of Fe polymer (rust) formed will be equivalent to between 2.8 and 7.5% of the Fe⁰ weight entered into the reactor (1st to 3rd quartile range). The reusability of the n-Fe⁰ is therefore also a function of its corrosion rate. An indication of the relationship between n-Fe⁰ corrosion and the proportion of a specific n-Fe⁰ charge remaining after y-reuse cycles is summarized in Figure A2.

This analysis indicates that desalination process routes based solely on magnetic n-Fe⁰ are unlikely to provide an economically viable route for producing partially desalinated irrigation water from saline groundwater or flowback water unless the costs associated with providing the n-Fe⁰ can be reduced by at least an order of magnitude.



Figure A2. Relationship between the proportion of an initial $n-Fe^0$ charge remaining and reuse cycle number. Blue line = 96% reusable in the next cycle; red line = 98.5% reusable in the next cycle; green line = 99% reusable in the next cycle; brown line = 99.5% reusable in the next cycle.

Appendix A.2. Magnetic n-Fe₃O₄ Desalination: US Patent US8636906B2

Patent US8636906B2 (2008) adds a ferrimagnetic or ferromagnetic nanoparticle (Figure 1) to the saline water. Magnetic nanoparticles include: n-Fe⁰, spinels, magnetite, ulvospinel, hematite, maghemite, trevorite, magnesioferrite, pyrrhotite, greigite, troilite, goethite, lepidocrocite, feroxyhyte, awaruite, and wairauite. The nanoparticle can be functionalized for chloride removal, sodium removal, or both Na⁺ and Cl⁻ ion removal.

Appendix A.2.1. Example Magnetic Nanoparticle Formation

An example is sol-gel particle precipitation, which is achieved by adding $1 \text{ M NH}_4\text{OH}$ to a mixture of ferric chloride and ferrous chloride, e.g., [26]:

$$FeCl_2 + 2FeCl_3 + 8 NH_4OH = Fe_3O_{4(solid)} + 4H_2O + 8NH_4^+ + 8Cl^-,$$
 (A7)

The magnetic nanoparticles form instantly, and the reaction reaches completion in 1 to 2 h at ambient temperatures. The settling nanoparticles can be concentrated and removed using magnetic separation. They are then washed prior to use. The bare nanoparticles can be functionalized by adding a coating prior to use. For example, they can be coated with a cation receptor, an anion receptor, or both, e.g., [27–31].

$$[Fe_{3}O_{4(solid)} @Function]^{+} + Cl^{-} = [Fe_{3}O_{4(solid)} @Function]^{+} @[Cl^{-}],$$
(A8)

$$[Fe_3O_{4(solid)} @Function]^+ Na^+ = [Fe_3O_{4(solid)} @Function]^- @[Na^+],$$
(A9)

Appendix A.2.2. Binding Capacity of a Nanoparticle

The binding capacity (BC) of the nanoparticle for a specific ion is determined as:

BC,
$$g g^{-1} L^{-1} = (C_{t=0} - C_{t=n})/P_w$$
, (A10)

 P_w = concentration of the nanoparticle in the water, g L⁻¹. Typical binding capacities are <0.1 g ion g⁻¹ nanoparticle.

Appendix A.2.3. Regeneration and Reuse of a Nanoparticle

The recovered magnetic nanoparticles are regenerated by first washing them in 0.2 M NaOH to remove Cl⁻ ions and 0.2 M HCl to remove Na⁺ ions. They are then washed

and returned to the reactor for reuse. The general recycle process flow is illustrated in Figure A3, where:

 $[Fe_{3}O_{4(solid)} @Function]^{+} @[Cl^{-}] + NaOH = [Fe_{3}O_{4(solid)} @Function]^{+} @[OH^{-}] + NaCl,$ (A11)

 $[Fe_{3}O_{4(solid)} @Function]^{-} @[Na^{+}] + HCl = [Fe_{3}O_{4(solid)} @Function]^{-} @[H^{+}] + NaCl, (A12)$

Regeneration in the next cycle takes the form:

 $[Fe_{3}O_{4(solid)} @Function]^{+} @[OH^{-}]@[Na^{+}] + HCl = [Fe_{3}O_{4(solid)} @Function]^{+} + H_{2}O + NaCl,$ (A13)

 $[Fe_{3}O_{4(solid)} @Function]^{-}@[H^{+}]@[Cl^{-}] + NaOH = [Fe_{3}O_{4(solid)} @Function]^{-} + H_{2}O + NaCl,$ (A14)



Figure A3. Process flow diagram for partial water desalination using an interpretation of the process described in patent US8636906B2, using seawater or saline groundwater feed to produce partially desalinated irrigation water.

Appendix A.2.4. Desalination Operation

The feed water and nanoparticles remain in the mixing chamber (Figure A3) for a period of time, e.g., 2 h. The particles and feed water are then separated (e.g., by one or more of magnetism, gravity separation, or another process), and the product water is then passed to a product water tank. Part of this water may be recycled and processed with a fresh charge of nanoparticles (Figure A3). The relative fluid volumes in each section of this reactor process are illustrated in Figure A4. No operating data for this desalination approach have been published to date, apart from a series of seven micro-reactor laboratory trials, which were used to validate the US8636906B2 process. Each validation trial used a micro-reactor containing 0.01 L and used an ISE to measure ion concentrations.



Figure A4. Fluid volumes associated with individual flow lines when the reactor incorporates a recycle loop. A = feed water (groundwater) flow rate, m³ d⁻¹; B = recycle water flow rate, m³ d⁻¹; C = water entering the reactor, m³ d⁻¹; D = water leaving the reactor, m³ d⁻¹; E = product water (partially desalinated irrigation water) flow rate, m³ d⁻¹.

Appendix A.2.5. Economic Viability

n-Fe₃O₄ can be obtained (FOB) from China for USD 15,000 to $60,000 \text{ t}^{-1}$ (www.alibaba. com, accessed on 16 October 2022). The particles, when coated, are not subject to corrosion losses to the same degree as n-Fe⁰ (Figure 3). Consequently, it is reasonable to expect that a single charge of n-Fe₃O₄ may have a life expectancy of >100 cycles, and possibly >1000 cycles, without requiring significant make-up, though periodic recoating may be required to retain functionality. This would potentially allow this approach to produce partially desalinated irrigation water for a cost of <USD 3 m⁻³.

This approach is considered in this study to be a potentially more viable route for the low-cost production of partially desalinated water for irrigation from saline groundwater, or flowback water, than the n-Fe⁰ route.

Appendix A.3. UK Patent GB2520775A

This 2013 patent (GB2520775A) describes a diffusion reactor that uses Fe^0 or $Fe_xH_yO_z$ polymers to treat water, including the desalination of water. It recorded a reduction in NaCl from 7.6 g L⁻¹ to 0.57 g L⁻¹ using n-Fe⁰ and a wider desalination outcome range when m-Fe⁰ was used (from 40 g L⁻¹ to <0.8 g L⁻¹).

It was the first patent to establish that m-Fe⁰ (costing USD 200 to 3000 t⁻¹ (www. alibaba.com, accessed on 16 October 2022) could potentially remove >98% of the salinity from saline water. This patent assumed that Fe⁰ corrodes to form a particle covered in a n-Fe polymer coating. The assumption made is that the Na⁺ and Cl⁻ ions are removed by this polymer. This patent formed the underlying basis for the four polymer-based desalination routes, which are described in references [4,6,7,20]. These analyses indicate that the ZVI must become functionalized (e.g., n-Fe⁰@OH⁻; n-Fe⁰@H⁺) or it must be covered in a functionalized polymer (e.g., n-Fe⁰:Fe(a,b,c)@OH⁻; n-Fe⁰:Fe(a,b,c)@H⁺) to be effective as a desalination agent. This patent also provides an apparatus for the construction of m-Fe⁰:n-Fe⁰(a,b,c)@C⁰ polymers.

Fe^0 :Fe(b)@C⁰ Polymers

m-Fe⁰:n-Fe(a,b,c)@ C^0 polymers [6] (Figure 1) when placed in saline water, increase the water's pH, and become functionalized, i.e.,:

$$2[m-Fe^{0}:Fe(a,b,c)@C^{0}] + H_{2}O = [m-Fe^{0}:Fe(a,b,c)@C^{0}@OH^{-}] + [m-Fe^{0}:Fe(a,b,c)@C^{0}@H^{+}],$$
(A15)

Removal of the Na⁺ and Cl⁻ ions [6] from the water follows the route:

$[m-Fe^{0}:Fe(a,b,c)@C^{0}@OH^{-}] + [m-Fe^{0}:Fe(a,b,c)@C^{0}@H^{+}] + Na^{+} + Cl^{-} = [m-Fe^{0}:Fe(a,b,c)@C^{0}@OH^{-}]@Na^{+} + [m-Fe^{0}:Fe(a,b,c)@C^{0}@H^{+}]@Cl^{-},$ (A16)

The polymers were constructed to contain dead-end porosity and open-pore porosity, which were in fluid communication with the saline water body [6]. The functionalized surfaces allow captured ion movement to occur through the polymer to transport the captured ion from the saline water body to an adjoining dead-end pore [6]. The adsorbed ions are removed from the polymer by the water contained within the dead-end pores as [6]:

$$[m-Fe^{0}:Fe(a,b,c)@C^{0}@OH^{-}]@Na^{+} + H_{2}O = [m-Fe^{0}:Fe(a,b,c)@C^{0}@OH^{-}]@H^{+} + NaOH,$$
(A17)

 $[m-Fe^{0}:Fe(a,b,c)@C^{0}@H^{+}]@Cl^{-} + H_{2}O = [m-Fe^{0}:Fe(a,b,c)@C^{0}@H^{+}]@OH^{-} + HCl, \quad (A18)$

This creates, within the dead-end pore, a generic reaction of the form:

$$NaOH + HCl = H_2O + NaCl,$$
(A19)

Once the concentration of NaCl in the dead-end pore fluids exceeds about 26.3% by weight [42], it will start to crystallize (Figure A5). The NaCl, which is removed from the water, is sequestered within the dead-end porosity (Figure A5) [6].





This observation has economic significance. For example, if a m-Fe⁰:Fe(a,b,c)@C⁰ pellet contains 5 cm³ of dead-end pores, then it will have the potential to sequester 10.8 g of NaCl within these pores. The process of removing NaCl from the water using the pellets is slow and can be described as a pseudo-zero-order reaction [6]. The required reaction time before the available pore capacity is filled may take between 1000 and 4000 h [6]. An individual m-Fe⁰:Fe(a,b,c)@C⁰ pellet may be constructed to have a porosity of 50 to 80% [6].

Desalination of water for irrigation, using this approach, requires the saline groundwater or flowback water to be placed in an impoundment for processing [6]. A 30 to 60% desalination is achievable over a 45-to-200-day time period [6]. This approach is not suitable for use in areas where insufficient storage in reservoirs or impoundments is available.

Appendix B. Classification of Common Desalination Patterns Associated with ZVI Desalination

The desalination patterns associated with more than 500 water batches, which have been desalinated using ZVI since 2010, have been examined. These water batches have allowed a number of ion removal patterns to be recognized and classified. The desalination pattern classification used in this study is:

- Pattern 1: Near-instantaneous ion decline followed by:
 - Pattern 1a: a stable ion concentration followed by:
 - Pattern 1aa: a rising ion concentration;
 - Pattern 1ab: an ion concentration decline followed by:
 - Pattern 1aba: a stable ion concentration;
 - Pattern 1abb: a rising ion concentration;
 - Pattern 1abc: a continued ion concentration decline, at a slower rate:
 - Pattern 1b: a rising ion concentration followed by:
 - Pattern 1ba: a stable ion concentration;
 - Pattern 1bb: an ion concentration decline followed by:
 - Pattern 1bba: a stable ion concentration;
 - Pattern 1bbb: a rising ion concentration;
 - Pattern 1bbc: a continued ion concentration decline, at a slower rate:
 - Pattern 1c: a declining ion concentration followed by:

- Pattern 1ca: a stable ion concentration;
 - Pattern 1cb: a rising ion concentration;
 - Pattern 1cc: a continued ion concentration decline, at a slower rate:
- Pattern 2: No initial ion decline followed by:
 - Pattern 2a: a declining ion concentration followed by:
 - Pattern 2aa: a stable ion concentration;
 - Pattern 2ab: a rising ion concentration;
 - Pattern 2ac: a continued ion concentration decline, at a slower rate:
 - Pattern 2b: an instantaneous decline followed by:
 - Pattern 2ba: a stable ion concentration;
 - Pattern 2bb: a rising ion concentration;
 - Pattern 2bc: a continued ion concentration decline
- Pattern 3: A slow initial ion decline followed by:
 - Pattern 3a: a stable ion concentration;
 - Pattern 3b: a rising ion concentration;
 - Pattern 3c: a continued ion concentration decline, at a slower rate:
 - Pattern 3d: a continued ion concentration decline, at a faster rate followed by:
 - Pattern 3da: a stable ion concentration;
 - Pattern 3db: a rising ion concentration;

Appendix C. Groundwater Chemical Indices

All groundwater comprises H_2O plus a mixture of cations and anions. The common cations are Na⁺, Ca²⁺, and Mg²⁺. The common anions are SO₄²⁻, HCO₃⁻, and CO₃²⁻. Most irrigation water quality assessment indicators use a variety of ratios that consider these ions. The early groundwater classifications were based on the presence of a dominant ion (e.g., the 1940s Piper classification [95]). More modern studies tend to use multi-variate statistics (e.g., principal components analysis) in order to classify and separate water compositional groups [96–98]. In this study, the focus is on changing Na⁺ and Cl⁻ concentrations. These changes decrease SAR, SI, PI, CAI-I, CAI-II, PS, KI, ESR, and SSP. The polymer analyses considered in this study add ions to the water, which will decrease SAR, SI, MAR, PI, CAI-II, RSCI, SSP, RSC, and RSBC. It is generally accepted that a decrease in these ratios will improve the suitability of groundwater for irrigation. These abbreviations are defined in Equations (A1) to (A14).

The 1940 Piper classification of ground water identified seven groups based on the dominant cation or anion: (A) Calcium type; (B) No dominant type; (C) Magnesium type; (D) Sodium type; (E) Bicarbonate type; (F) Sulphate type; (G) Chloride type. The relationship between the cations and anions creates a classification where the dominant species are: (1) CaHCO₃; (2) NaCl; (3) mixed CaNaHCO₃; (4) mixed CaMgCl; (5) CaCl; and (6) NaHCO₃.

Saline groundwater tends to be dominated by Na⁺ as the cation and Cl⁻ as the anion. The impact of desalination is to change the dominant cation to calcium or magnesium and the dominant anion to bicarbonate or sulphate. The common molar (moles L^{-1}) ratios used to assess the suitability of groundwater for irrigation are [41,94,98–102]:

Sodium Adsorption Ratio, SAR = $(Na^+/((Ca^{2+} + Mg^{2+})/2)^{0.5})$, (A20)

Sodium Percentage Index, $SI = (100(Na^+ + K^+))/(Ca^{2+} + Mg^{2+} + K^+ + Na^+)$, (A21)

Magnesium Adsorption Ratio, MAR = $((100 \text{ Mg}^{2+})/(\text{Ca}^{2+} + \text{Mg}^{2+})),$ (A22)

- Permeability Index, $PI = (100(Na^{+} + ((HCO_{3}^{-})^{0.5}))/(Ca^{2+} + Mg^{2+} + Na^{2+})),$ (A23)
 - Chloroalkaline Index-I, CAI-I = $(Cl^{-} (Na^{+} + K^{+}))/Cl^{-}$, (A24)

Chloroalkaline index-II, CAI-II =
$$(Cl^{-} - (Na^{+} + K^{+}))/(SO_{4}^{2-} + CO_{3}^{2-} + NO_{3}^{-}), (A25)$$

Potential Salinity,
$$PS = Cl^2 + 0.5SO_4^{2^2}/2$$
, (A26)

Residual Sodium Carbonate Index,
$$RSCI = ((CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})), (A27)$$

Total Hardness =
$$2.5 \text{ Ca}^{2+} + 4.1 \text{ Mg}^2$$
, (A28)

Kelly Index, KI, or Exchangeable Sodium Ratio,
$$ESR = Na^{+}/(Ca^{2+} + Mg^{2+})$$
, (A29)

Soluble Sodium Percentage, SSP =
$$Na^+/(Na^+ + Ca^{2+} + Mg^{2+})$$
, (A30)

Residual Sodium Carbonate, RSC =
$$(CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+})$$
, (A31)

Appendix D. Creating a Hydrodynamic Stationary Groundwater Plume or Mound

For the purposes of visualizing the groundwater fluid flow within the aquifer, the aquifer can be subdivided into a spatial grid of [n] cells of equal size. As an initial simplification, it can be assumed that within each cell, the porosity, permeability, and head (pressure applied) are constant (homogenous). A water balance is then created for each cell, which considers water flows in three directions, *x*, *y*, and *z*. The general flux equation defines water flow, J (m³ m⁻² s⁻¹) in a specific direction as:

J

$$= k P, \tag{A32}$$

k = permeability, m³ m⁻² s⁻¹ P⁻¹; P = head, pressure, or force applied, Pa, in the direction of flow relative to the adjacent grid cells. P can be negative or positive, and it controls the flow direction. The water balance for each grid cell, for each unit time, before factors such as differential factors such as porosity (storage) variation, saturation, etc., are considered is:

$$J_{cell} = J_x + J_y + J_z, \tag{A33}$$

There are a large number of different hydrological models that can complicate this simple flux equation, e.g., [103–105]. Fluid flows from cells containing a higher pressure to cells containing a lower pressure [106].

However, for the purposes of this study, it is clear from this simple equation that if a point with negative pressure is created and is surrounded by positive pressure points or natural barriers, such as faults, then it is possible to create a stationary fluid plume within the aquifer [106].

If the negative point(s) is an abstraction well and the positive points are infiltration or injection wells, then it is possible to change the composition of the stationary plume over time. This is achieved by processing the abstracted water to remove one or more components from the water or to add one or more components to the water prior to its infiltration or injection into the aquifer. This approach can be used to create a stationary, desalinated plume within the aquifer. This plume can be used to store desalinated irrigation water within the aquifer. This is a hydrodynamic plume [106], if the negative and positive point sources are removed, the plume will dissipate into the surrounding aquifer [106].

This concept, while not having previously been applied to the reconstruction of aquifer salinity, has been used to find hydrocarbons in the subsurface, e.g., [106–109]. These studies have defined the principal subsurface hydrodynamic processes as being either mainly gravity-driven (centripetal) or mainly compaction-driven (centrifugal) [109]. Antropogenic modification of the aquifer, by injection and infiltration/injection, creates an artificial centripetal modification of the poteniometric surface [109]. This concept is used in hydrocarbon production by: (i) providing enhanced oil recovery using water injection, gas injection, polymer floods, underground combustion, and CO_2 injection; (ii) fraced, acidized, and acid fracked wells to enhance hydrocarbon production. It is also being considered for use in some CO_2 sequestration projects [110].

The concept of forming stationary hydrodynamic plumes where the fluid is water, oil, hydrocarbon gas, other gases, or immiscible fluids is well established in the upstream

hydrocarbon industry but has not, to date, been applied to the active management of groundwater resources.

The hydrodynamics associated with non-stationary, dispersive contaminant plumes in an aquifer are well established [111]. The hydrodynamics of stationary plumes in shallow coastal outflow areas have also been defined [112].

Appendix D.1. Creating a Stationary Desalinated Plume

A simple conceptual model (Figure A6) for the formation of a desalinated is investigated, where a negative point source is used to abstract saline water from a stationary plume (an abstraction well). The abstracted water [C] is then partially desalinated. The product water [B] is then reinjected (by pumping or infiltration through infiltration wells, artificial recharge ponds, or another method) into the aquifer at a number of positive point source locations located around the periphery of the stationary plume.





The desalinated stationary plume could be constructed (Figure 2) using one of the following surface (reactor) based (Figure 1), ZVI desalination approaches: $n-Fe^{0}$; $n-Fe_{3}O_{4}$; Fe^{0} :Fe(b)@C⁰; Fe⁰:Fe(b)@urea; SiO₂@Fe(b)@urea; n-Fe(b).

Appendix D.1.1. Normalized Reactor Conditions

To allow for comparison of alternative reaction routes, the following standard reaction criteria are established:

- (i) The required product flow rate (D) is $4 \text{ m}^3 \text{ h}^{-1}$ or $40 \text{ m}^3 \text{ h}^{-1}$ (Figure A6). This equates to 96 m³ d⁻¹ or 960 m³ d⁻¹. The associated water abstraction rate (C) is $4 \text{ m}^3 \text{ h}^{-1}$ or $40 \text{ m}^3 \text{ h}^{-1}$ (Figure A6);
- (ii) The aquifer water (A) (Figure A6) is assumed to have the following composition $Ca^{2+} = 0.2669 \text{ g } L^{-1}$; $K^+ = 0.0302 \text{ g } L^{-1}$; $Mg^{2+} = 0.0381 \text{ g } L^{-1}$; $Na^+ = 6.9340 \text{ g } L^{-1}$; $Cl^- = 11.6500 \text{ g } L^{-1}$; $HCO_3^- = 0.5793 \text{ g } L^{-1}$; $SO_4^{2-} = 0.087 \text{ g } L^{-1}$; total salinity = 18.58 g L^{-1} ; total dissolved solids (TDS) = 19.58 g L^{-1} ; SAR = 148.35;
- (iii) The associated reaction temperature is 0 to 25 $^{\circ}$ C;
- (iv) The required product water (D) salinity is <2.5 g L⁻¹.

Appendix D.1.2. Modeling the Stationary Plume

For modeling purposes, the following assumptions are made:

- (i) Water abstraction is through a 150-mm-diameter well located in the center of the stationary plume;
- (ii) The regional potentiometric slope, within the aquifer, has a gradient across the plume area of <1 m per 1000 lateral meters;
- (iii) The surface ground area over the stationary plume is level;

- (iv) The top of the saline aquifer is located at 150 m depth;
- (v) The sandstone aquifer has a thickness of 5 m;
- (vi) The constructed stationary plume has a radius of 100 m and covers 31,415 m² (3.1 ha);
- (vii) The porosity of the aquifer is 30%. The effective storage volume of the stationary plume is 47,123 m³. As a simplification, for modeling purposes, it is assumed that [A] (Figure A6) = [E], and it is assumed that [A] is either positive or zero. Setting [A] as a negative value would result in the size of the stationary plume volume declining with time.

The energy potential of the hydrodynamic surface prior to creation of the stationary plume, Φ_r , is [106]:

$$\Phi_{\rm r} = gZ + P/D_r,\tag{A34}$$

Z = elevation of the aquifer relative to a datum; g = acceleration due to gravity; P = measured aquifer pressure; D_r = density of the formation water, e.g., 1.02 g cm⁻³. Within the stationary plume, two items change, D_r and P. The energy potential within the stationary plume, Φ_p , is [106]:

$$\Phi_{\rm p} = gZ + P/D_{pr},\tag{A35}$$

 D_p = water density within a stationary plume, e.g., between 1.0 and 1.02 g L⁻¹. The pressure gradient associated with *P* is a function of the water density. For example, for $D_p = 1.0$, the pressure gradient is 0.433 psi ft⁻¹ (9.79 kPa m⁻¹). The pressure gradient increases as *D* increases. The stationary plume potential surface, relative to saline water, V_{ps} , is [106]:

$$V_{vs} = (D_v / (D_r - D_v)) h_w,$$
 (A36)

 h_w = hydraulic head = Φ_p/g ; the expression $(D_p/(D_r - D_p))$ is a tilt amplification factor. These simple parameters can be used to define the boundaries of the stationary plume within an aquifer as a form of hydrodynamic trap [106].

A map of Φ_r relative to a static datum may take the form shown in Figure A7a. Following construction of the stationary mound Φ_p , the potential may take the form shown in Figure A7b. Water flows from a point of higher potential to a point of lower potential.



Figure A7. Reconstruction of the aquifer potentiometric surface. (a) Initial position; (b) Example potentiometric surface associated with a stationary plume. Green arrows = direction of water flow within the aquifer. The *x*-axis and *y*-axis scales are spatial coordinates. The *z*-axis (relative potential values) is represented by the color scheme in the legend.

Appendix D.1.3. Adsorption and Catalytic Reaction Modeling

The kinetic data sources can be used to model two scenarios for each ZVI desalination route. These scenarios are:

(i) Reactor with no recycle and a maximum residence time of the water in the reactor of 1 h;

A schematic process flow diagram that accommodates both scenarios is provided in Figure A8. The abstraction well is the central negative potential point in Figure A7b. The injection well schematically represents the ring of positive potential points surrounding the abstraction (negative potential) point (Figure A7b). The recycle water (Figure A8) will be directed to a series of injection wells or infiltration devices along this ring of positive potential points.



Figure A8. Process flow diagram used in the kinetic modeling. The section of aquifer shown is between the abstraction well (negative potential point) and the injection well (positive potential point) shown in Figure A7b. Fluid flow from the aquifer to the reactor via the abstraction well(s) = [C] (Figure A6); fluid flow from the reactor to the aquifer via the injection well(s) = [B] (Figure A6).

The hydrology of this process, while conceptually simple [106], is complex if the aquifer is not homogenous and isotropic and is not bounded by an upper and lower aquitard. For illustration purposes, in this study, the aquifer is assumed to be homogenous, isotropic, and bounded by an upper and lower aquitard.

The dominant fluid within a saline aquifer is water, though in some aquifers, one or more of natural gas, air, and immiscible hydrocarbon liquids may be present. Each fluid contained in the porosity will be subdivided into an irreducible saturation (e.g., for water, S_{wir}) and a moveable saturation (e.g., for water, S_w).

At the onset of the creation of the stationary plume, the salinity of $S_{wir} = S_1$ = the salinity of S_w , and the mass balance is $x \text{ m}^3$ porosity, which is filled by $y \text{ m}^3 S_{wir}$ and $z \text{ m}^3 S_w$.

Abstracting w m³ of S_w and desalinating the water before returning it to the aquifer (Figure A6) will result in a reduction in the salinity of S_w contained within the aquifer. The resultant difference in chemical potential between S_{wir} and S_w will result in a migration of Na⁺ and Cl⁻ ions from the S_{wir} to the S_w . Consequently, as an initial simplification, it can be assumed that $S_w = 100\%$ of the water within the porosity.

Adsorption Modeling: Constructing the Stationary Plume

Adsorption modeling requires an assessment to be made of the amount of Cl⁻ ions removed mg g⁻¹ Adsorbent, and Na⁺ ions removed mg g⁻¹ adsorbent during the reaction period within the reactor (Figure A8). This study considered both n-Fe⁰ and n-Fe₃O₄ as

adsorbents. Both are magnetic and require a magnetic separator for recovery from the product water (Figure A8).

There is insufficient data available for n-Fe⁰ (in the public domain) to judge its effectiveness for operation solely as an adsorbent/desorbent agent. The available data for n-Fe₃O₄ indicates that if the Fe₃O₄ was functionalized with amine cation receptors (for Na⁺ removal) and azide anion (for Cl⁻ removal) receptors to allow for the removal of both Na⁺ ions and Cl⁻ ions. The expected adsorption is 60 to 66 mg Cl⁻ g⁻¹ Fe₃O₄ or 37 to 41 mg Na⁺ g⁻¹ Fe₃O₄ for a residence time of 1 h in the reactor. Obviously, different functionalized loadings and receptors will give different results.

The Fe_3O_4 regeneration process (with NaCl recovery) is simpler if the water is first passed through a reactor where the n- Fe_3O_4 contains cation receptors and then a second reactor where the Fe_3O_4 contains anion receptors.

The example specifications indicate that the maximum acceptable NaCl concentration in the irrigation water is 2.5 g L⁻¹. The aquifer before the creation of the stationary plume has a salinity of 18.58 g L⁻¹. The plume has a design volume (V_d) of 47123.89 m³, and when its salinity (A_s) is 18.58 g L⁻¹ contains a salt content (S_c) of 875561872.6 g NaCl, where:

$$S_c = 1000(V_d \times A_s),\tag{A37}$$

For illustration purposes, the desalinated plume is created by the cyclic abstraction of 40 m³ h⁻¹ ([C] Figure A6), with a salt content (S_a) of:

$$Sa = 1000([C] \times A_s), \tag{A38}$$

The target salinity (S_t) is 2.5 g L⁻¹. Therefore, the amount of salt removed (S_r) within the reactor during a 1 h residence time is:

$$Sr = 1000([C] \times (A_s - S_t)),$$
 (A39)

If all the product water [D] (Figure A6) is injected into the aquifer ([B] (Figure A6)), the salinity of the stationary plume reduces to:

$$Sc_{(t=n)} = S_{c(t=0)} - S_r,$$
 (A40)

The new salinity of the stationary plume is:

$$A_{s(t=n)} = Sc_{(t=n)} / (1000V_d), \tag{A41}$$

This process is repeated progressively to desalinate the stationary plume. In this example, 100 mg NaCl are removed by 2 g Fe₃O₄ over an hour, and with $[C] = 40 \text{ m}^3 \text{ h}^{-1}$, the design removal of NaCl is 643.2 kg h⁻¹. The amount of n-Fe₃O₄ required within the reactors is 12.846 t. Once the amount of NaCl in the abstracted water [C] drops below 2.5 g L⁻¹, the reactor will continue to desalinate the water. In this example, the desalination is continued until the salinity of the stationary plume is reduced to 1 g L⁻¹. At this point, the stationary plume can be used to produce desalinated irrigation water.

The amount of water injection required to maintain the stationary plume will be site-specific and a function of aquifer properties, regional potentiometric surface, and the size of the stationary plume. It is obvious that the length of time taken to construct the stationary plume with a salinity of 1 g L⁻¹ will be a function of the properties of the adsorbent. For illustration purposes, an adsorbent efficiency of 50 mg g⁻¹ has been assumed. Increasing this efficiency to 500 mg g⁻¹, would substantially reduce the time required to achieve the target 1 g L⁻¹. Similarly, reducing the adsorbent efficiency to <50 mg g⁻¹, while maintaining a constant processing rate of 40 m³ h⁻¹ would

Adsorption Modeling: Operating the Stationary Plume

Once the stationary plume has been formed, there is a continual requirement for abstraction and injection to prevent the plume from dissipating or receiving fluids from the surrounding aquifer. These circulating fluids do not need to be passed through the Fe_3O_4 reactor. Once an irrigation requirement is identified, then the abstracted water [E] (Figure A6) will optionally be passed through the reactor prior to delivery for irrigation. It will be replaced in the stationary plume by an equal volume of water [A] (Figure A6).

This abstraction of [E] and replacement with [A] will result in a gradual rise in the salinity of the aquifer over time. If [E] is abstracted directly from the aquifer, then its salinity will be $A_{st} = n$. This aquifer volume will be replaced by [A] with a salinity A_s . The salinity of the aquifer following abstraction at time t = n + 1 becomes:

$$A_{st = n + 1} = (A_{st = n} \times V_d - [E]) + (A_s \times [A]),$$
(A42)

These equations allow both the stationary plume salinity and the irrigation water salinity to be modeled. An example modeling is summarized as follows:

- Stationary plume creation
 - Assumptions
 - $V_d = 47123.89 \text{ m}^3$,
 - $A_s = 18.58 \text{ g L}^{-1}$,
 - Target $A_s = 1.0 \text{ g L}^{-1}$,
 - Modeled plume salinity vs. time
 - Processing rate: $40 \text{ m}^3 \text{ h}^{-1}$,
 - Product salinity leaving the reactor: $<2.5 \text{ g L}^{-1}$,
 - n-Fe₃O₄ adsorbent used = 12.846 t.
 - Adsorption rate:
 - $25 \text{ mg g}^{-1} \text{ Fe}_3\text{O}_4$; Stabilization time = >500 days;
 - $50 \text{ mg g}^{-1} \text{ Fe}_3\text{O}_4$; Stabilization time = 346 days;
 - $100 \text{ mg g}^{-1} \text{ Fe}_3\text{O}_4$; Stabilization time = 173 days;
 - 500 mg g⁻¹ Fe₃O₄; Stabilization time = 36 days; The stabilization time required to achieve $A_s = 1$ g L⁻¹, decreases as the adsorbent quality increases (Figure A9a).
 - Modeled plume salinity vs. time during operation
 - Extracted Irrigation water [E]: $4 \text{ m}^3 \text{ h}^{-1}$,
 - Makeup water from aquifer [A]: $4 \text{ m}^3 \text{ h}^{-1}$,
 - Period of extraction of 96 m³ d⁻¹ = 42 days (4032 m³). Minimum salinity = 1 g L⁻¹; maximum salinity = 2.5 g L⁻¹,
 - Aquifer reconstruction period, to reduce salinity from 2.5 g L^{-1} to 1.0 g L^{-1} (Figure A9b–d)
 - $50 \text{ mg g}^{-1} \text{ Fe}_3 \text{O}_4$; Stabilization time = 30 days;
 - $100 \text{ mg g}^{-1} \text{ Fe}_3\text{O}_4$; Stabilization time = 16 days;
 - 500 mg g⁻¹ Fe₃O₄; Stabilization time = 5 days.



Figure A9. Modeled stationary plume. (a) Time required to reduce the plume salinity as a function of adsorbent quality; (b) relationship between periods of irrigation abstraction and periods of additional plume desalination and adsorbent quality = 50 mg g^{-1} ; (c) relationship between periods of irrigation abstraction and periods of additional plume desalination and adsorbent quality = 100 mg g^{-1} ; (d) relationship between periods of irrigation abstraction and periods of additional plume desalination and adsorbent quality = 100 mg g^{-1} ; (d) relationship between periods of irrigation abstraction and periods of additional plume desalination and adsorbent quality = 500 mg g^{-1} .

Catalytic Modeling

The principal difference between adsorbent modeling and catalytic modeling is that a catalyst reduces A_s by a fraction (F_c), while an adsorbent reduces A_s by a fixed amount (F_f). Catalysts tend to be more efficient than adsorbents, requiring a lower loading of catalyst to achieve a specific processing volume, though adsorbents may offer an outcome with a substantially lower outcome variability. Examples are provided as follows:

- Fe⁰:Fe(b)@Urea polymer: Further details in Reference [4];
 - Stationary plume creation
 - Assumptions
 - $V_d = 47123.89 \text{ m}^3$;
 - $A_s = 18.58 \text{ g L}^{-1};$
 - Target $A_s = 1.0 \text{ g L}^{-1}$.
 - Modeled plume salinity vs. time
 - Processing rate: $40 \text{ m}^3 \text{ h}^{-1}$,
 - Processing time: 3 h;
 - Product desalination leaving the reactor = 19%,
 - Fe⁰:Fe(b)@Urea catalyst used = 8.33 kg;
 - Stabilization time = >500 days (Figure A10).



Figure A10. Modeled stationary plume. Fe⁰:Fe(b)@Urea polymer catalyst: time required to reduce the plume salinity.

- SiO₂@Fe(b)@Urea polymer: Further details in Reference [7];
 - Stationary plume creation
 - Assumptions
 - $V_d = 47123.89 \text{ m}^3$,
 - $A_s = 18.58 \text{ g L}^{-1}$,
 - Target $A_s = 1.0 \text{ g L}^{-1}$,
 - Modeled plume salinity vs. time
 - Processing rate: $40 \text{ m}^3 \text{ h}^{-1}$,
 - Processing time: 24 h;
 - Product desalination leaving the reactor = 40%,
 - Fe⁰:Fe(b)@Urea catalyst used = 1.11 kg Fe (78 L catalyst);
 - Stabilization time = 365 days (Figure A11a); The stabilization time = time required to achieve $A_s = 1 \text{ g L}^{-1}$.
 - Modeled plume salinity vs. time during operation
 - Extracted Irrigation water [E]: $4 \text{ m}^3 \text{ h}^{-1}$,
 - Makeup water from aquifer [A]: $4 \text{ m}^3 \text{ h}^{-1}$,
 - Period of extraction of 96 m³ d⁻¹ = 42 days (4032 m³). Minimum salinity = 1 g L⁻¹; maximum salinity = 2.5 g L⁻¹,
 - Aquifer reconstruction period to reduce salinity from 2.5 g L^{-1} to 1.0 g L^{-1} is 113 days (Figure A11b)



Figure A11. Modeled stationary plume. SiO₂@Fe(b)@Urea polymer catalyst: (**a**) time required to reduce the plume salinity. (**b**) Salinity of irrigation water versus time, and aquifer recharge time.

• n-Fe(b)@Ca@Urea polymer: Further details Figure 18d; Table 2;

- Stationary plume creation
 - Assumptions
 - $V_d = 47123.89 \text{ m}^3$,
 - $A_s = 18.58 \text{ g L}^{-1}$,
 - Target $A_s = 1.0 \text{ g L}^{-1}$,
- Modeled plume salinity vs. time
 - Processing rate: $40 \text{ m}^3 \text{ h}^{-1}$,
 - Processing time: 24 h;
 - Product desalination leaving the reactor = 90%;
 - Fe⁰:Fe(b)@Urea catalyst used = 229.6 kg FeSO₄ + 547.8 kg CaO + 216.5 kg Urea;
 - Stabilization time = 160 days (Figure A12a); The stabilization time = time required to achieve $A_s = 1$ g L⁻¹.
- Modeled plume salinity vs. time during operation
 - Extracted Irrigation water [E]: $4 \text{ m}^3 \text{ h}^{-1}$;
 - Makeup water from aquifer [A]: $4 \text{ m}^3 \text{ h}^{-1}$;
 - Period of extraction of 96 m³ d⁻¹ = 42 days (4032 m³). Minimum salinity = 1 g L⁻¹; maximum salinity = 2.5 g L⁻¹;
 - Aquifer reconstruction period to reduce salinity from 2.5 g L^{-1} to 1.0 g L^{-1} is 50 days (Figure A12b).

This preliminary modeling indicates that, based on the earlier suggestions [4,7,113,114], it may be possible to partially desalinate a saline aquifer, either to combat seawater incursion or to provide subsurface storage of desalinated water, which both are technically viable.



Figure A12. Modeled stationary plume. n-Fe(b)@Ca@Urea polymer catalyst: (**a**) time required to reduce the plume salinity. (**b**) Salinity of irrigation water versus time and aquifer recharge time.

Appendix D.2. Modeling a Perched Pressure Mound

Salinized soil is a major problem in many areas affected by either freshwater aquifer depletion, or salinized irrigation [115–117]. Not all low-permeability soils are suitable for the creation of a perched groundwater mound within the soil. Conventional infiltration device design assumes that the permeability of soils is isotropic, where the soil permeability, k, in each of the x, y, and z directions is equal, i.e., $k_x = k_y = k_z$. It automatically follows that the water body placed in the infiltration device will flow both vertically and laterally with time until it reaches the underlying water table (potentiometric surface, phreatic surface), and the descending water body is adsorbed in the underlying groundwater body.

Perched groundwater mound design [118–124] creates a perched groundwater body, or mound, located with the soil or located on the surface of an aquitard. It requires the soil to have a number of characteristics. These are:

• The soil body is located above a regional or perched water table;

- The soil porosity contains an irreducible water saturation, an irreducible air saturation, a mobile air saturation, and when saturated contains a mobile water saturation. Additionally, salinized soil may contain dissolvable, crystallized ions and salts within their porosity.
- The soil contains a very low permeability, e.g., $<10^{-14}$ m³ m⁻² s⁻¹ Pa⁻¹.
- The soil contains a network of sealed nano-, micro-, and macro-fractures.
- Increasing the hydraulic pressure, *P*, applied will progressively and abruptly unseal the sealed nano-, micro-, and macro-fractures, and result in water flow into and water storage within the fractures. Reducing the hydraulic pressure applied will result in the progressive and abrupt resealing of the nano-, micro-, and macro-fractures.
- The fractures create an anisotropic permeability distribution where $k_x \gg k_z$ and $k_y \gg k_z$. The dominant fracture propagation direction is in the x and y directions.

The charge volume (V_{ch}) to the infiltration device can be expressed as a pressure load, ΔP_L , (potential energy), which is defined as [106]:

$$\Delta P_L = V_{ch} \, d_w \, g, \tag{A43}$$

 d_w = density of the water, g = gravitational constant. The charge volume will fill the infiltration device to a height, D_h , m. The actual pressure, $\Delta P_{x,y,z}$, applied to any point $D_{x,y,z}$ in the infiltration device or associated groundwater mound will be [106,118]:

$$\Delta P_{x,y,z}, \, \text{Pa} = 101325 \times (D_h - D_{x,y,z}) \, d_w, \tag{A44}$$

The infiltration rate, Q_t , m³ s⁻¹, between any two time points is calculated as [118]:

$$Q_t = (k_{x,y} A_{x,y} P_{x,y}) + (k_z A_z P_z),$$
(A45)

 $A = \text{area}, \text{ m}^2$, where $A_z = \text{area}$ of the device base; $A_{x,y} = \text{area}$ of the device sides. $k_z = \text{permeability}$ of the device base; $k_{x,y} = \text{permeability}$ of the device sides; $P_z = \text{pressure}$ applied to the device base = 101325 × D_h × d_w ; $P_{x,y} = \text{pressure}$ applied to the device side, which for any specific point is $\Delta P_{x,y,z}$. It is normally assessed for simple analyses as $(P_z + P_t)/2$, where $P_t = 101325 \times D_t \times d_w$; $D_t = \text{depth}$ to the top of the infiltration zone.

The stored water volume within the infiltration device at t = 0 is $V_{st(t = 0)}$. The stored water volume within the infiltration device at time t = n is $V_{st(t = n)}$. This volume is a result of [118]:

$$V_{st(t=n)} = V_{st(t=0)} + R_{t=n} - Q_{it=n}$$
(A46)

where $R_{t=n}$ = water placed in the infiltration device between time t = 0 and t = n, m³; $Q_{it=n}$ = water placed in the pressure mound between time t = 0 and t = n, m³. A typical clay example contains a matrix permeability, k_m , of 6.12×10^{-14} m³ m² s⁻¹ Pa⁻¹; The water entry rate into the porosity is dependent on the Knudsen diffusion rate of the displaced air. A permeability associated with the opening of the nano-fractures, k_n , e.g., 3.28×10^{-9} m³ m² s⁻¹ Pa⁻¹. A permeability associated with the opening and extension/propagation of the macropore-fractures, k_{mp} , e.g., 5.1×10^{-5} m³ m² s⁻¹ Pa⁻¹. A typical clay with these parameters may result in: (i) nano-fracture permeability becoming operative when $\Delta P_{x,y,z}$ exceeds 10,000 Pa; (ii) macropore-fracture permeability becoming operative when $\Delta P_{x,y,z}$ exceeds 25,000 Pa. These parameters were measured for Scottish Boulder Clay.

An example mound formulation is as follows:

- A 2 m × 2 m × 4 m pit is dug in the clay;
- A 1 m-deep, 1.2 m-wide perforated preformed concrete ring segment is placed in the pit. It is overlain by three 1 m-deep, 1.2 m-wide non-perforated pre-formed concrete segments;
- The perforated zone is surrounded by coarse gravel (5–15 cm particle size), estimated porosity = 30%. Estimated storage volume, net of the storage chamber = 0.86 m³. The

surrounding clay permeability is anisotropic, with a ratio of horizontal permeability to vertical permeability of 30. The remaining 3 m of the pit are infilled with clay.

The mound then receives 208 m³ over a 24 h period at a constant rate of 0.144 m³ min⁻¹ (8.67 m³ h⁻¹). The initial water charge results in a gradual increase in water depth within the infiltration device with time (Figure A13a). After about 15 min, the water depth reaches 1 m, the infiltration device holds about 2.17 m³. 2.17 m³ have been delivered to the device, and no water has infiltrated into the surrounding clay. After an additional 10 min the water depth reaches 2 m. This increases the amount of water stored in the device to 3.12 m³. 3.61 m³ have been delivered to the device, and a total of 0.49 m³ have infiltrated into the surrounding clay. Once the water depth reaches about 2.6 m³, (after an additional 7 min, with a total of 3.69 m³ stored in the device), the water level in the device remains constant, as all additional water received is discharged laterally into the groundwater mound. The average lateral discharge rate is 8.67 m³ h⁻¹. The observed infiltration rate is summarized in Figure A13b. Over a 24-h period, this approach created a perched groundwater mound containing 204.31 m³.





The upper surface of the perched groundwater mound is defined by its Dupuit envelope [118]:

$$z_x = (z_i^2 - [z_i^2 - z_D^2](x/D))^{0.5},$$
(A47)

where z_D = the elevation (m) of the groundwater mound at a distance *D* from the infiltration device where x < D; z_j = the elevation (m) of the groundwater mound in the infiltration device. The maximum width (m) of the groundwater mound during recharge (*D*) will approximate the base of the device [2], i.e., z_D = the elevation of the base of the infiltration device. *D* is not observed. The upper surface shape and lateral extension are modified by the pressure losses as *x* increases [118]. The methodology required to define both the lateral extent of the groundwater mound and its basal shape is defined in reference [118].

The perched groundwater mound, when the feed water is partially desalinated water, can be used to both desalinate the soil (by the dissolution of precipitated salts and the dilution of saline pore water). The stored water within the groundwater mound can be abstracted for irrigation or for reprocessing using the approaches summarized in reference [118].

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