

Towards a Custom Made Water Product- Potential Use of Electrodialysis for Coal Seam Gas Water Treatment using the Example of Copper Ions

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1. Abstract

This study provides a literature overview and an investigation of the possibilities of using electrodialysis for removal of copper ions and partial desalination of brackish river water and coal seam gas water. Copper is beneficial as a plant micronutrient in the soil and often deficient. Likewise, many plants and soils can be irrigated with slightly saline water. Therefore, partial removal of copper and sodium chloride is investigated, as well as the possibility to maintain micronutrients in the irrigation solution. Another research question was if an electrolyte solution consisting of sodium sulphate salt aids the removal of copper. The aim of this paper is to investigate methods to produce a custom made water product, suitable for different situations using the example of copper removal. A small preliminary experiment was conducted, and results are shown at the end of the paper.

Keywords: Desalination, Electrodialysis, Copper removal, Micronutrients, Salinity, Coal Seam Gas Water, Custom Made Water;

2. Introduction

Electrodialysis was discovered in 1890, parallel to the discovery of the presence of fixed charges and mobile counter ions in ion exchange membranes (Shaposhnik and Kesore [1]). Meyer and Straus [2] described the principles of electrodialysis in the 1930's. After 1940 alternating anion and cation exchange membranes in an apparatus were described. Later different resins were developed to improve the system. Electrodialysis is a method mainly used for desalination of seawater using an electrochemical generator that has an anode section through which the salt water runs. It is an electro-membrane process in which ions are transported through a membrane from a solution of high concentration to one of even higher concentration (concentrate or brine), producing a solution with low ion concentration (diluate) under the impact of an electrical potential and an electrolyte solution. The negatively charged anions are attracted by the anode, which is where the current (the flow of positively charged particles) enters the cell, and the positively charged cations go to the cathode. At the cathode, they are reduced and exit the cell. Lee, Hong [3] describe the setup of an electrodialysis plant. Electrodialysis (ED) can be utilised to perform several kinds of processes such as the concentration and separation of acids, salts, and bases from aqueous solutions, or the separation and concentration of monovalent ions from different charged components, or the separation of ionic compounds from uncharged molecules [4] [5]. Other uses for electrodialysis are organic acid production from whey [6], sugar demineralization, and blood and protein treatments [7]. Sadrzadeh et al. (2007) [8] state that the most extensively used desalination techniques are either membrane or thermal methods. Membrane systems are more energy efficient [9]. For example, Banasiak et al. (2007) conducted desalination experiments using ED with solutions containing different salt concentrations ranging from 1-35 g/L and established that the optimum voltage was 12V. In the same study, ED was also effective to eliminate fluoride and nitrate from brackish groundwater [10]. McGovern et al. (2014) established that the ED technology is the most energy efficient method for partial desalination of waters with high salinity. Korngold

et al. showed that the energy needed to concentrate a solution from 0.4%-1.8% salt content to a 20% salt content was about 1.5-7.1kWh/m³ [11]. Lower salinities limit the current density and therefore, desalination takes longer and is more inefficient [12] [13]. Mohammadi and Kaviani (2003) found that ED is suitable for sea water desalination, and the best conditions were a salt concentration of 30000 ppm, a voltage of 6V and low flow rates (0.3cc/s) [14]. On the other hand, in a study by Sadrzadeh et al. (2007), the lowest feed concentration, and flow rate (10000 ppm/ 0.07 mL/s) and the highest voltage, and temperature (9V and 55 degrees Celsius) lead to the maximum level of desalination in sea water. [9]. One major advantage of ED is that the brine component is small, with about 10%. A very significant use of ED is brine recovery for example from reverse osmosis (RO) applications. Brine, from an ED system, is highly concentrated. Brine is an environmental problem which can lead to soil degeneration and plant toxicity when released into the environment, and salt accumulation in surface waters. Also, nutrients and salts can easily be recovered from the concentrated brine. Kwon (2015) showed that brine recovery in reverse ED systems can be used successfully in energy recovery [15]. At present many desalination units are in use worldwide, a recent example is the large EU-funded plant Aigues ter Llobregat (ATLL) in Spain [16]. This plant processes over 200,000 cubic meters of water per hour and has an over 90% water recovery rate. The purpose of this drinking water plant is to reduce river water salinity and the organic compounds responsible for trihalomethane formation. After the ED process, the water is stored for some time on a Calcite bed to remineralize it. Although this is an excellent way to remineralize the water, it takes time and storage capacity and could be more expensive than just leaving these substances in the water from the beginning [16], [17].

3. Removal of Monovalent and Multivalent Ions

Güler et al. (2013) found that non-selective ion exchange membranes have a low ability to separate monovalent ions from multivalent ions [18]. Van der Bruggen (2003) established that the ED process was not as efficient as that achieved by Nanofiltration (NF) membranes for separation of monovalent ions from multivalent ions. [19]. NF membranes have a separation efficiency of monovalent from divalent anions of ca. 60%. Larger divalent ions cannot pass through the membrane. Conventional ED membranes have minor differences in transport properties for different ions, but these are not enough to obtain a separation. Selective anion or cation exchange membranes have considerably different passage conditions for monovalent and multivalent ions. A separation between these ions by their charge, the applied voltage (in ED) and the pressure (in NF) is possible [20, 21].

4. Sodium Chloride

The topic of salt removal appears in numerous desalination studies over the years. For example, a viability study of urban wastewater desalination using electro dialysis to deliver recycled water for horticultural irrigation was conducted by Goodman et al. in Melbourne, Victoria, Australia [22]. On Gran Canaria, Spain, Veza et al. (2004) set up an electro dialysis desalination plant driven by wind energy and tested it to treat brackish water [23]. Desalination of various substances, such as urine [24] and fish sauce is common. Galama et al. (2013) [25] studied the preferential removal of divalent ions in sea water, especially the effect of the current density. The lower the current, the more complete was the removal of divalent ions. Current is measured in Ampere or Coulombs/sec. It specifies how many electrons flow in a conductor at a given time past a certain spot (Equation 1). One Ampere signifies one Coulomb (6.24×10^{18}) electrons passing one point in a second (1 Amp= 1 Coulomb/sec). One mole of electrons has a charge of 1 Faraday (=96500 coulombs) [26].

*Number of ions flowing / second = (current in amps * Avogadro's number) / Faraday's constant*

Equation 1: Number of ions flowing per second through a membrane at a certain point.

The removal pattern of ions is explained in the Nernst-Planck flux equation. This equation is a conservation of mass equation which is used to account for the motion of a charged molecule or ion in a liquid. The flux of ions depends on an ionic concentration gradient and an electric field [27]. The lower the initial concentration of the divalent Ca, Mg, SO₄, and the beneficial K⁺ ions compared to Na and Cl the stronger the depletion of these ions in the transport layer adjacent to the membrane. The boundary layer effects are more pronounced at higher applied current densities resulting in reduced transport of ions with a low initial concentration [25].

5. Copper

Copper is a transition metal and can have multiple oxidation states and, therefore, no constant charge. Cu²⁺ is more stable than Cu¹⁺. "A transition metal forms one or more stable ions with partly filled d orbitals" [28]. CuCl₂ reacts with HCl or other chloride suppliers to form complex ions: the red CuCl₃⁻, and the green or yellow CuCl₄²⁻. Some of these complexes can form crystals from aqueous solution, and adopt a wide variety of structures [29]. CuSO₄ in a saline solution forms CuCl₂ (aq) and Na₂SO₄ (aq). Copper is present in rocks, soil and natural water as a mineral. It is essential to human nutrition as a trace element. Only about 10% of daily copper intake is through water consumption; the rest is from food. However, where copper pipes corrode, they can release copper into drinking water to a level that can affect its quality and safety and leave a metallic or bitter taste. Copper leaves a green-blue tint on taps, sinks, and showers [30]. An adult requires two to three milligrams of copper per day. Ingesting of higher levels of copper can cause queasiness, vomiting, diarrhea, stomach upset and headaches. Long-term exposure can cause liver damage and death. Blood and urine testing are the only accurate way to test for copper in blood [31]. Copper is also found in wine. Concentrations of more than 1mg/L have a strong influence on the quality of the wine, causing a bitter, metallic taste, and generating turbidity. Higher copper concentrations stem from the Bordeaux mixture, consisting of copper sulphate and hydrated lime, a fungicide in vineyards (Shimadzu method application SCA-120-026 Spectroscopy) [32]. ED could be used to remove this undesired copper residue. Copper is also a plant micronutrient and fertilizer [33] and as such is quite expensive. Another possible usage of the ED system is the treatment of compost leachate [34]. The leachate obtained from chicken manure piles is high in nutrients like copper, but also high in sodium chloride. While the organic matter present in the leachate may lead to membrane fouling over time, pre-filtering and a change in the direction of the current (reverse ED) could minimise the effect. Compost leachate and tea have been shown to suppress fungal diseases in plants and to improve overall yield and plant health [35]. The same applies to abattoir waste waters which often have high sodium content, limiting their use as fertiliser. Surface water and groundwater near coal mines are also polluted with copper. Shi (2013) found elevated levels of copper, zinc and arsenic in agricultural soils and wheat crops in Huaibei, China. One site was near the Shuoli coal mine. Concentrations of Cu and Zn in wheat samples from this area were above the permissible limits in edible plants set by the Food and Agriculture Organization/World Health Organization [36].

6. Coal Seam Gas (CSG) Water

Another promising application of ED is the desalination of coal seam gas water, a waste product from fracking. The Australian National Water Commission stated that the Australian CSG industry extracts more than 300 gigalitres of water each year, although estimates vary widely. Simultaneously, the industry will produce 31 million tonnes of waste salt over the next 30 years (Queensland Gas Company, QGC). This water also contains copper, heavy metals and radionucleotides. Currently, the wastewater is stored in brine ponds and evaporated, and the salt stored in salt pits. The brine cannot be discarded into the ocean. Most aquatic organisms are sensitive to increases in salt content and cannot survive such an impact. For example, in Dubai highly salty brine from reverse osmosis drinking water production is pumped into the sea, and most marine life dies. CSG water also contains considerable amounts of copper and other contaminants (Table 1). Tularam and Ilahee discuss this problem in an Australian context [4].

Table 1: Contaminants in Coal Seam Gas Water

Contaminant	Max. Detected concentration in water discharged into Condamine River (ug/L)	Toxic to aquatic organisms when undiluted
Boron	1200	yes
Bromide	48	yes
Iodine	25	yes
Aluminium	20	yes
Chloroform	6.8	
Zinc	4	yes
Barium	3.2	
Chromium	1	yes
Copper	1	yes
Nickel	0.8	yes
Cadmium	0.6	yes
Lead	0.2	yes

Fairview Project Area EMP Appendix B, Santos library [37], [38].

7. Materials and Methods

Figure 1 shows the instrument in the laboratory of USQ, Toowoomba, Australia. This unit provides three independent hydraulic circuits with flow meters (40-400l/h), power supply and pumps. The ED cell stack ED 20 contained 20 cell pairs, formed by 20+1 cation exchange membranes, 20 anion exchange membranes, and 2x20 spacers. The experiments were conducted using the recycling batch mode [39]. There are three circuits. The diluate circuit is where the ions are removed, the concentrate circuit is where the ions are collected, and the electrolyte circuit is where the electrolyte solution circulates. Table 2 shows the membrane specifications.



Figure 1: PCell electro dialysis unit at USQ, Toowoomba, Australia

Table 2: Two Chamber Electro dialysis Cell Membrane Specifications

Membrane Size	262x 125mm
Active membrane area	207 sq cm/ membrane
Processing length	220 mm
Cell thickness	0.5 mm
Number of cell pairs	20
Material Anode	Pt/Ir-coated Titanium
Material Cathode	V4A Steel
Electrode housing material	Polypropylene

The other instruments used were as follows: Speer Scientific handheld Conductivity-TDS-Salinity meter from Pro Sci Tech. TPS smartChem pH Meter with ATC Temperature probe. Power supply HCS-3400/3402/3404 Laboratory Grade; and High Immunity Switching Mode Power Supply with Rotary Encoder Control provided with the instrument. A small electric pump was used to empty the tanks before commencement.

8. ED solutions

- Diluate: Two and a half grams of Copper II Sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), a fungicide, and 250 g of laboratory grade sodium chloride were dissolved in 25L of distilled water. The initially measured conductivity was 16 mS/cm or 10720 ppm Total Dissolved Solids (TDS); the copper content was a calculated 35.2 ppm.
- Concentrate: The initial electric conductivity (EC) of the concentrate was 23.7mS. The solution was a leftover from a previous experiment. The volume at the start was four litres.
- Electrolyte: The electrolyte solution consisted of 14.2g sodium sulphate/L (approx. 1 molar). The EC of the electrode rinse was 16.78mS/cm. It did not decrease significantly until the end of the experiment. The electrode rinse volume was about four litres and did not change significantly.

- Standards: A commercial copper standard solution (High-Purity Standard, from Choice Analytical, 1000 $\mu\text{g/L}$, in 2% HNO_3) diluted to different concentrations with distilled water was used. Each diluted standard had 1% NaCl added.
- Voltage: The voltage was 10V. The Amperage during this time decreased from 1.6 to 0.8A. The resulting pressure at the inlet and outlet of the membrane was around 0.3 bars at the inlet and 0.4 bars at the concentrate outlet. The flow rates for the diluate and concentrate streams were about 50-60L/hr. The electrolyte flow rate was approximately 125 L/hr.

The samples for the Atomic Absorption Spectroscopy (AAS) analysis were taken 10 minutes apart from the outlet at the top of the testing unit where the water flows back to the diluate tank. The experiment run over 180 minutes; two concentrate samples were taken at the beginning and the end of the experiment. Copper was measured with the AAS absorption method. The lamp was a combination lamp for foundry effluents, with a measurement range of 1-25 ppm Cu. The lamp current (low peak) was 20 mA. The wavelength of copper is 324.8 nm, the slit width 0.7 nm, and the lamp mode BGC-D2 (Background correction with a Deuterium lamp). The fuel gas flow rate (L/min) was 15 l/min, the flame type Air- C_2H_2 , the burner height 7 mm and the burner angle degree zero. The calibration curve (Figure 2) shows a range of 0.1- 25ppm. The regression coefficient was 0.9967, which is excellent.

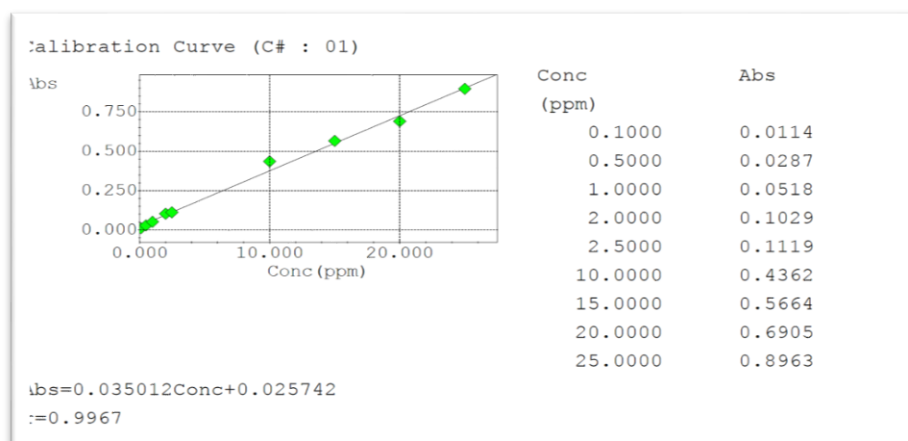


Figure 2: AAS Copper calibration curve. Standards had 1% NaCl added.

9. Results Copper and Salinity Removal in Copper Sulphate Solution

Copper was removed with a constant voltage of 10 V. Copper was measured undiluted in the AAS absorption mode. The diluate had an initial salt concentration of 10,000 ppm (10g NaCl/L). Emission mode proved unsuitable to measure the high Na concentrations in both the diluate and the concentrate. A dilution with a factor of 1000 gave unsatisfactory results for both sodium and especially for copper, as the dilution error was too big. Therefore, the ppm (mg/L) TDS, containing both copper and NaCl , was calculated from the EC in $\mu\text{S/cm}$, and a conversion factor of 0.67 was used [40]. The copper content in the diluate went down logarithmically from the calculated concentration of 35.2 ppm Cu to 1 ppm which is a removal rate of 97% (Figure 3).

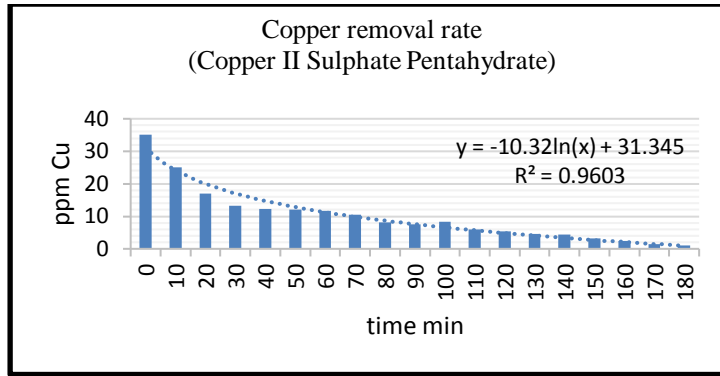


Figure 3: Removal rate of Copper in a saline Copper II sulphate solution at 10V.

The conductivity of the diluate at the beginning of the experiment was 16 mS/cm (10.72g TDS/L). The conductivity of the diluate at the end of the experiment was 10.14 mS/cm (6.79 g TDS/L) (Figure 4). The difference was 3.93 g TDS/L. The removal was linear. The conductivity of the concentrate at the start was 23.7 mS/cm (15.88 g TDS/L) at the end it was 41.4 mS/cm or 27.74 g TDS/L. The difference between start and end was 11.86 g TDS/L in the concentrate. As the concentrate solution increased from 4L to 5.8L over the run, $1.8L * 27.74g + 4L * 11.86g = 97.37$ g TDS were transferred from the diluate to the concentrate.

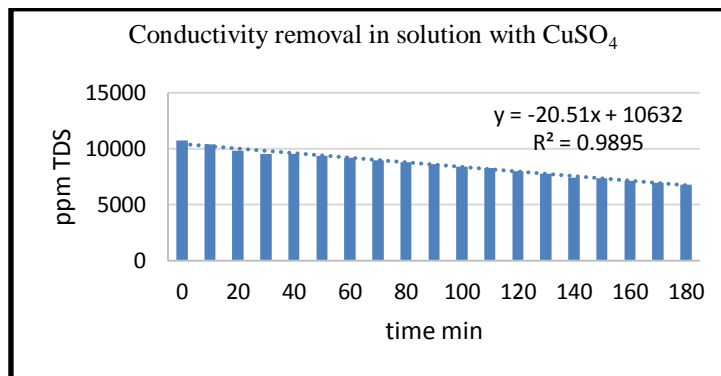


Figure 4: Conductivity removal rate of Copper in a saline Copper II sulphate solution at 10V.

Sulphate was removed in a linear way, and its removal rate was faster than that of the conductivity. The starting concentration was 46.33 ppm, and the end concentration was 15.92 ppm (Figure 5).

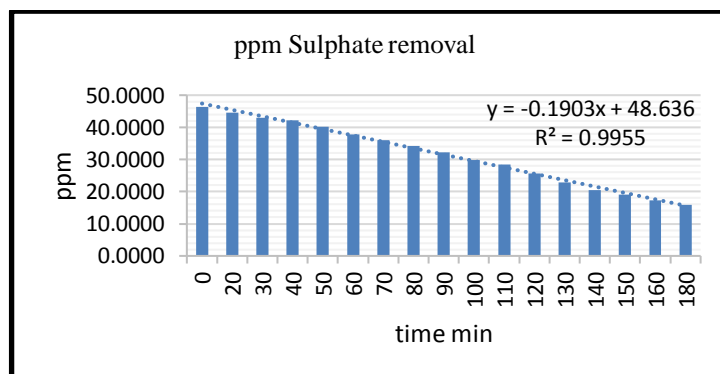


Figure 5: Sulphate removal rate in the diluate, measured with an ICS-2000.

The pH went up insignificantly from 5.7 to 6.18 during the run. The temperature increased from 23.7 to 28.1 degrees Celsius. The volume of the diluate went down from 25L to 23.2L. Conversely, the volume of the concentrate increased from 4 to 5.8 L. The diluate lost about

10% of its volume. The current went down from 1.6 A to 0.8 A. There were strong positive correlations between Ampere and conductivity in the diluate, Ampere and copper content in the diluate, as well as the conductivity in the diluate to copper content in the diluate. Conversely, there were negative correlations between these in the concentrate. The correlations between conductivity and copper content as well as sulphate content were the same (Table 3).

Table 3: Correlations between results

Correlations in Diluate Solution	Correlation Coefficient r
Ampere: Conductivity (mS/cm)	0.86
Ampere: Cu content (ppm)	0.95
Conductivity (mS/cm): Cu content (ppm)	0.91
Conductivity (mS/cm): SO ₄ content (ppm)	0.91

10. Different Experiment using Copper Chloride Solution

In this experiment, instead of copper sulphate, 2.5g copper chloride was added. Copper was removed with a constant voltage of 10 V. The copper content in the diluate went down logarithmically, and the removal rate of copper was 98% (Figure 6). The concentrate solution looked greenish- blue at the end, (the colour of the copper II chloride in water solution, which is greener when more Cl⁻ is present, and bluer when less Cl⁻ is present [41]) which implies that copper surpassed the membrane. The diluate still had a slight bluish tinge at the end of the experiment. The colour in the concentrate was the same as the diluate but a darker hue.

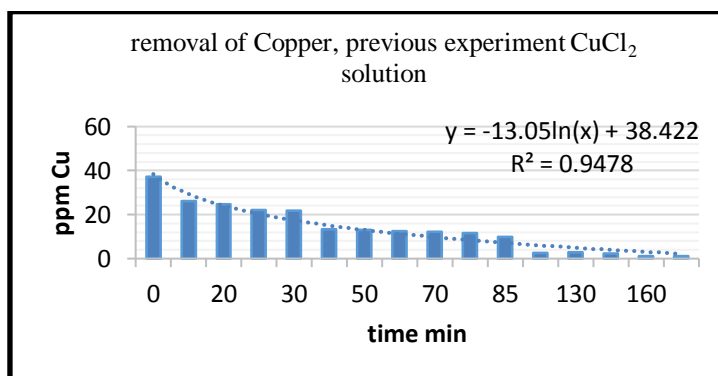


Figure 6: Removal of copper from a copper chloride solution in a previous experiment, 10V.

Figure 7 shows an experiment where the conductivity removal rate was faster than in the first experiment. In this experiment, the membrane has been cleaned before the experiment. This data shows that it is hard to compare measurements in this ED system.

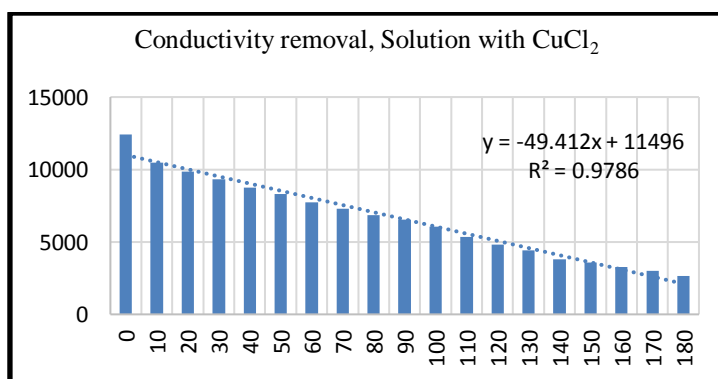


Figure 7: Decrease in conductivity in the diluate in another run, also 10V.

11. Discussion

We investigated the removal rate of copper chloride and copper sulphate in comparison to sodium chloride using a non-ion selective ED membrane with a sodium sulphate electrolyte solution. Conventional ED membranes have minor differences in transport properties for different ions, and the electrolyte solution influences removal efficiency, but these differences are not enough to obtain a separation. Selective anion or cation exchange membranes have considerably different passage conditions for monovalent and multivalent ions. A separation between these ions by their charge, the applied voltage (in ED) and the pressure (in NF) is possible [20, 21]. In water desalination, it is currently standard practice to remove as many sodium, calcium and other cations from the water as possible as well as organic matter, algae, colour and other impurities. But not all applications require total removal of these elements, in fact, it is often better to leave them in the water where they can act as fertilisers and nutrients. If beneficial cations like calcium, potassium, magnesium, and to a certain extent plant micronutrients like copper and other minerals remain in the water, it leads to a saving in fertiliser and soil improvement costs. Micronutrient fertiliser is expensive and could be saved when using partially desalinated water treated with the ED method. If copper and other micronutrients are preserved in the diluate, it could be beneficial from a plant nutritional standpoint. Calcium and magnesium in water prevent heart disease in humans. In soils they prevent sodium from causing too much damage (hard setting) by keeping the sodium adsorption ratio (SAR) of soil water low. SAR describes the ratio of sodium to calcium and magnesium in soil water and irrigation water. Usually, the higher the SAR, the more the soil structure is damaged by this water [42].

$$SAR = \frac{Na^+}{1/2\sqrt{Ca^{2+} + Mg^{2+}}}$$

Equation 2: Sodium Adsorption Ratio (SAR)

Another valuable formula for the determination of the toxicity of an irrigation solution on soils is the Exchangeable Sodium Percentage (ESP); (Equation 3). ESP is the ratio of sodium ions in the soil solution to the sum of calcium, magnesium and potassium ions [43]. The presence of Ca and Mg in irrigation water automatically decreases the Exchangeable Sodium Percentage (ESP) of the irrigation/ fertigation solution. Lower ESP means that larger amounts of salt in the irrigation water can be tolerated without causing harmful effects and soil conductivity for water can be preserved.

$$ESP = \text{Exchangeable} \left\{ \frac{Na}{Ca+Mg+K+Na} \right\} * 100$$

Equation 3: Exchangeable Sodium Percentage

The partial desalination of brackish ground and river water, as well as CSG water using electro dialysis, also leads to a saving of energy. To use partial demineralisation, it is necessary to determine the best parameters for any given water.

The main findings of this study were that in the range of this experiment, the conductivity was removed linearly, and the copper was removed logarithmically. Copper can be present as oxidation stages 1⁺, 2⁺ and 3⁺. In copper from a copper sulphate solution, most copper should be Cu²⁺. Possibly the Cu²⁺ was removed faster than the Cu¹⁺ which created the logarithmic curve. The copper was removed faster than sodium chloride. When looking at the effective ionic radii (which is a function of spin and ionic charge) of these elements, the faster removal of copper is explained. Copper in all its oxidative stages has a much lower effective ionic radius than sodium and chloride (Na¹⁺ has a radius of 102pm, Cl¹⁻ has 181, Cu¹⁺ has 77, and Cu²⁺ 73 [44]). The removal rate also depends on the charge of the ion. The higher the charge, the faster

the ion is removed (Mass/charge ratio). With the methods available to us, it could not be determined how much of each species of copper was present. ICP-MS analysis would be needed to determine the copper species exactly. However, Cu^{2+} is the more common species [28], therefore it is assumed that it was present in the solution in a higher percentage. The typical copper concentration in a hydroponic fertigation solution is 0.08-0.2 ppm. For the copper sulfate solution to reach a concentration of 0.2 ppm copper, the instrument would have to run approximately 304 min, when projecting the curve into the future. After this time, the salt content would be 4.192 g TDS/L, which equates to an EC of approximately 6.25 mS/cm which would still be far too high for fertigation/irrigation. To completely reduce 0.93g of Cu^{2+} at a current of 10 Ampere in an ideal situation where no membranes are involved, would only take about 4.6 minutes (stoichiometric calculation). Sulphate should be present at 50-120 ppm in the fertigation solution [45]. After a 304 min run the sulphate would be zero when forecasting the curve (Figure 5). The sulfate was removed linearly as well. Because the sulphate is divalent, it was removed at a slightly faster rate than salt. Although the curve for sodium chloride (or TDS) elimination in both experiments was linear, previous experiments by the author showed it is also logarithmic when higher starting concentrations were used.

A sodium sulphate solution was used as the electrolyte rinse. In the PCELL instruction booklet, the stronger sodium amido sulphonate solution is recommended when the pH of the diluate is neutral and mono- and divalent ions are present. One result of this study was that for the non-ion selective ED membrane used, an expensive electrolyte solution like sodium amido sulphonate is not necessary to remove most of the copper. The copper chloride concentrate solution looked greenish- blue at the end, which implies that copper surpassed the membrane. The diluate still had a bluish tinge at the end of the experiment. The results show that most copper ions passed the membrane into the concentrate, but complex formation could also have led to some deposit on the membrane. Depending on the temperature and concentration copper chloride can form complexes [46]. These can be the blue $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, or the halide complexes of $[\text{CuCl}_{2+x}]^{x-}$. These can be red or yellow. Further investigation, for example, analysis of the membrane with a Scanning Electron Microscope, is recommended. The literature review showed that the lower the initial concentration of the divalent Ca, Mg, SO_4 , and the beneficial K^+ compared to Na and Cl, the stronger the depletion of these ions in the transport layer adjacent to the membrane. The boundary layer effects are more pronounced at higher applied current densities resulting in reduced transport of ions with a low initial concentration [25]. In this experiment, the initial concentration of copper and sulphate to sodium chloride was less than one percent. This could also be a reason for the faster removal of copper and sulphate. The experiments were conducted with low flow rates which reduced permeate flux. The pH results were mainly inconclusive. Measuring the pH in the saline solutions proved difficult and is not recommended because the salt interferes with the measurement. In the copper sulphate diluate, the pH increased slightly during the run from 5.7 to 6.18. The increase of the pH could be due to the temperature increase in the diluate although the pH meter had a temperature correction. At high currents, the pH tends to go down because water is split [47]. As the current was low (the max. voltage of the benchtop unit is 30V) there was no water splitting in the diluate, and possibly none in the electrolyte solution, which can accumulate hydrogen gas at the top. Hydrogen gas can be re-used as an energy source. However, higher voltages would be necessary to achieve this. The current in the diluate went down from approximately 1.6 to 0.8 Ampere, which can be explained by the depletion of ions in this solution. There were positive correlations between Ampere: Conductivity in the diluate and Ampere: Cu removal. The current went down when the conductivity and copper content in the diluate went down. On the other hand, there were negative correlations between conductivity in the diluate and pH, and current (Amp) and pH. All these correlations were not very strong. There was, however, a significant correlation between removal of salt and copper. Please note that this is a comparison

between a logarithmic and a largely linear curve for conductivity. The correlation between copper and conductivity and sulphate and conductivity were the same, which shows that the measurements in this run were correct. The diluate in all runs lost about 10% of its volume. Therefore, the efficiency of the benchtop unit is in the range of industrial electro dialysis plants. In the diluate, the temperature went up by four to five degrees Celsius during the runs. This energy could be re-used. Relatively easy benchtop experiments can be conducted to estimate the removal rates of different micronutrients compared to salinity by extrapolation of the generated curves. However, the reproducibility of the experiments is not ideal. Membrane fouling and aging are an issue. It is important that the membranes be kept in a clean state, and the testing conditions are always the same. Furthermore, the membrane should never be allowed to dry out but stored in a saline solution. Different starting temperatures also result in different removal rates; therefore, a temperature controlled environment must be used, or the influence of the temperature must be accounted for in a correction formula. There was no temperature control in this experiment.

12. Conclusions and Outlook

The literature review revealed that although there are many studies concerning the electro dialysis process, the comparability of these studies regarding the removal of individual cations or anions is often difficult due to a large range of different testing conditions. Although there are some studies relating to the elimination of copper in brackish water using ED, not enough research has been done. This preliminary study only aimed to show one set of possible conditions. It demonstrated that partial desalination and partial copper removal was possible with a very low energy input, which could be supplied for example by solar energy. Forecasting of desalination and de-mineralisation curves obtained from the benchtop ED instrument could provide valuable insights into the exact time necessary to get irrigation water of a certain quality. For example, clay soils can tolerate water that has a higher salinity due to its higher cation exchange capacity, and plants like tomatoes can tolerate a higher level in their irrigation water. However, the complexity of ions present and interactions between ions and other substances in the water, like humic acids or other organic matter, makes modelling challenging. As different soils and plants tolerate varying levels of salinity and custom made water products can save precious resources, especially in a context where these are limited, this research is essential for the future. Similar ED methods could be used to treat CSG water and saline river water to produce a custom made product according to the proposed use in an energy and resource efficient way. Different voltages and temperatures should also be assessed. Also, various micronutrients should be tested under different conditions. Finally, ion-selective membranes can also be utilised. Using ED for desalination and leaving the beneficial divalent ions in the treated CSG water could result in an enormous cost reduction for coal seam gas companies. Also, it would lead to a beneficial effect on soil and human health and a cost saving for the farmers.

13. Acknowledgements

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15. Appendix

Table 4: Raw data Copper Sulphate experiment

Time (min)	Volt (V)	Amp	mS/cm Dil.	mS/cm Conc.	pH dil	Temp dil	Vol dil	Vol conc	ppm TDS	Cu ppm Dil	Cu ppm Conc	SO ₄ ppm Dil
0.0	10.0	1.6	16.0	23.7	5.7	23.7	25.0	4.0	10720.0	35.2	0.0	46.32
10.0	10.0	1.5	15.5	-	5.9	24.1	25.0	4.0	10385.0	25.1	-	-
20.0	10.0	1.3	14.7	-	6.0	24.5	25.0	4.0	9835.6	17.1	-	44.55
30.0	10.0	1.2	14.3	-	6.0	24.9	24.8	4.2	9560.9	13.3	-	43.03
40.0	10.0	1.1	14.2	-	5.9	25.1	24.8	4.2	9514.0	12.2	-	42.14
50.0	10.0	1.0	14.0	-	5.9	25.4	24.5	4.5	9353.2	12.0	-	40.09
60.0	10.0	0.9	13.7	-	-	25.7	24.5	4.5	9179.0	11.6	-	37.69
70.0	10.0	0.9	13.4	-	6.0	26.0	24.4	4.6	8978.0	10.6	-	35.9
80.0	10.0	0.9	13.1	-	6.0	26.2	24.4	4.6	8790.4	8.1	-	34.23
90.0	10.0	0.8	12.8	-	6.0	26.4	24.3	4.7	8596.1	7.6	-	32.2
100.0	10.0	0.8	12.5	-	6.0	26.7	24.2	4.8	8401.8	8.3	-	29.9
110.0	10.0	0.8	12.3	-	6.0	26.8	24.1	4.9	8261.1	6.0	-	28.35
120.0	10.0	0.8	12.0	-	6.1	27.1	24.1	4.9	8013.2	5.4	-	25.69
130.0	10.0	0.8	11.6	-	6.1	27.1	24.0	5.0	7765.3	4.6	-	22.83
140.0	10.0	0.8	11.1	-	6.1	27.7	23.9	5.1	7416.9	4.4	-	20.45
150.0	10.0	0.8	11.0	-	6.1	27.8	23.8	5.2	7390.1	3.2	-	19.1
160.0	10.0	0.8	10.6	-	6.1	28.1	23.5	5.5	7128.8	2.4	-	17.29
170.0	10.0	0.8	10.4	-	6.2	28.2	23.5	5.5	6954.6	1.5	-	-
180.0	10.0	0.8	10.1	41.4	6.2	28.1	23.2	5.8	6793.8	1.0	9.9	15.92