ZVI (Fe^0) desalination: catalytic partial desalination of saline aquifers

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Abstract

Globally, salinization affects between 100 and 1000 billion $\text{m}^3 \text{a}^{-1}$ of irrigation water. The discovery that zero valent iron (ZVI, Fe^0) could be used to desalinate water (using intra-particle catalysis in a diffusion environment) raises the possibility that large-scale in situ desalination of aquifers could be undertaken to support agriculture. ZVI desalination removes NaCl by an adsorption–desorption process in a multi-stage cross-coupled catalytic process. This study considers the potential application of two ZVI desalination catalyst types for in situ aquifer desalination. The feasibility of using ZVI catalysts when placed in situ within an aquifer to produce $100 \text{ m}^3 \text{d}^{-1}$ of partially desalinated water from a saline aquifer is considered.

Keywords Zero valent iron (ZVI) · Irrigation · Aquifer · Catalyst · Desalination

List of symbols and abbreviations

A_r	Required aquifer abstraction rate ($\text{m}^3 \text{d}^{-1}$)	E_a	Measured apparent activation energy (kJ mol^{-1})
A_v	The gross rock aquifer volume (m^3), required to produce A_r	EC	Electrical conductivity (mS cm^{-1})
a	Year	ΔE°	Standard potential (V)
a_i	ZVI particle size (nm)	F	Farad
a_s	ZVI surface area ($\text{m}^2 \text{g}^{-1}$ or $\text{cm}^2 \text{g}^{-1}$)	F	Faraday constant ($96,485.33289 \text{ C mol}^{-1}$)
c	Concentration of Na^+ (mol cm^{-3})	g	Grams
C	Charge associated with Cl^- removal (Coulombs)	G_a	The gross area (m^2), encompassed by the aquifer treatment zone
C_a	Capacitance (F g^{-1})	G	Gibbs free energy (kJ mol^{-1})
$C(\text{NaCl})$	Desorbed removed NaCl product	ΔG°	Standard Gibbs free energy (kJ mol^{-1}) = $-RT \ln(K)$. $\Delta G^\circ = \Delta H - T\Delta S$ (Ebbing and Gammon 2005)
C_e	Concentration of NaCl at equilibrium (g L^{-1})	ha	Hectare
$C_{t=0}$	Feed water salinity (mol L^{-1})	ΔH	Enthalpy (kJ mol^{-1})
$C_0 = \text{NaCl}_{t=0}$	Concentration of NaCl in the feed water (g L^{-1})	ΔH_1	Enthalpy associated with Stage 1 (kJ mol^{-1})
$C_t = \text{NaCl}_{t=n}$	Concentration of NaCl in the product water (g L^{-1})	ΔH_2	Enthalpy associated with Stage 2 (kJ mol^{-1})
d	Day	I	Current associated with desalination (A)
D_r	Required level of desalination ($1 - C_t/C_0$)	k	Rate constant = $\text{Ln}[C_0/C_t]/t$ and is the dimensionless logarithmic change in the ratio $\text{Ln}[C_0/C_t]$ per unit time
E_1	Activation energy for Stage 1 (kJ mol^{-1})	k_a	The observed rate constant associated with a water flow rate of 0.37 L m^{-1} and a single Type B catalyst charge containing 57.6 g Fe
E_2	Activation energy for Stage 2 (kJ mol^{-1})	k_c	Pseudo-first-order cathodic rate constant

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k_n	Normalized rate constant. It is calculated as either $k_n = k/(P_w a_s)$ or $k_n = k/(P_w)$ (Wilkin and McNeil 2003; Antia 2015b); k_n is the rate constant following normalization for the amount of catalyst placed in the reaction environment (P_w), i.e., rate constant per unit volume of water processed (L) per unit weight of ZVI catalyst (g L^{-1}), $k_n = k/P_w$; since catalytic reaction rates can be expressed as a function of the surface area of the catalyst, k_n can be expressed (Antia 2015b) in terms of the catalyst surface area (m^2) per unit volume of water (L), i.e., $k_n = k/(P_w a_s)$; the actual surface area (a_s) is not known in most ZVI studies and changes during catalysis (Antia 2015b). P_w is always known and is simple to measure and define (Antia 2015a, b)	ORP	Oxidation–reduction potential [Volts (mV)]. ORP is translated to Eh, V, using the quinhydrone method documented in Antia (2016a, 2017), i.e., Eh, $\text{mV} = -65.667 \text{ pH} + 744.67 + \text{ORP}$
k_1	Rate constant at temperature T_1	P_{sc}	The effective pseudo-specific capacitance (normalized charge) associated with desalination (F g^{-1})
k_2	Rate constant at temperature T_2	P_w	ZVI concentration (g L^{-1})
K	Dimensionless equilibrium constant (Ebbing and Gammon 2005) = rate constant forward reactions/rate constant reverse reactions = $1/(\text{NaCl}_{\text{equilibrium}}/\text{NaCl}_{t=0}) = 1/(C_e/C_0)$	PES	Polyether sulphone
kW	Kilowatt	Q	Reaction quotient, e.g., $1/(\text{NaCl}_{t=n}/\text{NaCl}_{t=0})$ (Pourbaix 1974; Ebbing and Gammon 2005)
kWh	Kilowatt hour	q_e	Equilibrium absorbance of NaCl by ZVI (catalyst), $\text{g NaCl g}^{-1} \text{ Fe}$, q_e for a Type A catalyst is typically in the range $0 < q_e < 0.3$ (Antia 2015b), q_e for a Type B catalyst is typically in the range $0 < q_e < 1000$ (Antia 2015b, 2016a, 2017, 2018a, b, c)
L	Litres	r	The radius (m) of the treatment zone around the abstraction well
LDH	Layered double hydroxide	R_{ext}	External cell resistance
m	Minutes	R^2	Coefficient of determination
m	Number of protons transferred	R	Gas constant ($8.3144598 \text{ J mol}^{-1} \text{ K}^{-1}$)
m^3	Cubic metre	ΔS	Entropy (J K^{-1})
M_w	Molecular weight of $[\text{Cl}^-]$, $35.453 \text{ g mol}^{-1}$	S_1	Catalytic site
n	Number of 0.8 m^3 batches of saline water processed by a single Type B catalyst charge	S_w	Aquifer mobile water saturation
n_e	Number of electrons transferred	T, T_1, T_2	Temperature (K)
n	Number of samples or trials considered	T_h	Aquifer thickness (m)
NaClS_1	Catalytic site with adsorbed NaCl	t	Time spent in the reaction environment (s)
$\text{NaCl}_{t=0}$	C_0	t_r	Time spent in the reaction environment within the aquifer (s)
$\text{NaCl}_{t=n}$	C_t	t	Tonnes
$\text{NaCl}_{\text{aquifer}}$	NaCl concentration in the saline aquifer (g L^{-1})	V_w	The volume of water required within the aquifer in the ZVI-influenced desalination zone (m^3)
$\text{NaCl}_{\text{product water}}$	Required NaCl concentration in the product water (g L^{-1})	W_r	Weight of Cl^- removed (g L^{-1} , i.e., concentration reduction, g L^{-1})
N_G	Net to gross ratio within the aquifer [i.e., aquifer/(aquifer + aquitard ratio) within the gross aquifer unit]	Z_1	The amount of ZVI catalyst required (t) to desalinate the aquifer
		ZVI	Zero valent iron, Fe^0
		\$	US dollar
		ϕ	Aquifer porosity

Introduction

About 17% of global arable cropland is irrigated, of which at least 20% is adversely affected by salinization (Lekakis and Antonopoulis 2015). Irrigated crop land accounts for more than 30% of global agricultural production (Lekakis

and Antonopoulos 2015) and more than 65% of global anthropogenic water usage (e.g., Knapp and Baerenklau 2006; FAO 2011; Amarasinghe and Smakhtin 2014; Wada and Bierkens 2014; Panta et al. 2014; Lekakis and Antonopoulos 2015).

Globally salinization affects between 100 and 1000 billion $\text{m}^3 \text{a}^{-1}$ of irrigation water (e.g., Knapp and Baerenklau 2006; FAO 2011; Amarasinghe and Smakhtin 2014; Wada and Bierkens 2014; Panta et al. 2014). Salinized irrigation water adversely affects crop yields and the long-term viability of agricultural land, and the underlying aquifers receiving salinized infiltration water (e.g., Ayers and Westcot 1994). A small decrease in salinity (e.g., 25–50% reduction) can have the potential to increase crop yields (depending on the crop, and initial water salinity) by between 25 and 10,000% (e.g., Ayers and Westcot 1994; Antia 2015b, 2017, 2018a, b, c).

Agricultural crops have a low value ($\text{\$ ha}^{-1}$) and can have a high irrigation requirement ($\text{m}^3 \text{ha}^{-1}$). This irrigation requirement may (depending on crop type and location) fall within the range 100–10,000 $\text{m}^3 \text{ha}^{-1}$ (e.g., Tabieh et al. 2015; Antia 2015b). It is unlikely that widespread usage, for irrigation, of partially desalinated water, will occur if the delivery cost of the irrigation water is $> \$0.2 \text{ m}^{-3}$ (e.g., Tabieh et al. 2015; Antia 2015b, 2016a, b, 2017, 2018a, b, c). The economics of irrigation (and increased agricultural crop yields) using partially desalinated water is addressed elsewhere (Antia 2017, 2018a, b, c).

Conventional desalination plants use a physical process (e.g., membrane separation (reverse osmosis), or thermal distillation (e.g., multi-stage flash distillation) to produce desalinated (or partially desalinated) water containing a 50–99% reduction in water salinity. The full cycle cost

of producing this desalinated water falls within the range $\text{\$}3 \text{ m}^{-3}$ – $\text{\$}5 \text{ m}^{-3}$ for a plant producing about $100,000 \text{ m}^3 \text{d}^{-1}$ (Antia 2017), but may, in the future, reduce to the range $\text{\$}0.7 \text{ m}^{-3}$ – $\text{\$}4 \text{ m}^{-3}$ (Bitar and Ahmad 2017).

In 2010, it was discovered that zero valent iron (Fe^0 , ZVI) can be used to partially desalinate water (Fronczyk et al. 2010, 2012; Antia 2010, 2015a, b, 2016a, b, 2017, 2018a, b, c; Hwang et al. 2015; Noubactep, 2018). The desalination process is a complex, multi-stage, cross-coupled, catalytic, adsorption and desorption series of reactions which concentrate Na^+ and Cl^- ions in the vicinity of the ZVI and in related products (Fronczyk et al. 2010, 2012; Antia 2010, 2015a, b, 2016a, b, c, 2017, 2018a, b, c; Hwang et al. 2015). The simplified, desalination, cross-coupled, catalytic process (Antia 2016c) is summarized in Fig. 1. The catalytic process cycles (Fig. 1) between oxidative addition of Fe (i.e., an increase in oxidation number) and reductive elimination (i.e., a decrease in oxidation number). The oxidation number for Fe oscillates within the range -2 to $+8$ during catalysis (Antia 2015a, b, 2016a, 2017, 2018a, b). This cross-coupled catalytic process has been demonstrated to also remove (during desalination) nitrates, nitrites, fluorides, phosphates, sulphates, Fe, Al, Cu, Mg, Mn, As, K, Ca, B, Ba, Sr from water (Antia 2010, 2014, 2015a, b, 2016c). The desalination process has been demonstrated to operate over the temperature range -10 to 90°C (Fronczyk et al. 2010, 2012; Antia 2010, 2015a, b, 2016a, b, 2017, 2018a, b, c; Hwang et al. 2015).

In 2013, small-scale trials using a 300 cm^2 pressured dead-end filtration cell established that polyether sulphone (PES) membranes impregnated with 5–10% Fe_3O_4 nanoparticles could achieve NaCl rejection rates of 62–82% from nitrogen-saturated pressured water containing $< 2 \text{ g NaCl L}^{-1}$ (Abuhabid et al. 2013; Alam et al. 2013). A control PES membrane with no Fe_3O_4 nanoparticles

Fig. 1 Schematic flowsheet for each desalination catalytic cycle. The cations M and N can vary on each cycle. The anions R and X can vary on each cycle. A similar cross-coupled catalytic cycle has been proposed for water treatment using ZVI (Antia 2016c)

showed no NaCl rejection. These trials established that (i) Fe_xO_y selectively removes NaCl from a flowing body of water, and (ii) NaCl removal is a function of particle size, pore size, particle surface area, porosity, particle concentration, fluid pressure, and gas partial pressure. Similar observations have been made in the ZVI desalination studies (Fronczyk et al. 2010, 2012; Antia 2010, 2015a, b, 2016a, b, 2017, 2018a, b, c; Hwang et al. 2015).

The desalination catalysts are $[\text{Fe}_x\text{O}_y(\text{OH})_z(\text{H}_2\text{O})_r]_n$ polymers (Antia 2015b, 2018a, b, c). These particles can be charged, $[\text{Fe}_x\text{O}_y(\text{OH})_z(\text{H}_2\text{O})_r]_n^{m+/-}$ and can incorporate one or more anions (A_n^-), or cations (C_a^+) (Antia 2015b, 2018a). They exhibit capacitance, and are conductive (Antia 2015b, 2018a). This capacitance can exceed 300 F g^{-1} (Antia 2015b) and the associated pseudo-capacitance increases as the nano-porosity and surface area increases (Antia 2015b, 2018a). The capacitance increases as the Debye length decreases, the surface area of the reactive surfaces increases (Antia 2018a). The desalination rate constant is a function of the capacitance (Antia 2015b, 2018a). Capacitance increases as the dead-end porosity of the catalyst increases (Antia 2015b, 2018a).

Desalination is associated with capacitor discharge (Antia 2015b, 2018b). The catalyst complex (capacitor) comprises a central metal atom (e.g., Fe^{n+}) and neutral molecules or ions attached to it (Antia 2018b, 2018c). In saline water containing Fe, the dominant acids (within the catalyst) include one or more of H^+ , Na^+ , K^+ , Fe^{n+} , Ca^{n+} , Al^{n+} , Mg^{n+} , Cu^{n+} , and CO_2 (Antia 2015b, 2016a, 2017, 2018b). The dominant bases (within the catalyst) include one or more of H_2O , Cl^- , HCO_3^- , O_2^- , O^{n-} , $\text{C}_x\text{H}_y\text{O}_z^-$, $\text{C}_x\text{H}_y\text{O}_z^{n-}$, CO_3^{2-} , NO_3^- , HS^- , H^- (e^-), OH^- , HO_2^- , ClO^- , ClO^{n-} , SO_4^{2-} , Fe^{n-} , N_3^- , NO_2^- , SO_3^{2-} , and CO .

The oscillation between capacitor discharge and recharge drives the catalytic desalination reaction (Antia 2010, 2015b, 2018b). In acidic water, the basic capacitor discharge reaction is: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$. The associated capacitor recharge reaction is $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$. In alkali water, the basic capacitor discharge reaction

is: $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$. The associated capacitor recharge reaction is $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$. Within the recharge–discharge reaction, O_2 can be replaced by one or more of CO , CO_2 , CH_4 , C_xH_y , $\text{C}_x\text{H}_y\text{O}_z$, $\text{C}_x\text{H}_y\text{O}_z\text{N}_a$, or $\text{C}_x\text{H}_y\text{O}_z\text{N}_a\text{Cl}_b$, e.g., $2\text{H}_2\text{O} + \text{C} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$, $\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{C}$ (Antia 2015b, 2018b); $2\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2\text{CO}_3 + 2\text{H}^+ + 2\text{e}^-$, $\text{H}_2\text{CO}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{CO}$ (Antia 2015b). $\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$, $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 8\text{H}^+ + 8\text{e}^-$ (Antia 2015b); $2\text{CO} + 12\text{H}^+ + 12\text{e}^- \rightarrow 2\text{CH}_4 + 2\text{H}_2\text{O}$ (Antia 2011a, 2015b, 2018b).

This oscillating process (Antia 2010, 2014) allows the ZVI catalyst to remove, or transform, a variety of other pollutants within the water (e.g., pesticides, herbicides, fungicides, nitrates, hormonal pollutants, chlorates, phosphates, nitrogenous pollutants, As, B, Ba, Ca, Cu, Cd, Fe, Mg, Mn, Pb, Sr, Se, etc.). A more detailed list of the pollutants that can be removed, or transformed, is provided elsewhere (Antia 2010, 2011a, 2014, 2016c). The removal process includes one or more of direct reaction to an alternative product, precipitation, reduction, oxidation, adsorption, or adsorption/desorption. The removal of pollutants increases with increased contact time in the reaction environment to a new equilibrium level (Pourbaix 1974; Antia 2010). The equilibrium level is a function of the Eh and pH of the product water and the nature of the other components in the water (Pourbaix 1974; Antia 2010, 2011a, b, 2014). The removal process is commonly multi-stage (Antia 2011a, 2016c) with numerous pollutants being removed simultaneously (Antia 2015a, b).

This study considers the potential application of two groups of ZVI desalination catalysts (termed Catalysts A and B) for in situ aquifer desalination.

Type A catalysts (Figs. 2, 3, 4, 5, 6, 7) operate as catalyst pellets (or powders), which are placed in water (Antia 2015b). These catalyst pellets slowly remove NaCl from a water body over a period of 50–1200 d (Antia 2015a, b). The NaCl is concentrated within the dead-end pores

Fig. 2 Schematic energy versus reaction co-ordinate graphs illustrating the desalination process. **a** E_a is positive. **b** E_a is negative

Fig. 3 Catalyst A: rate constants. **a** k and k_n versus feed water salinity. **b** k_n versus time required to reduce the water salinity by 50%. **c** k versus probability of a lower value. **d** Probability versus residence time required to achieve a 50% reduction in salinity. Further details

of the trials are provided in Antia (2015b). Probability (P) calculated by ranking values, where $P = \text{rank number}/(\text{total number of samples} + 1)$: methodology after Antia (1986)

Fig. 4 Catalyst A: activation energy assessment. **a** Isothermal temperature versus k_n and **b** $\log(k_n)$ versus $1/T$. Trial details: reactor size 0.2 L, $P_w = 18.91 \text{ g L}^{-1}$, $C_0 = 8.2 \text{ g L}^{-1}$, $t = 24 \text{ h}$, number of analyses,

$n = 73$, $k_n = k/P_w$. The saline water was constructed by adding NaCl to natural spring water. The composition of the natural spring water is provided in Antia (2015a, b)

within the catalyst as both hypersaline water and halite (Antia 2017, 2018a, b). The salinity of the water is reduced to an equilibrium level which is typically between 5 and 80% of the feed water salinity (Antia 2015a, b, 2016a, b, 2017, 2018a, b, c). The required pellet concentration in the water is in the range 20–100 g Fe L⁻¹ (Antia 2015b), i.e., provision of 10,000 m³ of irrigation water may require 200–1000 t of catalyst pellets.

Type B catalysts (Figs. 8, 9, 10, 11) gradually remove the Cl⁻ and Na⁺ ions from a batch of water over a period of 1–36 h (Antia 2015b, 2016a, 2017, 2018b, c). The salinity of the water is reduced to an equilibrium level which is typically between 10 and 80% of the feed water salinity (Antia 2017, 2018a, b, c). Each batch of catalyst can be reused for successive batches (e.g., > 50) without loss of activity (Antia 2017, 2018a, b, c). The rate of desalination commonly

Fig. 5 Catalyst A: interpreted electrochemical parameters. **a** Pseudo-specific capacitance versus k_n . **b** Current versus k_n . **c** Capacitance versus k_n . Raw data source trials ST1a–ST5j (50 trials Antia 2015b)

Fig. 6 Catalyst A: interpreted thermodynamic parameters. **a** Equilibrium constant versus salinity. **b** Gibbs free energy versus salinity (trials ST1a–ST5j (50 trials Antia 2015b)). **c** Standard potential versus salinity (trials ST1a–ST5j (50 trials Antia 2015b)). **d** Interpreted reaction co-ordinate versus energy diagram for the generic Catalyst

A desalination reaction, assuming that the principal Stage 1 reaction produces $\text{Fe}(\text{OH})_3$ and the principal Stage 2 reaction produces NaClO (standard enthalpy from Lide 2008). Raw source data trials ST1a–ST5j (50 trials Antia 2015b)

Fig. 7 Catalyst A: simplified schematic diagram illustrating the interaction of OH with the ZVI. LDH layered double hydroxide. e^- interactions with the reduction of FeO_x and Fe(OH)_x to Fe^{n+} are not shown

Fig. 8 Catalyst B: rate constants. **a** k and k_n versus feed water salinity. **b** k_n versus time required to reduce the water salinity by 50%. **c** k versus probability of a lower value. **d** Probability versus residence time required to achieve a 50% reduction in salinity. The primary control on k_n is the O_2 saturation of the water. Trial details:

reactor size 240 L, $P_w = 0.5 \text{ g L}^{-1}$, $T = 5\text{--}25^\circ\text{C}$, air discharge rates $= 0.5 \text{ L L}^{-1} \text{ h}^{-1}$, air bubble–water contact surface area is $1 \text{ m}^2 \text{ L}^{-1} \text{ h}^{-1}$, air discharge pressure 0.01 MPa; see Antia (2015b) for further operating details associated with Catalyst B

increases with increasing feed water salinity (Antia 2017, 2018a, b, c). A typical Bronsted relationship (Antia 2018b) is $\text{Log}_{10}(k_a) = 1.9768 (C_{t=0})^{0.5} - 5.8078$ ($n = 40$; $R^2 = 40\%$; valid for salinities in the range $1\text{--}9 \text{ g NaCl L}^{-1}$). The current

generation (2018) of Type B catalysts requires $< 0.02 \text{ t Fe}$ to partially desalinate $10,000 \text{ m}^3$ of irrigation water.

The commercial cost of partial desalination (for irrigation) using a surface-based ZVI reactor system processing

Fig. 9 Catalyst B: interpreted electrochemical parameters. **a** Pseudo-specific capacitance versus k_n . **b** Current versus k_n . **c** OH^- added versus k_n (OH^- calculated from change in pH; methodology: Ebbing and Gammon 2005) and **d** apparent capacitance versus k_n

Fig. 10 Catalyst B: simplified schematic diagram illustrating the interaction of OH^- with the ZVI. LDH layered double hydroxide

$100 \text{ m}^3 \text{ d}^{-1}$ was initially estimated at being $< \$0.1 \text{ m}^{-3}$ (Antia 2015b, 2016a, 2017). Subsequent trialling (2016–2018) of a commercial-scale ZVI desalination reactor train (processing $0.53 \text{ m}^3 \text{ d}^{-1}$) has established (e.g., Antia 2018b, c) that the actual cost (excluding profit, financing, labour, facility/site costs, administration, etc.) approximated to $\$0.02 \text{ m}^{-3}$ for Type B catalyst, plus a depreciated capital cost of $\$0.01 \text{ m}^{-3}$ (excluding operating costs, feed and product water storage costs, site cost, financing costs, insurance costs, profit, taxes, administration costs, etc.). These trials have confirmed that a

multi-train ZVI reactor system processing $100 \text{ m}^3 \text{ d}^{-1}$ can be expected to reduce the feed water salinity ($1\text{--}9 \text{ g NaCl L}^{-1}$) by 40–60%, for a target full cycle cost of $< \$0.2 \text{ m}^{-3}$.

Moving the desalination process from a reactor environment into the aquifer (providing the saline irrigation water) has the potential to further reduce costs.

In situ placement of ZVI within aquifers [either by injection or placement in permeable reactive barriers (PRBs)] has been extensively used to decontaminate aquifers (e.g., Henderson and Desmond 2007; Fu et al. 2014; Guan et al.

Fig. 11 Disrupted cross-coupling catalytic cycle associated with ZVI desalination resulting in the production of ClO–OCl dimers, Cl₂, and HO₂[•] ions/radicals (demonstrated by Antia 2015b); ClO dimer kinetics are defined by von Hobe et al. (2006). Cl₂O₄^{•-} reaction is from Kortvelyasi and Gordon (2004). This cycle demonstrates the formation of electrochemical capacitance (e.g., Wang et al. 2015)

2015) and will remove an extensive suite of cations, anions and microbiota from the aquifer (e.g., Antia 2014, 2016c). Placing ZVI in an aquifer will modify the Eh and pH of the surrounding groundwater (e.g., Antia 2010, 2011a, 2014, 2016a) and can create a requirement for an environmental impact assessment and regulatory approval (e.g., Dougherty and Hall 1995; Mak and Lo 2011; Albergaria et al. 2013; Lynch et al. 2014; Jang et al. 2014; Alvarenga et al. 2016).

To date, aquifer-based ZVI environmental impact assessments have focused on freshwater aquifers. ZVI interacts with NaCl to create an oxidic intra-particle nano-redox environment (Antia 2018a) which can facilitate the formation of H_xCl_yO_z species (Antia 2015b, 2016a). ZVI is known to deactivate common aquifer bacteria (e.g., Kim et al. 2010; Tellen et al. 2010; Barzan et al. 2014; Zabetakis et al. 2015). However, the oxidative redox conditions (which can develop within the intra-particle porosity during desalination) can favour the growth of an extensive microbiota (e.g., Barzan et al. 2014; Antia 2018a, b). The predatory iron bacterium *Leptothrix discophora* can be present in the ZVI catalyst during desalination, and will remove other bacterial species from the product water (Antia 2018a).

Data set and methodology

The non-isothermal ZVI desalination trials (trial identifiers: ST1a–ST5j, E146a–E146q and E147 series Antia 2015b, 2016a, A–K catalysts Antia 2017, 2018a, b, c) were used as the data base for this study. This data set recorded the feed water salinity (1–20 g L⁻¹), the product water salinity, Eh, pH, electrical conductivity (EC),

temperature (non-isothermal fluctuating within the range – 10 to 25 °C), pressure (0–0.01 MPa above atmospheric pressure), operating conditions, reactor volumes (0.2–800 L/batch), ZVI composition, ZVI particle size ($a_1 = 44,000$ –77,000 nm), ZVI particle surface area, ZVI concentration (0.5 to > 100 g L⁻¹) and ZVI treatment. ZVI was held as pellets (Catalyst A), or in cartridges (Catalyst B) (Antia 2015b, 2017, 2018a, b, c).

Catalysts A and B were trialled on synthetic water containing: (i) Catalyst A: Na–Cl, Na–Cl–HCO₃⁻, Na–Cl–NO₃–HCO₃⁻ and Na–K–Cl–NO₃–HCO₃⁻, (ii) Catalyst B: Na–K–Cl–Mg–SO₄ and Na–K–Cl–Mg–SO₄–HCO₃⁻ (Antia 2015b, 2016a). The feed water also contained Ca, Mg, Mn, B, Ba, Cu, Si, Sr, Zn (Antia 2016a). The synthetic water was manufactured by adding NaCl to natural spring water (Catalyst A trials) or by adding Zechstein Halite to natural spring water (Catalyst B trials).

pH measurements were calibrated at pH 4, 7, 10 [Equipment manufactured/branded by Hanna Instruments Ltd. (Leighton Buzzard, Bedfordshire, UK), HM-Digital, Inc. (Culver City, CA, USA) and Extech Instruments, Inc., Nashua, NH, USA]; Eh measurements were calibrated to the standard hydrogen electrode using a quinhydrone calibration at pH of 4 and 7. Oxidation–reduction potential (ORP) measurement equipment was manufactured/branded by Hanna, HM-Digital and Extech; direct ion (Na⁺ and Cl⁻) concentration measurements were based on ion calibration at 0.001, 0.01, 0.1 and 1.0 mol L⁻¹ (Catalyst B), equipment manufactured by Bante Instruments Ltd., Shanghai, China; salinity measurements were based on EC (Catalyst A) and direct ion analysis. EC measurement equipment was manufactured/branded by Hanna, HM-Digital and Extech.

The efficiency of the desalination process can be measured directly using the observed rate constant, k (Ebbing and Gammon 2005; Kent 2007; Antia 2016a), where

$$\ln[\text{NaCl}_{t=0}/\text{NaCl}_{t=n}] = \ln[C_0/C_t] = kt = k_n t P_w. \quad (1)$$

In this study k_n is defined as $k/(P_w)$ as both Catalysts A and B are constructed using the same-sized ZVI particles (44,000–77,000 nm). The expected surface area of the resultant catalyst is within the range 20–200 m² g⁻¹ (Antia 2015b). The charge (C) associated with Cl⁻ removal is (Ebbing and Gammon 2005):

$$C \text{ (Coulombs)} = F(1/M_w)W_r. \quad (2)$$

The effective pseudo-specific capacitance (normalised charge) (P_{sc}) associated with desalination is (e.g., Brousse et al. 2015):

$$P_{sc} \text{ (C g}^{-1}\text{)} = C/P_w. \quad (3)$$

The associated current, I (A) is (e.g., Sarkar et al. 2013):

$$I = P_{sc}/t. \quad (4)$$

The capacitance, C_a , is (e.g., Kuo et al. 2007; Yagmur et al. 2013; Chen et al. 2013):

$$C_a \text{ (F g}^{-1}\text{)} = I/\text{voltage}. \quad (5)$$

Voltage is defined (Shen et al. 2016) as: Voltage = (average Eh (V) – initial Eh (V))/ P_w/t . The applied working electrochemical voltage = (average Eh (V) – initial Eh (V)). The change in voltage during desalination is principally due to the effectiveness of the cathodic sites (Shen et al. 2016). The capacitance is a measure of external cell resistance, R_{ext} , where (Shen et al. 2016)

$$R_{ext} = \text{Voltage}/I. \quad (6)$$

k_n increases as the amount of OH in the water increases and as the amount of available electrochemical energy increases (Antia 2015b; Wang et al. 2015). The catalyst effectively operates (e.g., Antia 2014, 2015b, 2016b; Shen et al. 2016) with a cathodic surface, a solid electrolyte transfer surface (ion conductor) and an anodic surface. The interaction of this electrochemical cell with Cl and Na ion species results in the removal of Na⁺ and Cl⁻ ions (Antia 2015b, 2016a, 2017).

Desalination is a multi-stage, multi-pathway process, involving catalytic adsorption and desorption (Antia 2015a, b, 2016a, 2017, 2018a). This allows catalysts to be designed whose rate constant (i) increases with decreasing temperature, (ii) remains constant with changing temperature, (iii) increases with increasing temperature, (iv) increases with increasing feed water salinity, (v) remains stable with increasing feed water salinity, (vi) decreases with increasing feed water salinity, (vii) increases with increasing catalyst concentration, and (viii) decreases when the catalyst

concentration increases beyond a critical level (e.g., Antia 2015b, 2016a, b).

The apparent activation energy, E_a (for a pseudo-first-order reaction) is derived from the slope (s) of a regression line for $\ln(k_n)$ (or $\log(k_n)$) vs. $1/T$ (Ebbing and Gammon 2005). Figure 2 schematically illustrates the relationship between the experimentally measured activation energy (E_a) and the actual activation energy (E_2). The observed activation energy is: $E_a = E_2 - \Delta H_1$ (Revell and Williamson 2013; Antia 2016a).

The cross-coupled desalination catalytic reaction (Fig. 1) can be simplified into a two-stage reaction (Fig. 2), where

- (i) Stage 1 is $\text{NaCl} + \text{Catalyst } (S_1) \rightarrow \text{NaClS}_1$;
- (ii) Stage 2 is $\text{NaClS}_1 \rightarrow [\text{Product (C) NaCl}] + \text{Catalyst } (S_1)$;
- (iii) The net reaction is $\text{NaCl} + \text{Catalyst } (S_1) \rightarrow [\text{Product (C) NaCl}] + \text{Catalyst } (S_1)$.

The observed activation energies (e.g., Antia 2016b) can be positive (Fig. 2a), or negative (Fig. 2b).

Catalyst A

Catalyst A (trial series ST1a–ST5j ZVI Antia 2015b, 2016a): (i) composition: (Antia 2015b), (ii) particle size, $a_i = 44,000\text{--}77,000$ nm (Antia 2015b), (iii) principal catalyst characteristics: (Fig. 3), (iv) external energy requirement = none (Antia 2015b), and (v) equilibrium absorbance, $q_e = 0.30\text{--}0.50$ g g⁻¹ (Antia 2015b).

The key characteristics of the ST catalyst pellets (illustrated in Antia 2015b, 2016a, 2017, 2018a, b) are (i) a rate constant (k, k_n) which increases with increasing feed water salinity (Fig. 3a), (ii) the time required to reduce the water salinity by 50% increases with increasing P_w (Fig. 3b), (iii) k decreases with decreasing catalyst concentration, and there is a range of potential rate constants which are associated with a specific catalyst concentration (Fig. 3c), and (iv) the rate constant data (Fig. 3c) can be used to predict the time required [with a specific catalyst concentration (P_w)] for the aquifer salinity to reduce by 50% (Fig. 3d).

50 trials operated under identical temperature conditions established equilibrium absorbance, g NaCl g⁻¹ Fe, q_e , for a Type A catalyst after 70–130 d (Antia 2015b). The trials were continued to give a total duration of 280 d. The k_n values in Fig. 3 are based on $t = 280$ d. Incremental k_n values before the equilibrium salinity levels are reached are in the order of $10^{-8}\text{--}10^{-6}$ (Fig. 4a, b), where $k_n = \ln(C_i/C_{t+24h})/tP_w$, k_n varies with temperature (Fig. 4a, b). The apparent activation energy is calculated, from the data in Fig. 4, using the method described in Ebbing and Gammon (2005) as:

$$E_a = \ln(k_1/k_2)/(1/T_1 - 1/T_2)R \quad T_1 < T_2. \quad (7)$$

The measured apparent activation energy, E_a , is $-109.9 \text{ kJ mol}^{-1}$ (Fig. 4b).

The principal electrochemical parameters (e.g., capacitance) for Catalyst A are summarized in Fig. 5. The effectiveness of this catalyst is inversely proportional to its capacitance (Fig. 5). A relationship between the standard rate constant, k_n , and capacitance, C_a , has been defined (Kisa and Kazmierczak 1991) as:

$$k_n = [RT/n_e^2 F^2 a_s(c)^{0.5}] k_c C_a. \quad (8)$$

The relationship between pseudo-specific capacitance (Eq. 3) and k_n (Fig. 5a) indicates that k_n increases with pseudo-specific capacitance, and that the associated current discharge associated with the ZVI catalyst (Eq. 4) decreases as k_n increases (Fig. 5b). The measured residual capacitance [following desalination (Eq. 5)] associated with the ZVI catalyst (Fig. 5c) decreases with increasing k_n . This is interpreted (Antia 2015b, 2018b) as indicating that desalination (and k_n) is associated with the discharge of capacitance in the ZVI catalysts.

These relationships (Fig. 5) indicate, that for a specific value of C_a , the variation in k_n can be attributed to changes in a_s and k_c (if it is assumed that the other parameters are constant). The cathodic rate constant, k_c , increases with the increased availability of O_2 (Ebbing and Gammon 2005; Shen et al. 2016). k_c may increase as C_a decreases. Catalyst B provides an example where k_n is increased by increasing k_c (Antia 2018a, b, c).

The principal thermodynamic parameters for Catalyst A (ST catalyst) are summarized in Fig. 6. At equilibrium, when C_0 is between 8 and 10 g L^{-1} , k_n decreases with increasing salinity (Fig. 6a). When C_0 is $< 8 \text{ g L}^{-1}$, k_n increases with increasing salinity (Fig. 3a). At equilibrium (Ebbing and Gammon 2005):

$$G = 0 = \Delta G^\circ + RT \ln(K). \quad (9)$$

The values of G are negative within the range -4 to -9 kJ mol^{-1} , and decrease as C_0 increases (Fig. 6b). Negative G values in the range 0 to -9 kJ mol^{-1} indicate that the desalination reaction will produce an equilibrium mixture containing both reactants and products (Ebbing and Gammon 2005), i.e., the saline water will only be partially desalinated at equilibrium (e.g., Antia 2015b, 2016a, 2017). The standard potential, ΔE° , is calculated as (Ebbing and Gammon 2005):

$$\Delta E^\circ = \Delta G^\circ / -n_e F. \quad (10)$$

ΔE° is related to Eh and pH as (Pourbaix 1974):

$$Eh = \Delta E^\circ - (RT/n_e F) \text{pH} - RT/n_e F \ln(Q). \quad (11)$$

ΔE° decreases with increasing feed water salinity (Fig. 6c), decreasing k_n (Fig. 6a) and increasing G (Fig. 6b).

This change reflects the composite nature of the desalination reaction (Antia 2016a). The Bronsted relationship illustrated in Fig. 6a is: $\text{Log}_{10}(k) = -8.855 (C_{t=0})^{0.5} - 6.3213$. This indicates that the transition state complex [Product (C) NaCl] (Fig. 6d) has a lower charge than the reactants and has a lower stability at higher ionic strengths than the reactants. The observed (Fig. 6a) increase in k with decreasing ionic strength (decreasing salinity) indicates that the transition state complex is formed by two or more ions with a different charge sign.

If the dominant primary reaction is associated with the interaction of ZVI and water (Antia 2014, 2015b, 2016a, b), e.g., $\text{Fe}^0 + 3\text{HO}^- = \text{Fe}(\text{OH})_3 + 3\text{e}^-$, $\Delta H_1 = -134.2 \text{ kJ mol}^{-1}$ (thermodynamic data from Lide 2008), then $E_2 = -24.3 \text{ kJ mol}^{-1}$ (Fig. 6d).

An interpretation of the relationship between activation energy, enthalpy and reaction sequencing is provided in Fig. 6d. Catalyst A is suitable for aquifer partial desalination when the aquifer water temperature is in the range 0 – 90°C (Antia 2015b).

The primary cathodic reaction ($\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$) (Pourbaix 1974) is a function of the availability of both O_2 and H^+ . The bulk of the O_2 entering the water will react to form OH radicals and ions (i.e., $0.5\text{O}_2 + \text{H}_2\text{O} = \text{H}_2\text{O}_2$; $\text{H}_2\text{O}_2 + 2\text{e}^- = 2\text{OH}^-$ Pourbaix 1974). Catalyst A is present as a layered double hydroxide (LDH) and derives an O_2 and OH supply from four sources within the aquifer (Fig. 7): (i) oxygen diffusion across the air–water interface with subsequent OH^- formation (Antia 2016a), (ii) dissolved oxygen within the water body with subsequent OH^- formation (Antia 2015b), (iii) natural alkalinity within the water body (Antia 2015b), (iv) ZVI catalysed water decomposition to form H^+ and OH^- (Antia 2014, 2016b).

All water containing ZVI shows a natural oscillation between higher and lower values for both Eh and pH (Antia 2010, 2011a, 2014, 2016c). This Eh and pH oscillation is associated with an oscillation in Fe valency within the range -2 to $+8$ (Antia 2016a, 2017, 2018b). The pH oscillation reflects changes in the $\text{H}^+:\text{OH}^-$ ion ratio in the water while the Eh oscillation reflects changes in the $\text{O}_2:\text{O}^{n-}:\text{OH}^-:\text{O}_2\text{H}^-$ ratio in the water (Antia 2014, 2016b, 2017, 2018b). During desalination catalysis (Figs. 1, 7), the Fe oxidation number cyclically increases, before cyclically decreasing (Antia 2016a, 2017, 2018b).

Catalyst B

Catalyst B (trial series E146 Catalyst Antia 2015b, 2016a): (i) composition: (Antia 2015b), (ii) $a_1 = 44,000$ – $77,000 \text{ nm}$ (Antia 2015b), (iii) principal operating characteristics (Figs. 8, 9, 10, 11), (iv) external energy requirement $< 0.17 \text{ kW m}^{-3}$ (for air compression, Antia 2016a),

and (v) q_e = potentially $> 1 \text{ kg NaCl g}^{-1} \text{ Fe}$ (Antia 2015b, 2016a, 2018b); treatment is potentially $> 52,000 \text{ m}^3 \text{ t}^{-1}$ (Antia 2015b, 2016a); removed NaCl is concentrated in (and on) the ZVI and in the ZVI cartridge (Antia 2016a).

Type B catalysts show a general trend where k_n increases with increasing feed water salinity (Fig. 8a). These rate constants indicate (Fig. 8b–d) that a Type B catalyst (with a concentration of $< 1 \text{ g L}^{-1}$) could achieve a 50% desalination of a feed water. The measured rate constant can increase, as P_w decreases, with some Type B catalysts, when P_w exceeds a critical level (Antia 2018b).

The electrochemical parameters associated with this catalyst (Fig. 9) demonstrate, like Catalyst A, that k_n increases with decreasing pseudo-specific capacitance (Fig. 9a), decreasing current (Fig. 9b), decreasing OH^- addition to the water (Fig. 9c), and decreasing residual capacitance (Fig. 9d). The substantially higher values of k_n [relative to Catalyst A (Fig. 3)] reflect the substantially higher values of k_c resulting from the oxygenation of the water with air. The desalination reaction is driven by the reaction couple $3\text{O}_2 + 6\text{H}_2\text{O} + 12\text{e}^- = 6\text{H}_2\text{O}_2 = 12\text{OH}^-$ (Antia 2015b, 2016a). This also allows (Fig. 10) the formation of secondary products.

Secondary reactions

Cl^- and Na^+ ions interact with OH^- and H^+ within the water to form ion adducts and radicals of the form $\text{H}_x\text{Cl}_y\text{O}_z$, Cl_xO_y , NaOH (Antia 2015b, 2016a). Their concentration in the water and in ZVI varies with catalyst type and with the operating mode selected. Their presence can allow a microflora to grow in the ZVI. This can require careful handling of both the ZVI and the water. These factors may need to be considered in an environment impact assessment.

The primary reactant is HClO (formed from the anodic reaction: $\text{H}_2\text{O} + \text{Cl}^- = [\text{OH}-\text{Cl}] + \text{H}^+ + 2\text{e}^-$ Pourbaix 1974). An excess of HClO , or ClO^- , is generated in the inter-particle porosity when the water is saturated with air, or CO_2 (Antia 2015b). This can result in the basic cross-couple cycle being disrupted (Fig. 11) to produce $\text{ClO}-\text{OCl}$ dimers (Cl_2O_2 species) as an initial primary by-product (Antia 2015b).

The $\text{ClO}-\text{OCl}$ dimer (product from Fe^{III} desorption) decomposes to form $\text{ClO}_2 + 0.5\text{Cl}_2$ (Figs. 10, 11). The ClO_2 product is adsorbed by Fe^{I} (Fig. 11). This product is then desorbed from Fe^{III} as 0.5Cl_2 . The O_2 product then interacts with water to produce H_2O_2 and OH^- . In the presence of excess O_2 , the OH^- interacts with Fe^{I} to produce HO_2^- . The principal product (Antia 2015b) of this cycle is HO_2^- .

The primary reaction outcomes from $\text{ClO} + \text{ClO}$ are (i) $\text{Cl}_2 + \text{O}_2$, (ii) $\text{Cl} + \text{ClO}_2$, and (iii) $\text{ClO}-\text{OCl}$ (Mollina and Mollina 1987; von Hobe et al. 2005). $\text{ClO}-\text{OCl}$

decomposes to produce $\text{Cl} + \text{ClO}_2$ (Mollina and Mollina 1987; von Hobe et al. 2005). $\text{ClO}-\text{OCl}$ can react with ClO to produce $\text{Cl}_2\text{O} + \text{ClO}_2$ (Zhu and Lin 2011). The catalysed decomposition of ClO_2 produces $\text{Cl} + \text{O}_2$ (Mollina and Mollina 1987; von Hobe et al. 2005). This then initiates the coupled reaction $2\text{O}_2 + 2\text{OH}^- = 2\text{HO}_2 + \text{O}_2$ (e.g., Kingston 1987). In an oxygenated environment the O_2 will react with water to produce an intermediate product H_2O_2 (Pourbaix 1974). The H_2O_2 will decompose to form 2OH^- (Pourbaix 1974). Some of the H_2O_2 will react with the ClO (i.e., $\text{ClO} + \text{H}_2\text{O}_2 = \text{HOCl} + \text{HO}_2$ Levanov et al. 2015).

The disrupted oxygenated cycle (Fig. 11) dechlorides the water to produce two principal products $\text{Cl}_2(\text{aq})$ and HO_2^- . The equilibrium relationship $[2\text{Cl}^- = \text{Cl}_2 + 2\text{e}^- \text{ (Eh} = 1.395 + 0.295 \log (\text{Cl}_2/(\text{Cl}^-)^2)]$ is independent of pH (Pourbaix 1974). The Cl_2 product can react with water to form one or more of HClO , ClO^- , HClO_2 , ClO_2^- , ClO_3^- and ClO_4^- (Pourbaix 1974). Their equilibria relationships are a function of Eh and pH (Pourbaix 1974).

HClO forms part of the pH-dependent equilibrium continuum (e.g., McElhatton and Marshall 2007; Hu et al. 2010; Lefrou et al. 2012; Lichtfouse et al. 2012; Sandin 2013) from $0.5\text{Cl}_2(\text{aq})$ to Cl^- to HClO to ClO^- , where (i) $\text{pH} = 7.49 + \text{Log}(\text{ClO}^-/\text{HClO})$ (Pourbaix 1974), (ii) $\text{Eh} = 1.494 - 0.0295 \text{ pH} + 0.0295 \text{ Log}(\text{HClO}/\text{Cl}^-)$ (Pourbaix 1974), and (iii) $\text{Eh} = 1.494 - 0.0295 \text{ pH} + 0.0295 \text{ Log}(\text{ClO}^-/\text{Cl}^-)$ (Pourbaix 1974).

The expected change in the Eh and pH (Hasab et al. 2012; Valenzuela et al. 2013) of the intra-particle porosity in the presence of NaCl (during desalination) is (i) a progressive drop in pH [relative to the situation without NaCl from 11 (e.g., Antia 2010, 2011a, b) to 4–5 (e.g., Antia 2015b, 2016a)], and (ii) an increase in Eh from < 0.6 (e.g., Antia 2015b, 2016a) to $> 1.1 \text{ V}$ (Pourbaix 1974).

The NaClO product entering the main water body will decompose (e.g., Pourbaix 1974; Falbe 1986) to form the equilibrium relationships $[3\text{NaClO} = 2\text{NaCl} + \text{NaClO}_3]$, $[2\text{NaClO} = \text{NaCl} + \text{NaClO}_2]$ and $[2\text{NaClO} = \text{O}_2 + 2\text{NaCl}]$.

The secondary reactions associated with ZVI in fresh water are largely benign and are associated with the removal or inactivation of microbiota (e.g., Antia 2014). In saline water, the secondary reactions produced during desalination can allow microbiota to flourish. The elevated Eh nano-redox conditions ($> 0.7 \text{ V}$) within the ZVI intra-particle porosity are suitable for the growth of *Escherichia coli*, *Listeria monocytogenes*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* (e.g., Deza et al. 2005). These species are natural constituents of many shallow aquifers (e.g., Ridgway et al. 1990; Hossain and Anwar 2009; Feighery et al. 2013; Penny et al. 2015). The sheltered intra-particle nano-environment will, in some aquifers, result in colonies of these species growing within the ZVI during desalination.

The Gram-positive bacteria *S. aureus*, which is inhibited by concentrations of NaClO above 7.5 mM, is not inhibited in water containing NaCl + NaClO₃, or in water containing < 7.5 mM NaClO (Melvin et al. 2011). The water within the ZVI can contain an extensive flora of the predatory oxic bacterium *L. discophora* (Antia 2018a, b). This bacterium operates by releasing acetaldehyde dehydrogenase enzyme and the associated by-product acetaldehyde into the pore waters within, and surrounding the ZVI (Antia 2018a). Therefore, appropriate biological precautions may be required during catalyst changeover, or water sampling from the catalyst bed.

UV–visible absorbance spectra associated with the ZVI nanoparticles produced during desalination (e.g., Antia 2015b) have identified the presence of Cl[−] (210–220 nm), Cl₂O₆ (215 nm), Cl₂O₂ (230 nm), Cl₂O₄ (230–235 nm), HClO (240 nm), ClO–OCl (240–250 nm), Cl₂ (250 nm), ClO (270 nm), ClO[−] (290 nm), ClO₂ (292 nm), HO₂[−] (225 nm), Na⁺ (225–230 nm), NaO[−] (265 nm) and NaClO (294 nm) (Thomas and Burgess 2007; Antia 2015b, 2016a). Therefore, appropriate chemical precautions may be required during catalyst changeover, or water sampling from the catalyst bed.

Aquifer desalination

Aquifer desalination using a Type A catalyst requires a radial treatment zone to be established around an abstraction well (e.g., Huang et al. 2015). The treatment zone contains a number of wells, or infiltration devices, containing ZVI (Fig. 12). The ZVI is held in removable open-ended cartridges, or in removable permeable containers which are placed in the well, or in an infiltration device (e.g., Antia 2015b, 2016a, 2017). The number of wells/infiltration devices required and amount of ZVI (Z_i) required are

defined by the required level of desalination, D_r , k_n and the required abstraction rate, A_r (m³ d^{−1}). A_r is defined by the irrigation requirements for a specific crop. The required D_r is defined by a cost–benefit analysis of D_r versus crop yield. k_n is defined by the selected catalyst. There is precedent for the placement of ZVI in aquifers, as ZVI has been widely used in PRBs for > 20 years to decontaminate aquifers (e.g., Wilkin et al. 2014).

Aquifer-specific parameters such as permeability, homogeneity and porosity will affect both the number of wells or infiltration devices and their micro-siting (Antia 2017). Local factors such as land ownership, land usage, aquifer geometry, aquifer distribution and regulatory constraints will also impact on the feasibility of in situ aquifer desalination.

The primary parameter required to undertake in situ aquifer desalination is:

$$1/D_r = \text{NaCl}_{\text{aquifer}}/\text{NaCl}_{\text{product water}} \quad (12)$$

Each crop type (and variety) will have a yield decrement relationship with salinity. The exact relationship is a function of local conditions (e.g., temperature, soil, operating conditions, irrigation, etc.).

Saline water from riparian water, ground water and saline drainage water from irrigated land (salinity = 0.9–9 g L^{−1}) have been used to irrigate crops (e.g., Rhodes 1984; Zaman and Ahmad 2009; Jiang et al. 2010; Wang et al. 2016). A decrease in irrigation water salinity from 5 to 2.5 g NaCl L^{−1} ($D_r = 0.5$) would have the potential (Antia 2015b) to increase (depending on the planting strategy, variety and irrigation strategy adopted) soybean seed yields by between 0.8 and 10.8 t ha^{−1} (e.g., Khan and Khaliq 2004; Ali et al. 2013; AGDM 2016).

The average residence time, t_r (s), required for the water within the ZVI-influenced desalination zone (e.g., Ebbing and Gammon 2005; Kent 2007) is:

Fig. 12 Process flow diagram for the partial desalination of an aquifer using a Type A catalyst

$$t_r = \text{Ln}[1/D_r]/(k_n P_w). \quad (13)$$

Increasing D_r reduces the cost of the desalination project by reducing the average residence time required for the water in the reaction environment. The volume of water required within the aquifer in the ZVI-influenced desalination zone, V_w (m^3), is:

$$V_w = A_r t_r / 86,400. \quad (14)$$

The amount of ZVI required (t) is:

$$Z_I = V_w / (1000/P_w). \quad (15)$$

The required gross rock aquifer volume (A_v , m^3) is:

$$A_v = V_w / (\phi S_w N_G). \quad (16)$$

The gross area, G_a (m^2), encompassed by the aquifer treatment zone is:

$$G_a = A_v / T_h. \quad (17)$$

The radius, r (m), of the treatment zone around the abstraction well

$$r = (G_a / \pi)^{0.5}. \quad (18)$$

The land take required for ZVI desalination can be assessed by considering a hypothetical saline aquifer located 2–3 m below the ground surface which is used for irrigation. The hypothetical parameters are provided in Table 1. These are integrated with the catalyst data to

Table 1 Example saline aquifer parameters

Parameter	Value	Parameter	Value	Parameter	Value
Common parameters					
$\text{NaCl}_{\text{aquifer}}$	5 g L^{-1}	$\text{NaCl}_{\text{product water}}$	2.5 g L^{-1}	N_G	90%
Φ	50%	S_w	70%	T_h	1 m
A_r	100 $\text{m}^3 \text{d}^{-1}$	P_w (Catalyst A)	0.030 t m^{-3}	P_w (Catalyst B, 2015)	0.0005 t m^{-3}
	1st Quartile		Median		3rd Quartile
Catalyst A—Position in 2015 as demonstrated by batch trials (0.2 to 10L·batch ⁻¹)- Fig. 2-7,12. $D_r = 0.5$ or 50% desalination					
k_n	8.425×10^{-10}		1.47×10^{-9}		3.95×10^{-9}
t	317 days		182 days		68 days
V_w	31,741 m^3		18,192 m^3		6770 m^3
A_v	100,765 m^3		57,751 m^3		21,492 m^3
G_a	100,765 m^2		57,751 m^2		21,492 m^2
r	179.1 m		135.6 m		82.7 m
Z_I	952 t		546 t		203 t
	1st Quartile		Median		3rd Quartile
Catalyst B—Position in 2015 as demonstrated by technical scale(pilot) trials- Fig 8-11, (30–100 L d^{-1}). $D_r = 0.5$ or 50% desalination					
k_n	2.121×10^{-6}		4.496×10^{-6}		6.660×10^{-6}
t	7.6 days		3.6 days		2.4 days
V_w	756 m^3		357 m^3		208 m^3
A_v	2400 m^3		1133 m^3		660 m^3
G_a	2400 m^2		1133 m^2		660 m^2
r	27.6 m		19.0 m		15.6 m
Z_I	0.38 t		0.18 t		0.12 t
Air required ($\text{m}^3 \text{d}^{-1}$)	9072		4284		2496
	1st Quartile		Median		3rd Quartile
Catalyst B—Position in 2018 as demonstrated by a commercial scale reactor train (0.53 $\text{m}^3 \text{d}^{-1}$) Observed D_r approximates to $[1 - (0.0292 C_0^2 + 0.6484 C_0)/C_0]$, $R^2 = 76\%$, i.e. $D_r = 38\text{--}50\%$ for $C_0 < 5 \text{ g L}^{-1}$ and $D_r = 50\text{--}61\%$ for $5 \text{ g L}^{-1} < C_0 < 9 \text{ g L}^{-1}$. This relationship will vary with catalyst, feed water composition, and operating conditions. k_n varies with D_r					
k_n	Function of D_r		Function of D_r		Function of D_r
t	1.6 days		1.4 days		1.2 days
V_w	160 m^3		140 m^3		120 m^3
A_v	507 m^3		444 m^3		381 m^3
G_a	507 m^2		444 m^2		381 m^2
r	12.7 m		11.9 m		11.0 m
Z_I	0.01 t		<0.01 t		<0.01 t
Air required ($\text{m}^3 \text{d}^{-1}$)	<270		<270		<270

cfm cubic feet/minute. Quartile analyses are based on the probability distributions associated with k_n

provide (Table 1) an indication of the required aquifer sizes required to deliver $100 \text{ m}^3 \text{ d}^{-1}$ of partially desalinated irrigation water. Four desalination strategies are considered.

The first (passive) strategy places Catalyst A in a number of infiltration devices or wells. This strategy is illustrated schematically in Fig. 12. The water is retained within the reaction zone in the aquifer for a period of 60–1200 d while it gradually desalinates (Fig. 12).

The second (active) strategy places Catalyst B in a reactor (Fig. 13) with water storage, which is located in surface-based tanks (Fig. 13). In this strategy, an abstraction well is used to provide saline feed water for the reactor (Fig. 13). A reactor containing a Type B catalyst, processing $100 \text{ m}^3 \text{ d}^{-1}$ of feed water and producing $100 \text{ m}^3 \text{ d}^{-1}$ of product water, would require 150 m^3 of water storage (Fig. 13) and could be placed within a standard 6-m-long shipping container. This allows the reactor and water storage units to be both mobile and temporary facilities. In many regulatory jurisdictions these units can be employed without requiring specific regulatory consents.

The third (active) strategy places Catalyst B in a reactor (Fig. 14) with water storage, which is located within an aquifer (Fig. 14). In most regulatory jurisdictions, this strategy will require specific regulatory consents.

The fourth (active) strategy places Catalyst B in a reactor, where each reactor is located within an infiltration (recycle) borehole and the water storage is located within an aquifer (Fig. 15). This strategy will require specific regulatory consents and in some regulatory areas this strategy will require a waiver from existing regulations. This is because the water composition entering the aquifer will be different to the water composition entering the infiltration borehole(s).

In some regulatory environments, permits (with associated regulatory fees) and environmental impact studies will be required to allow a specific aquifer to be partially desalinated.

The principal differences between conventional desalination and ZVI desalination are summarized in Table 2.

Commercial-scale trials (2016–2018) of a reactor train (using a Type B catalyst) operating at $0.53 \text{ m}^3 \text{ d}^{-1}$ have achieved an average desalination in the range 45–55% (Antia 2017, 2018b, c) from a feed water (constructed by dissolving halite in natural spring water) with a salinity which varies within the range $1\text{--}9 \text{ g L}^{-1}$ (Figs. 13, 14, 15). These trials (Antia 2017, 2018b, c) indicate that (i) a reactor (Figs. 13, 14, 15) processing $100 \text{ m}^3 \text{ d}^{-1}$ will contain 19.4 kg Fe, and will require about 150 m^3 water (including recycle water) to be held in storage within the reaction environment (Figs. 13, 14, 15), (ii) a single catalyst charge (19.4 kg Fe) will be able to catalytically partially desalinate $> 54,000 \text{ m}^3$ of saline water (i.e., $> 2,780,000 \text{ m}^3 \text{ t}^{-1}$ Fe). This compares with the historical (large scale, e.g., $1000\text{--}7000 \text{ m}^3 \text{ d}^{-1}$) commercial ZVI municipal water treatment (Anderson process), which established that 1 t Fe could purify $> 2,400,000 \text{ m}^3$ of feed water (Anon 1889), (iii) the average desalination increases, as the feed water salinity increases (e.g., Figs. 13, 14, 15), when the feed water salinity is $< 9 \text{ g L}^{-1}$ (Antia 2018b).

Saline aquifers extend under a large number of neighbouring agricultural holdings. This allows Type A (Fig. 12) and Type B catalysts (Figs. 14, 15) to be potentially used (by co-operatives and state/municipal authorities) to partially desalinate, in situ, large aquifer volumes, e.g., $100,000\text{--}10,000,000 \text{ m}^3$. These partially desalinated aquifers can be used for irrigation, or to provide a feed stock for

Fig. 13 Process flow diagram for the partial desalination of irrigation water using a Type B catalyst

Fig. 14 Process flow diagram for the partial desalination of an aquifer using a Type B catalyst and surface-based reactors

Fig. 15 Process flow diagram for the partial desalination of an aquifer using a Type B catalyst and sub-surface-based reactors

conventional desalination plants. This type of large-scale aquifer desalination will be associated with a decrease in the nitrate content of the aquifer water (Antia 2015a, b).

Conclusions

This study has demonstrated that it is technically feasible to use ZVI catalysts to partially desalinate a saline aquifer, using a radial treatment zone, where water is being continuously removed through an abstraction well. The economics

is a function of location, water composition, salinity reduction required, aquifer geology and hydrology, crops selected, planting strategy, land management strategy, anticipated increase in crop yield, local cost structures and commodity prices. The initial technical screening indicates that ZVI catalysts could potentially be used to deliver 100 m^3 (partially desalinated water) d^{-1} , for a potential cost of $< \$0.2 \text{ m}^{-3}$, by the in situ treatment of a saline aquifer.

The practical feasibility of using this technology for in situ aquifer remediation will require appropriate regulatory consents and will require pilot testing (e.g.,

Table 2 Comparison of conventional desalination with ZVI desalination. Source Antia 2017, 2018a, b, c)

Parameters	Reverse osmosis	ZVI desalination
Amount of NaCl removed (%)	50–99.9	30–70
Amount of energy required (kW m ³)	> 0.7	0–0.1
Amount of feed water discarded as		
Waste water (% of feed water)	20–80	0
Cost for 1 m ³ d ⁻¹ product water	> \$100 m ³	< \$0.2 m ³
Cost for 10 m ³ d ⁻¹ product water	> \$20 m ³	< \$0.1 m ³

5–1000 m³ d⁻¹) within an aquifer which is designed to establish and test: (i) ZVI design layouts within the aquifer (including geological/hydrological data requirements), (ii) methods for placing the ZVI in the aquifer (and removing it), (iii) material and equipment requirements (including command and control systems), (iv) personnel requirements, (v) desalination time frame and achievable desalination levels, (vi) safety codes which have to apply during installation and operation, (vii) environmental constraints (including energy conservation), (viii) appropriate installation and operating standards and codes, (ix) resources required, (x) economic constraints (including operating cost structures, administrative cost structures, utility cost structures, supplies and equipment cost structures, capital and operating cost structures, insurance cost structures) and (xi) quality of the product water and its suitability for irrigation.

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