

# **HYPO, FRRRIC AND ARSENIC; A TALE OF OXIDATION AT MACARTHUR**



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# HYPO, FRRRIC AND ARSENIC; A TALE OF OXIDATION AT MACARTHUR

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## ABSTRACT

Macarthur is a small town in Western Victoria. The water supply was classified as non-potable due to the high arsenic levels found naturally in the bore. The source of the arsenic is from the local geology surrounding the aquifer. The water supply in Macarthur has been classified as non-potable since the Department of Health changed the arsenic requirement from 50ppb to 7ppb in the 2004 Australian Drinking Water Guidelines.

This paper outlines the treatment process optimisation for arsenic removal and the results of a new granular ferric oxide media arsenic sorption plant. The success of this project resulted in Macarthur Water Treatment Plant producing water with arsenic below detectable limits. The supply has been reclassified as a potable supply from the 01<sup>st</sup> July 2011.

## KEY WORDS

Arsenic, Ferric Chloride, Granular Ferric Oxide, Oxidation, Optimisation.

## 1.0 INTRODUCTION

### 1.1 Plant Background

Macarthur is serviced by the Macarthur Water Treatment Plant (WTP) (figure 1). The primary treatment process train contains; pre-chlorine oxidation, clarification and pressure filtration (dual media). The primary plant is capable of removing arsenic from background concentrations of 400 parts per billion (ppb) to a filtered water arsenic concentration of 10-20ppb.

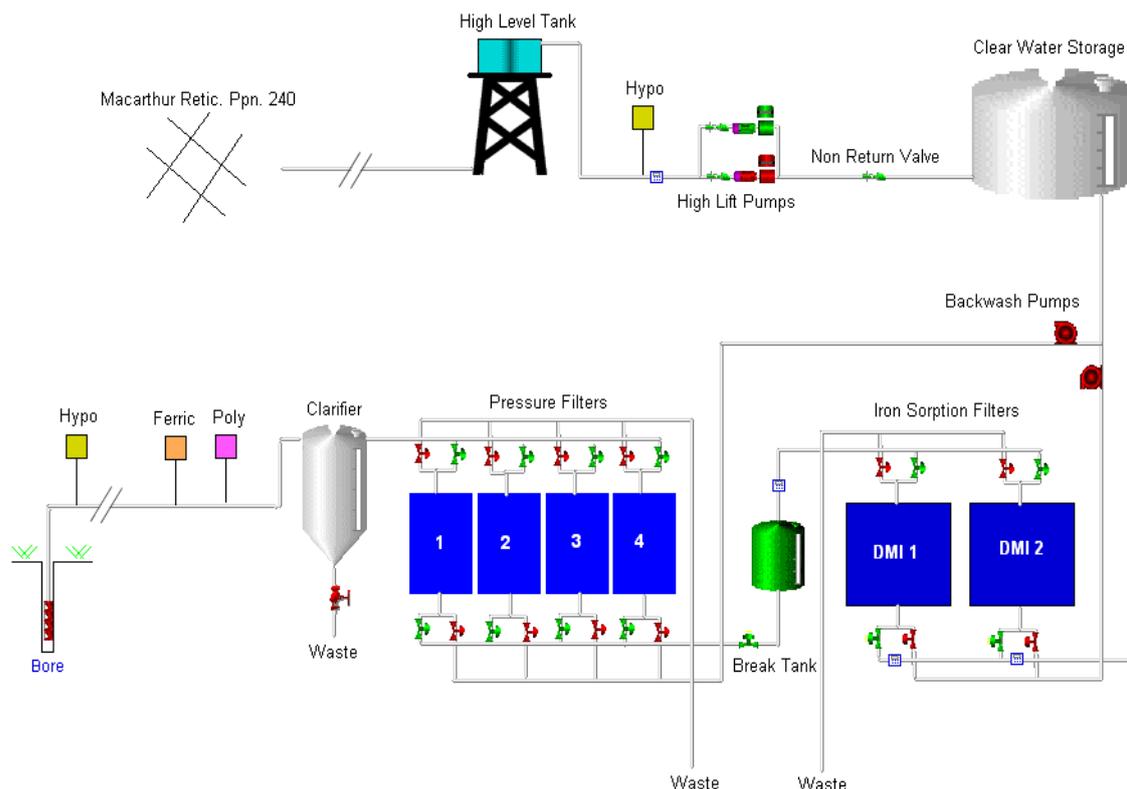
A secondary process was required to reduce arsenic to below 7ppb to meet the Australian Drinking Water Guidelines (ADWG) 2004. A contractor was engaged to design and build a secondary treatment plant to remove this arsenic. The secondary process originally involved further oxidation with chlorine and adsorption by a media called DMI-65. The DMI – 65 media failed to meet expectations in terms of arsenic removal. This media was later replaced with another adsorptive media called Granular Ferric Oxide (GFO). This media was found to be quite effective in removing arsenic below the ADWG limit. In fact, this media removed arsenic below the detection limit of 1ppb.

There were a number of issues during the commissioning of the secondary plant, including the poor arsenic removal by the primary plant. The primary plant required optimisation before the final commissioning could be completed.

Like many small regional WTP's there was very few man hours spent at Macarthur. Since it was a regulated supply, there was also a lack of understanding of the process involved in arsenic removal. A full plant assessment and optimisation was required to:

- 1) Understand the arsenic removal process; and
- 2) Find the cause of the process failure.

The primary plant optimisation process is the focus of this paper (Figure 1).



**Figure 1:** *Plant Schematic*

## 1.2 Arsenic Oxidation Background

As arsenic is a relatively rare contaminant in Australian water supplies, below is a brief outline of the oxidation chemistry.

Arsenic is most commonly found in two chemical charges (oxidation states). Arsenite [As(III)] is soluble and is most commonly found in bore supplies. Arsenate [As(V)] is insoluble and therefore rarely found naturally in water as it generally settles out.

The key to arsenic removal is converting As(III) to As(V). As(V) can be easily removed through a clarification and filtration processes. Conversion of As(III) to As(V) is called oxidation as the charge (or oxidation state) increases from 3 to 5. There are a number of useful chemicals for arsenic oxidation. Sodium hypochlorite (liquid chlorine) is used at Macarthur as it is also used as a disinfectant. Other oxidants include; potassium permanganate, ozone and other proprietary solid phase oxidants.

The oxidation reaction equation of sodium hypochlorite and arsenic is:



The oxidation of As(III) to As(V) is reported to be relatively independent of pH (Ghurye and Clifford 2001). However, our experience is that, for sodium hypochlorite oxidation, the lower the pH the greater the oxidation rate. Ghurye and Clifford 2001 also found that the oxidation would occur relatively quickly (<60 seconds), this was confirmed on site.

## 2.0 DISCUSSION

The initial site inspection revealed an old, but well functioning plant, with no obvious mechanical, dosing or process issues. There was little process information and virtually no data about the plants operating conditions before the optimisation process began. To further complicate the optimisation, the primary plant had no flow meters, no turbidity analysers and practically no online equipment. All changes would need to be monitored on site and confirmed with laboratory analysis. It was clear from the outset that this process would take some time.

### 2.1 Process Optimisation

As with all optimisation processes a systematic approach was required. Initially Wannon Water looked for any obvious problems that may be affecting the plant. This involved, checking for blockage in dose lines, failure of pumps and other equipment. Everything was operating effectively so, Wannon Water decided to review and optimise each process step.

The plant review started with optimisation of the clarifier, filters and clear water storage. The clarifier was optimised in terms of desludge timing, chemical dose rates and outlet turbidity and iron levels. This had little effect on the arsenic concentration but did help to improve turbidity and reduce loading on the filters.

Filters were then assessed for turbidity, iron and arsenic removal. This optimisation process saw a number of improvements. The total arsenic post filter was about 50ppb. This was a good start but there was still room to improve. Filters were then caustic washed to remove any arsenic build up and prolong media life. The caustic washing process increased the pH in the filters causing a spike in arsenic concentrations.

The clear water storage had a layer of ferric type sludge and silt of unknown depth. This was removed by a diving service to ensure the sludge was not leaching arsenic. The sludge was only 1cm deep. Figure 2 below shows the sediment build up in the clear water storage.



**Figure 2:** *Sludge layer in clear water storage*

### 2.2 Dose Rate Optimisation

Now that the WTP hardware was running at optimum and ruled out as a cause of the high arsenic, the chemicals and dose rates were the last potential cause and thus the solution.

### 2.3 Chlorine Dose Rate (Hypo)

Chlorine is the main oxidant and was the first chemical targeted. The stoichiometric demand for arsenic is 0.95mg/l of chlorine per 1.0mg/l of arsenic. So the bore's 400ppb (0.4mg/l) of arsenic should in theory require 0.38mg/l of chlorine plus any natural demand. The chlorine dose increased to 3.5 mg/l total residual to exceed the required demand. But, there was little improvement in arsenic oxidation. So the chlorine was put back to the original setting (2mg/l) and was ruled out as the cause of our problem.

Since there was already some arsenic removal occurring, a test was conducted to identify the process step where most removal occurs to further improve that step specifically. This proved to be the biggest breakthrough in understanding the arsenic removal process. The test included As(III) and As(V) at various locations along the process train. It was expected that the pre chlorine dose step to have the most impact. But we were in for a surprise. Wannon Water found that most of the oxidation from As (III) to As (V) occurred not after pre chlorine dose but after the ferric chloride dose.

## **2.4 Ferric Chloride Dose Rate (Ferric Chloride)**

Over the next two weeks the ferric dose rate was slowly raised and Wannon Water monitored the iron levels to prevent over loading the clarifier and filters. As the ferric dose increased the iron residual also increased, but the arsenic concentration started to fall!

Wannon Water believes, there are 2 reasons for this:

1. Using the same logic applied to the hypo over dose, the extra ferric was decreasing the pH increasing the oxidation rate
2. Ferric has a catalytic effect on the oxidation rate.

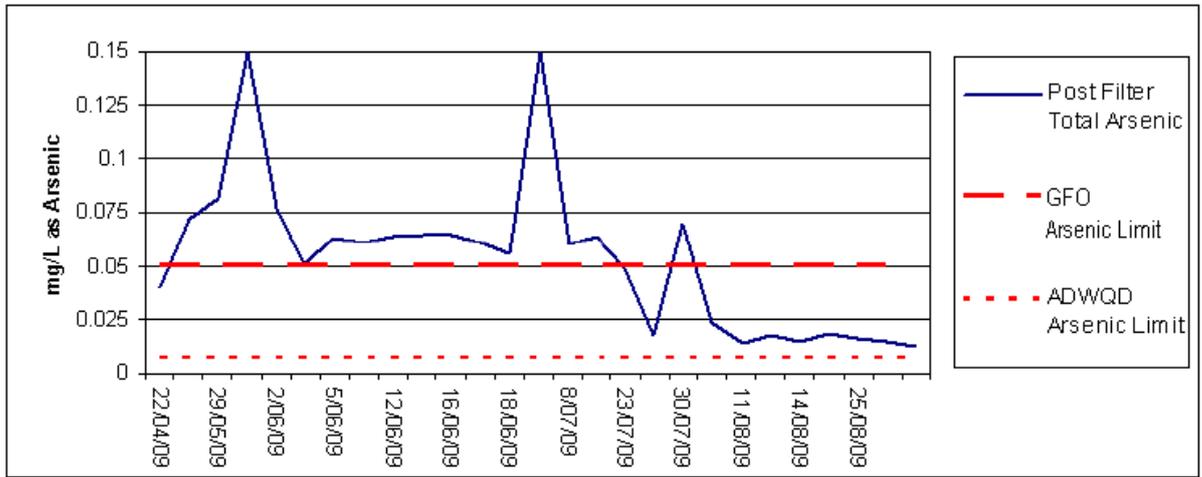
To be more precise the high ferric dose was instantaneously dropping the pH creating an acidic environment for arsenic oxidation to take place. This works because chlorine is a more efficient oxidant at lower pH. This low pH may only last a few minutes or even seconds but is enough to allow the oxidation to take place.

## **2.5 Polymer**

The arsenic concentrations spiked a month after the ferric dose was optimised. On site Wannon Water identified an empty poly hopper. Poly dosing is in many plants underrated or even forgotten. Macarthur WTP was no exception. Ferric produces a weak floc and poly is essential in controlling floc carry over and break through. With a new batch of poly the plant was back on track. It just goes to show that everything is equally important.

## **2.6 Primary Plant Results**

Figure 3 shows the filtered water arsenic concentration over the optimisation period. Note the three peaks caused by filter cleaning, chlorine over dose and polymer failure respectively.

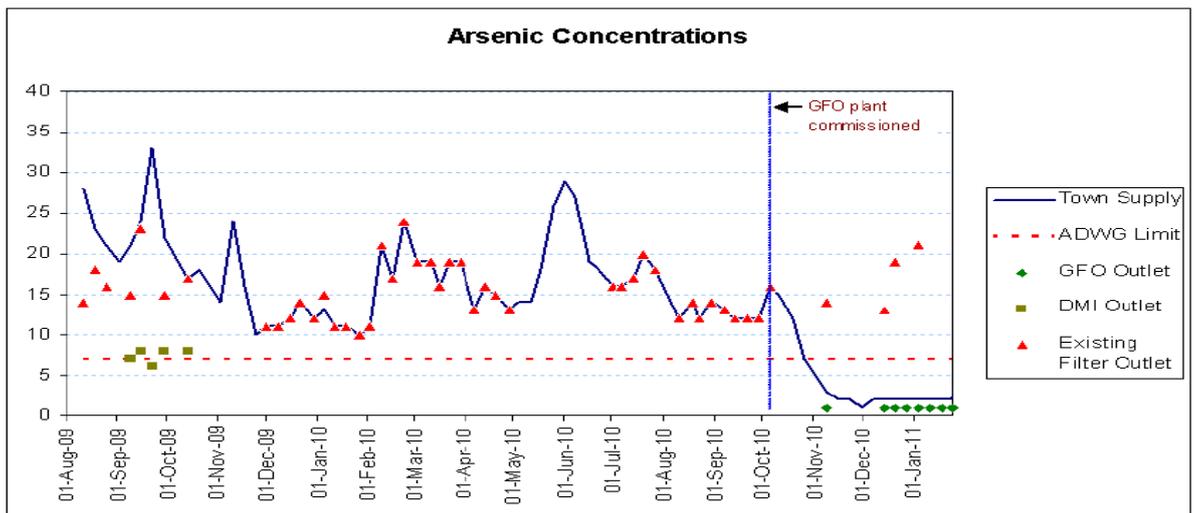


**Figure 3:** Primary plant filtered water arsenic concentrations

## 2.7 Secondary Plant Commissioning

The Granular Ferric Oxide (GFO) has a number of strict operating requirements. These conditions include total arsenic <50ppb, total iron <0.3mg/l, total manganese <0.05mg/l, turbidity <5NTU and has an expected life span of 6-36 months. The primary plant now meets these requirements and the GFO media is proving to be an excellent arsenic removal technology.

The secondary plant was commissioned in the months following the optimisation. Figure 4, below shows the operational results in the months before and after the commissioning. The DMI-65 media results are on the far left of Figure 4 below, the media removed approximately half of the arsenic but this did not meet the ADWG limit of 7ppb. The GFO media was installed in October 2010, the results are in green on the right of the graph. The media has consistently met the 7ppb requirement.



**Figure 4:** Arsenic results during the DMI-65 and GFO media commissioning.

### **3.0 CONCLUSIONS**

Arsenic contamination is relatively rare in Australia, but the lessons learnt in Macarthur WTP can be applied at most treatment plants. Optimisation is a very effective way to improve treatment plant performance and to understand the treatment process.

The primary plant is now producing water with less than 20ppb of total Arsenic. The primary plant arsenic reduction rate is 95% of the bore water arsenic level. The plant has had very few treatment issues since the optimisation.

The GFO media has proven to be a robust media with all results below the detection limit of 1ppb. GFO media is an adsorptive media that is capable of adsorbing both Arsenite [As(III)] and Arsenate [As(V)]. The greatest drawback is that the media will reach adsorption capacity and will need to be replaced. Pilot scale tests indicate this will be necessary after three to five years of service

As a result of this project, the secondary plant commissioning was completed. From December 2010 there has been no arsenic recorded in the Macarthur reticulation. On the 1<sup>st</sup> of July 2011 the water supply was reclassified as potable. This is the first new arsenic removal plant in Victoria to meet the ADWG requirement of 7ppb.

### **4.0 ACKNOWLEDGEMENTS**

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