

# ELECTROCHEMICAL OXIDATION OF IRON AND MANGANESE IN GROUNDWATER

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## **ABSTRACT**

Groundwaters in the Waikato region are often naturally contaminated with iron and manganese at levels of up to 20.0 mg/L and 0.9 mg/L respectively. When present with elevated levels of silica and/or organic matter, these waters upon oxidation can form highly stable and difficult to filter brownish colloidal suspensions. Usual treatment methods involve either ion exchange to remove the metal, when present at low concentrations, or chemical oxidation using calcium hypochlorite to remove the metal as hydrous oxide precipitate. An electrochemical method using a novel porous electrode flow through (PEFT) cell design was found to be 100% effective in oxidizing iron and manganese after a single pass through the cell providing 3 g/L sodium chloride was added. Without sodium chloride addition the 10 to 12 mg/L of naturally occurring chloride gave 47% instant oxidation at 25 V. This percentage was increased to 70% when the chloride concentration was raised to 250 mg/L (well below the chloride drinking water standard). Complete oxidation and rapid settling was achieved by four passes through the cell at voltages as low as 10.5 V. The power consumption required to produce drinkable water was 18 kWh/m<sup>3</sup>.

## **KEYWORDS**

**Iron water, Porous electrode flow through cell, water treatment**

# 1 INTRODUCTION

New Zealand groundwaters are known to have high levels of iron and manganese, naturally derived from water rock interactions (Rosen, 2001). Iron and manganese will be present in groundwater if dissolved oxygen levels are very low because the reduced forms of iron and manganese are much more soluble than the oxidized forms. High iron and manganese containing aquifers are commonly associated with peat layers, slow moving waters and consequent oxygen depletion. Groundwater makes up to 90 percent of Waikato Region's freshwater supplies and is used for drinking water, industrial, agricultural and horticultural supplies. About 400 bore wells are drilled annually (Hadfield, 2001). The ground water in the region is often naturally contaminated with iron and manganese of the order of 20.0 mg/L iron and 0.9 mg/L manganese. The problem associated with the removal of this iron and manganese is that oxidation by forced aeration often forms highly stable brownish colloidal suspensions which do not settle on standing and are also difficult to filter. Currently, bores with this problem groundwater are often abandoned because treatment requires both expensive addition of chemicals and filtration. These problem waters have also been found to contain high levels of dissolved organic carbon and silica (derived from the peat layers and the volcanic subsoil) which are believed to be implicated in the formation of the stable colloidal suspensions. It has been found that rapid chemical oxidation favours the formation of aggregated flocs which facilitates the removal of the contaminant metal ions (Carlson and Schwertmann, 1987). This paper describes an electrochemical method that provides an effective means of achieving the rapid oxidation necessary to treat iron and manganese contaminated groundwater to drinking water standards.

Electrochemical oxidation of contaminants in water can occur through two different oxidation mechanisms, first the direct oxidation and the second is indirect oxidation (Anglada et al., 2009). Direct oxidation involves two steps: (1) diffusion of pollutants from the bulk solution to the anode surface and (2) oxidation of pollutants at the anode surface. During indirect electrochemical oxidation, a strong oxidizing agent is electrochemically generated at the anode surface and this oxidizes the contaminants. The indirect oxidation mechanism is more favourable in contaminant removal processes and is used frequently in the water treatment applications (Chiangi et al., 1995, Deng and Englehardt, 2007, Murphy et al., 1992, Yang and James, 2007). While convenient, electrochemical methods have not found widespread application in water treatment because of the high cost of electrodes, high voltages and high power consumption. The present work has addressed these drawbacks by the development of a novel PEFT cell using carbon and stainless steel electrodes, and a cell configuration that achieves good current densities at voltages below 25 V. The present work describes cell performance as a function of sodium chloride concentration, cell voltage and number of passes through the cell.

## 2 A NOVEL POROUS ELECTRODE FLOW THROUGH (PEFT) CELL

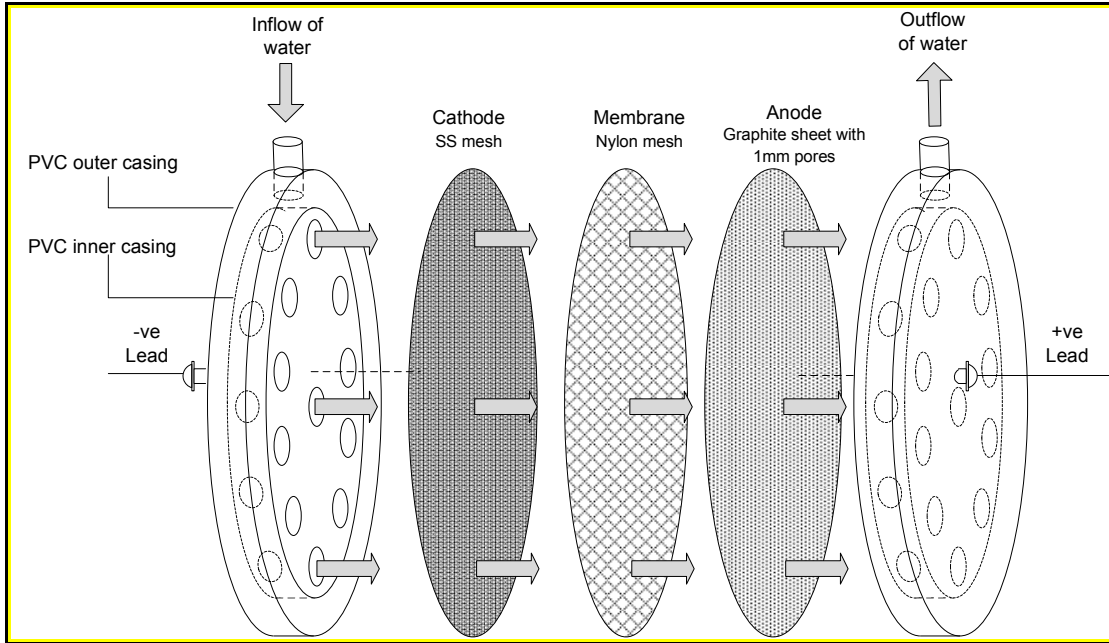
The porous electrode flow through cell design provides a dynamic electrolytic system, stepping away from the conventional static plate electrodes immersed in a bath. The greatest advantage of the design is that it can function as an inline in-situ water treatment system. The complete sealed design allows it to be functioning as an inline device which can be pressurized and vary the flow rates to match the treatment level. A key feature of the cell is that the assembly of electrodes allows reduction of the inter-electrode gap to a fraction of a millimeter, reducing resistive losses and allowing less efficient but lower cost materials to be used for the electrodes. The cost of electrolytic treatment can thus be made comparable with other available water treatment technologies (Guohua, 2004).

### 2.1 DEVELOPMENT OF THE CELL

A schematic diagram of the components of the novel flow through cell is given in Figure 1. The cathode used was a stainless steel mesh (0.25 mm sieve size, wire diameter 0.10 mm) cut into a disc. The anode was constructed from 2.5mm thick graphite sheet. This material was chosen because of its electrical properties, resistance to oxidation and compatibility with drinking water supplies. The anode had a hole density of 8 holes per square centimeter giving an effective surface area of 48.3 cm<sup>2</sup>. Titanium wires were used as the electrical connecting leads. The membrane or the electrode separator was a nylon mesh (1.0 mm sieve size, fiber diameter 0.12 mm) giving a constant calculated from the cell geometry of approximately 2.5 x 10<sup>-4</sup> cm<sup>-1</sup>. The water enters into the cathodic end of the PVC outer casing and moves into the inner casing where the influent distributes

evenly and moves horizontally through electrodes into the anodic inner PVC casing and flows out to the outer casing and discharged as the treated electrolyte. The electrodes separated by the nylon mesh were sandwiched using the cathodic and anodic PVC compartments and were held together by 8 stainless steel nuts and bolts.

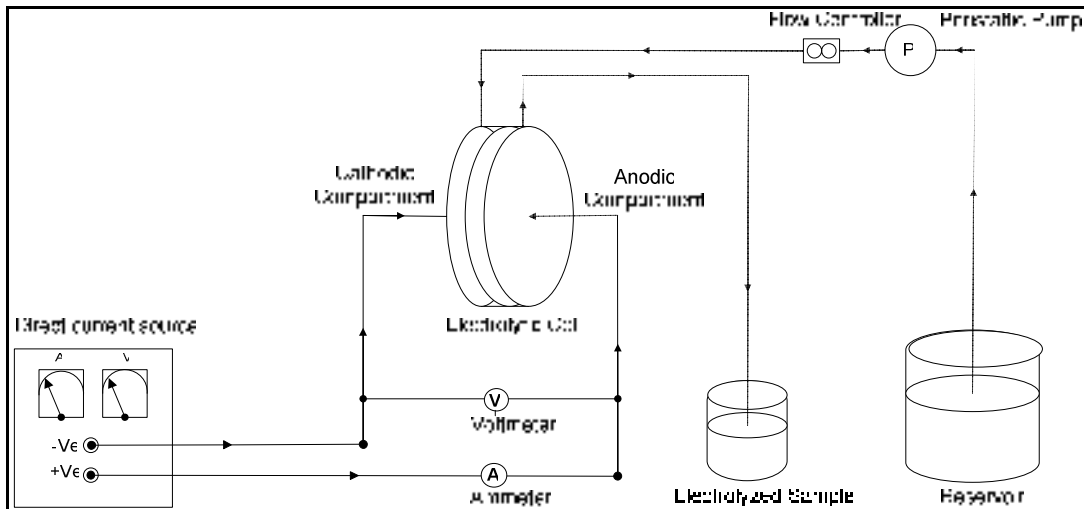
Figure 1: Schematic diagram of the porous electrode flow through electrolytic cell assembly.



## 2.2 EXPERIMENTAL SETUP

The experimental arrangement is shown in Figure 2. The flow through cell was connected to a direct current source with a maximum of 5A and 30V (Dick-Smith Electronics, 0-30V, 5A regulated DC power with variable current limit, input 230-240V ac 50Hz) through an ammeter (Fluke 73 III Multimeter) and a voltmeter (Fluke 77 Series II Multimeter) to measure the current and voltage. A peristaltic pump (Watson Marlow 504S, with regulated DC power supply) with a flow controlling knob was feeding the water to the cell and the out flow was collected in a measuring cylinder. The pH was measured using a Mettler Toledo (Seven Easy) pH meter, and the conductivity was measured using a CyberScan100 Con. Eutech Instrument.

Figure 2: Diagram of the chlorine electro-generator.



### 3 OXIDATION OF IRON AND MANAGANESE IN BORE WATER

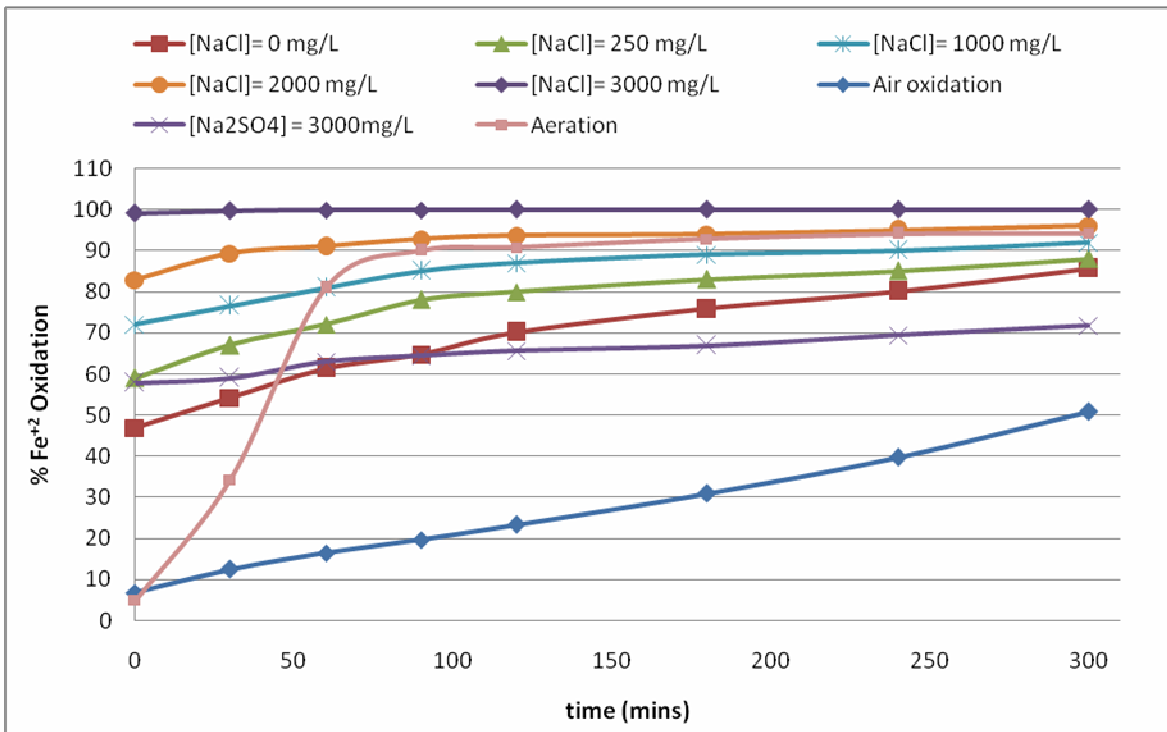
#### 3.1 MATERIALS AND METHODS

The groundwater was passed through the cell to electro-oxidize the metal ions and to allow subsequent aggregation and settling. The percentage of ferrous to ferric oxidation was determined by 1,10 Phenanthroline, spectrophotometric method using CARY 100 Scan UV-VIS spectrophotometer (Vogel, 1997). The supernatant was filtered with a 0.45 $\mu$ m filter and analysed using ICP-MS PerkinElmer SCIEX ELAN DRC II for residual metal ions. The sodium chloride added to the groundwater was BDH Analar grade reagent. Turbidity of the treated groundwater samples were measured using a HACH 2100P Turbidimeter. The active chlorine level in treated water was determined by an iodometric titration (Vogel, 1997).

#### 3.2 ELECTRO-OXIDATION OF IRON

Electro-oxidation of natural groundwater with a conductivity of 266  $\mu$ S/cm (10 to 12 mg/L NaCl) achieved only 47% immediate iron oxidation at 5 A and 24.7 V. Addition of sodium chloride to the groundwater increased instantaneous oxidation efficiency. Oxidation efficiency was studied at constant current density (78.6 mA/cm<sup>2</sup>) and with increasing additions of sodium chloride, shown in figure 3. At a level of 3.0 g/L of added salt and at electrolytic conditions of 5A, 6.1V, conductivity 3.9 mS/cm and a flow rate of 190 mL/min, instantaneous oxidation of 99% of the iron was achieved (Fig. 3). In contrast, the addition of 3.0 g/L sodium sulphate immediately oxidized only 58% of the iron present in the groundwater. Also shown on figure 3 is data for natural and forced air oxidation. While forced air oxidation is much more rapid than natural air oxidation, neither air oxidation curves indicate significant instantaneous oxidation.

Figure 3: Electro-oxidation of iron in groundwater at constant current density 78.6 mA/cm<sup>2</sup> and flow rate of 190 ml/min, single pass through the cell.

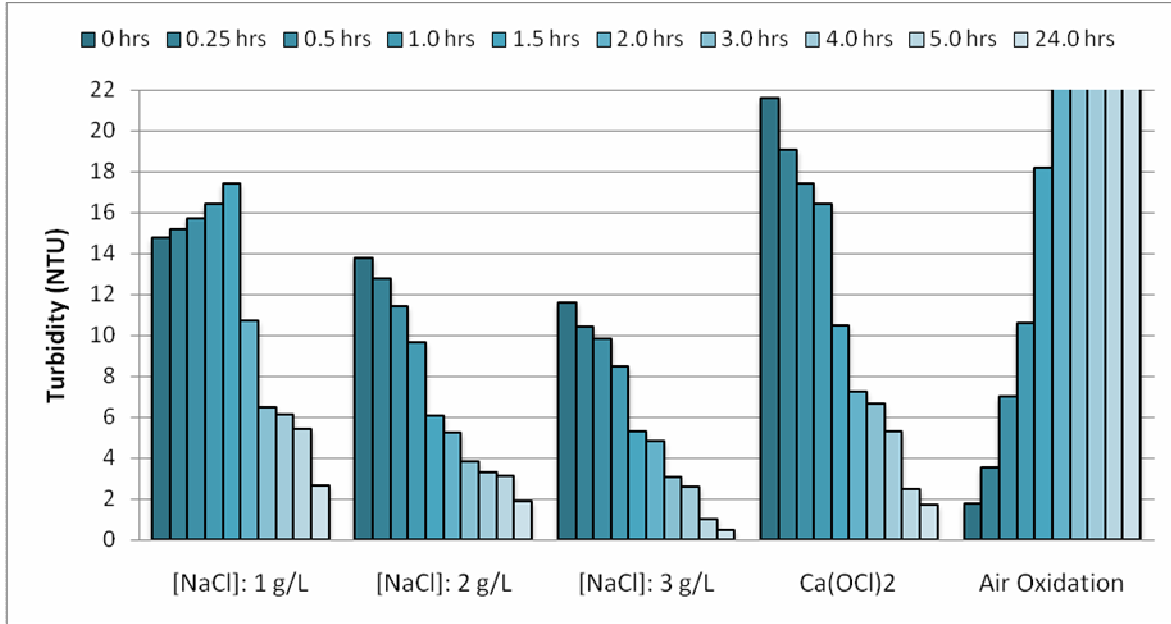


#### 3.2 OXIDATION AND TURBIDITY

The turbidity of the 100% oxidized groundwater sample with the 3 g/L of NaCl added settled rapidly and lowered metal to levels well below drinking water standards within 5 hours (fig.4). Under these conditions the ferric ions hydrate, hydrolyse and precipitate as ferric hydroxide. Rapid aggregation and settling is probably facilitated by the relatively high ionic strength (Gregory, 2006). At 2 g/L added NaCl, results are similar but do not achieve the same levels of oxidation or clarification, presumably because of the lower levels of chlorine

generated (see figure 5). At 1 g/L added NaCl, lower initial oxidation (see figure 3) meant that oxidation continued after exiting from the cell and turbidity also increased in sharp contrast to the higher chloride concentrations where turbidity decreased immediately after the water exited the cell.

Figure 4: The turbidity measurements of the electro-oxidized bore water with time.

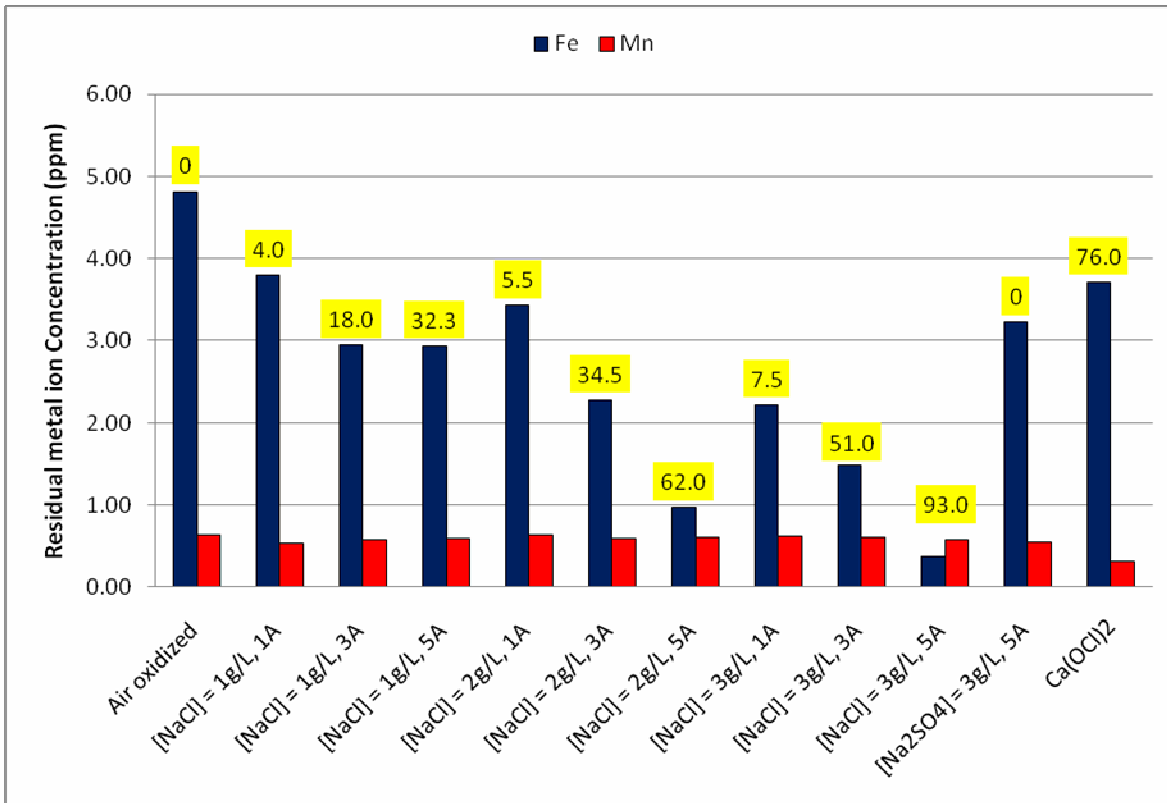


The fraction of iron that does not undergo instantaneous in-cell oxidation appears to undergo further slow (air) oxidation upon exiting the cell. It settles quickly but not to the low turbidity levels achieved at 2 and 3 g/L. Results for chemical oxidation using calcium hypochlorite (see figure 4), indicate that the amount of chlorine liberated from the hypochlorite was less effective than a similar amount of chlorine produced electrochemically in the 3 g/l experiment. Even after 24 hours, drinking water turbidity threshold (Less than 1 NTU) was not achieved. In sharp contrast to these results the turbidity of the air oxidized bore water rose sharply with increasing degree of oxidation, reaching a maximum after approximately 5 hours and 24 hours respectively for the natural and forced air oxidation experiments. There was no significant settling after many months

### 3.3 METAL REMOVAL SINGLE PASS TREATMENT

Data for metal remaining after filtration for a single pass through the cell at three NaCl concentrations using three current densities are shown in Figure 5. Data for Na<sub>2</sub>SO<sub>4</sub> at a concentration equal to the highest NaCl concentration and at the highest current density, along with data for air oxidation, are also included for comparison. The treated water was allowed to stand for 3 hours and then filtered through 0.45 μm filters and the filtrate analysed for soluble (non oxidized) iron and manganese. Also included on Figure 5 above each data bar are the amounts of chlorine that were produced in an analogous experiment with solutions made up to contain the same electrolyte concentrations but no iron or manganese.

Figure 5: Soluble iron and manganese content in water after 3 hrs post single pass electro-oxidation at a flow rate 190 mL/min.



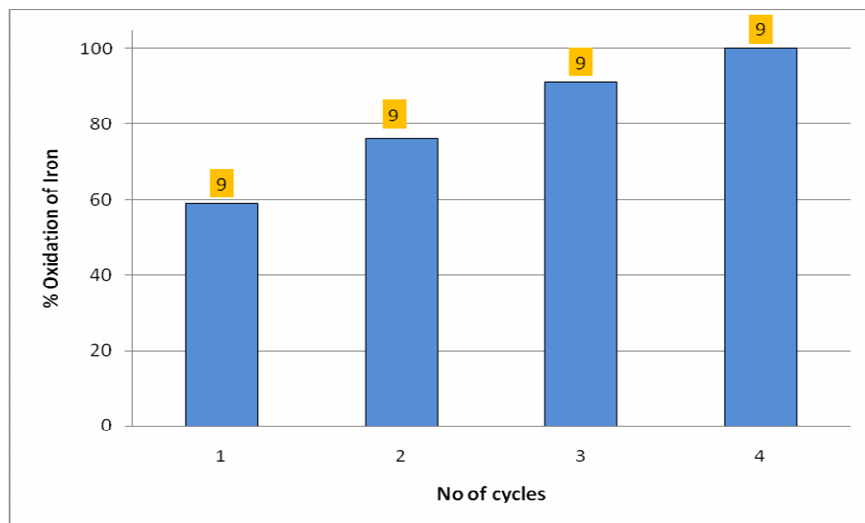
Increasing the chloride concentration reduced the concentration of remaining non-oxidised iron consistent with the greater production of chlorine. The oxidation and removal of manganese was very much less than that of iron presumably because the reduction potential of manganese is much higher. Even at the highest concentration of sodium chloride and highest current density iron and manganese concentrations (0.3 and 0.5 mg/L respectively) were higher than the New Zealand drinking water standard levels (0.2 mg/L and 0.4 mg/L respectively). The result obtained when sodium sulphate electrolyte was used, when compared with the result for air oxidation alone, indicated a level electro-oxidation where chlorine species were absent. This could be due to transient reactive oxygen species (ROS) reported to be formed during the electrolysis of water (Fiessinger et al., 1981, Kerwick et al., 2005, Panizza and Cerisola, 2005, Polcaro et al., 2007) or be the result of direct oxidation of the metal species at the electrodes (Anglada et al., 2009, Chiangi et al., 1995, Deng and Englehardt, 2007). However the effect could be due to the higher oxygen concentrations produced as a result of water electrolysis.

The problem of these high residuals, both of the high metal and when used the high chloride, was addressed by designing a multiple pass system.

### 3.3 MULTIPLE PASS TREATMENT

An acceptable chloride level in drinking water is 250 mg/L (Ministry of Health, 2005). The problem to be solved was how to use the electrochemical device to achieve adequate metal removal at this salt concentration. The approach adopted was to use a multiple pass system. Data for successive treatment cycles at 250 mg/L NaCl are shown in Figure 6. Total oxidation of the iron was achieved after 4 cycles.

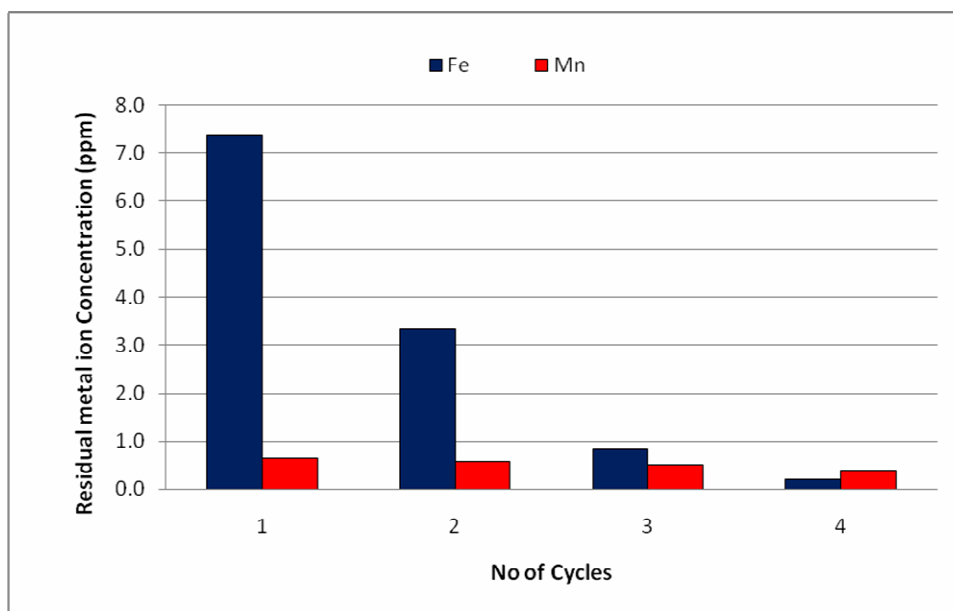
Figure 6: Percentage of iron oxidized in groundwater at each cycle in the multiple pass system, flow rate: 190 mL/min, [NaCl]: 250 mg/L, current density: 78.6 mA/cm. (value on top of each bar indicates the estimated chlorine generated during each cycle)



Data above each bar on the chart are the amounts of chlorine that would be generated under the same electrolysis conditions if a pure solution of NaCl was used. The total chlorine after four passes would be 36 mg/L. This compares favourably with the 93 mg/L chlorine that would be generated from the 3 g/L experiment which produced a similar level of oxidation. This reduced chlorine requirement is an important factor in treating groundwater because it will reduce the possibility of formation of chlorinated organics (Bull et al., 1995, Chang et al., 1996, Hsu et al., 2000, Kool and Van, 1984, Yang, 2004), believed to be carcinogenic.

It is likely that the reduce chorine requirement is a result of the direct oxidation taking place at the electrodes during each pass through the cell. In the single cycle experiment the contaminant metal ions meets the anode surface only once and relies on indirect oxidation by chlorine to achieve complete oxidation. Data for metal remaining after filtration of the treated water are summarized in figure 7.

Figure 7: Residual concentration of iron and manganese in groundwater after each cycle through the PEFT cell, measured one hour post electro-oxidation, flow rate: 190 mL/min, [NaCl] : 250 mg/L, current density: 78.6 mA/cm.



It is clear that the four cycles that are required for complete oxidation of the metal allow almost complete removal of the metal upon filtration so that the product water meets the New Zealand drinking water guidelines.

### **3.5 THE IMPORTANCE OF RAPID OXIDATION**

Waikato bore water containing elevated levels of iron and manganese and also elevated levels of silica and/or organics are difficult to treat by conventional means. They oxidize in air slowly and also form stable colloidal suspensions of hydrous oxide colloids. Treatment with a novel electrochemical cell has been found to be effective in achieving rapid oxidation and enhanced settling. The oxidation can be achieved either by using elevated NaCl levels or by multiple pass treatment with NaCl levels that lie within drinking water standards. Similar results can be achieved using hypochlorite but involve much higher levels of chlorine.

The importance of rapid oxidation in the treatment of these waters is not fully understood. The most commonly used explanation is that under condition of natural air oxidation, the slowly oxidized metal ions undergo hydrolysis to form sub units of hydrous oxide. In the presence of negatively charged silica particles or humic macromolecules, these particles have time to become coated with negatively charged silica or organic species resulting in their acquiring a net negative charge. This charge effectively stabilizes them against further aggregation. If the oxidation takes place rapidly, high concentrations of the primary hydrous oxide particles are formed in close proximity and aggregate before their surface become coated with the negative particles. Thus flocs are formed and the oxidized metal settles.

The poor removal of manganese, even when harsh oxidizing conditions are employed is consistent with the greater magnitude of the manganese reduction potential ( $E^0$ :  $Fe^{3+}/Fe^{2+} = +0.77V$ ,  $MnO_2/Mn^{2+} = +1.23V$ )(Rosen, 2001, Vogel, 1997). Evidence for this is provided in Figure 7 which shows that most of the iron is removed before there is significant manganese decrease.

### **3.6 POWER CONSUMPTION**

While the multiple pass experiment achieves 100% oxidation at a lower level of chlorine production than the single pass experiment at 3 g/L, the multiple pass experiment requires almost six times more power (multiple pass: 18.4 kWh/m<sup>3</sup> and single pass 3g/L: 2.7 kWh/m<sup>3</sup>) to achieve the same level of metal removal. This is mainly due the low current efficiency of chlorine production at the low concentration (2.0%) but increased cell resistance is also a factor in the multiple pass experiment (conductivity of 250 mg/L of NaCl: 595  $\mu$ S/cm, conductivity of 3 g/L NaCl: 3.9 mS/cm). There can be other effects such as the adhering of fine gas bubbles to electrode surfaces causing resistance increases and greater power consumption. This is one reason why it is preferable to use multiple passes at a high flow rate than expose the water to the same level of electrolysis at a slower flow rate. Gas bubbles can be swept from the electrodes at higher flow rates.

## **4 CONCLUSIONS**

Multiple passes through a porous electrode flow through (PEFT) cell fitted with a graphite anode and a stainless steel cathode and operated at low voltages has been effective in oxidizing iron and manganese in problem Waikato bore water. With added sodium chloride concentrations as low as of 250 mg/L, the technology coupled with filtration or modest storage residence times, is capable of removing the metals to drinking water standards. The electrochemical oxidation has advantages over chemical oxidation using  $Ca(OCl)_2$  because the less chlorine is involved and settling is faster. Power consumption was 18.4 kWh/m<sup>3</sup>. We believe this desired result could also be achieved by single pass through a cell consisting of four of the porous electrodes in series.

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