The Removal of Arsenic and Silica from Geothermal Fluids by Electrocoagulation

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1. Abstract

Electrocoagulation treatment offers a simpler and more cost-effective method of removing arsenic from separated geothermal water than the traditional treatment methods of coagulation and flocculation. It is an electrochemical process that uses direct current to remove a wide range of contaminants. This method has the potential to allow efficient downstream utilization of heat in low enthalpy fluids through cascaded direct use applications and provides a more cost effective disposal option than reinjection. Laboratory scale experiments showed that the process was capable of rapidly removing both silica and arsenic from aged solutions leaving a floc which readily settled on standing. In a full scale process the silica and arsenic can be removed as two separate components allowing an arsenic free silica sludge to be disposed of to a landfill and thereby leaving a much smaller arsenic/iron fraction to be disposed of by reinjection.

2. Introduction

Coagulation and flocculation are traditional methods used for the treatment of water to remove contaminants prior to discharge to surface waters or reuse. In these processes, coagulants (e.g. alum or ferric chloride) and other additives (e.g. polyelectrolytes) are dosed into the water to produce particulates (e.g. ferric hydroxide, aluminium hydroxide) that adsorb trace metals. The particles aggregate allowing them to be separated by a physical process such as filtration, dissolved air flotation or settling. Plants are generally multi-stage processes that require a considerable land area and a continuous supply of chemicals and were the basis of pilot plant trials conducted at Wairakei (NZ) since the early 1970's looking at the removal of arsenic from separated geothermal water (SGW).

Although superficially similar to chemical dosing electrocoagulation (EC) treatment appeares to offer a simpler and more cost-effective method of removing arsenic from SGW than any of the above methods.

3. Electrocoagulation

EC is an electrochemical process that uses direct current to remove a wide range of contaminants from wastewater. For an excellent review article discussing the benefits and drawbacks of the technology see Chen (2004). Recent published work (see for example Kumar et al., 2004; Parga et al., 2005) demonstrates the effectiveness of this technology for As removal. Potapov et al., (2002) appear to have published the only studies reporting laboratory electrocoagulation experiments in geothermal fluids. Their purpose was to investigate silica removal with aluminium, stainless steel, copper and galvanized steel electrodes and the effect of current strength, current density, voltage, temperature, pH, electrode separation and sedimentation rates.

Their work showed that silica could be efficiently removed from geothermal fluids with the rate of coagulation being fastest with aluminium electrodes. Power consumption decreased with increasing temperature but the process became less efficient at temperatures > 60°C due to the formation of non-porous adhering scale on the aluminium surface. Their study was a useful starting point for our work, particularly for suggesting optimum values of current strength/density and voltage. In this study we used either aluminium (Al) or iron (Fe) sacrificial electrodes. The application of a voltage results in the release of charged Al or Fe ions depending on the electrode material being used. The ions subsequently hydrolyse to aluminium hydroxide or iron hydroxide. The metal hydroxides agglomerate the colloidal and monomeric silica and the solid mass also adsorbs arsenic (As). The floc can then be easily separated by any suitable separation technology.

4. Experimental

The laboratory electrolytic cell shown in Figure 1 consisted of a 1 L reactor and a 1.5 L reservoir for settling the floc. Wairakei geothermal fluid (typically pH 8.61 (@ 20°C, SiO_2 533 mg/L, Cl 2070 mg/L, As 4 mg/L) was circulated through the apparatus past electrodes (80 cm^2 geometric surfaced area, separation ~ 5 mm) connected to a power supply through which the current and voltage could be varied independently. Samples were taken at known time intervals for the analysis of dissolved As, SiO_2, pH and Fe or Al.

Five series of experiments of were undertaken:

- Aged water cooled to ambient temperature
- Aged water cooled to ambient temperature and acidified
- Aged water cooled to ambient temperature with arsenic oxidation by H_2O_2
- Fresh water at elevated temperature (~ 60 and 80°C)
- High and low circulation rates (300 and 100 ml/min respectively).

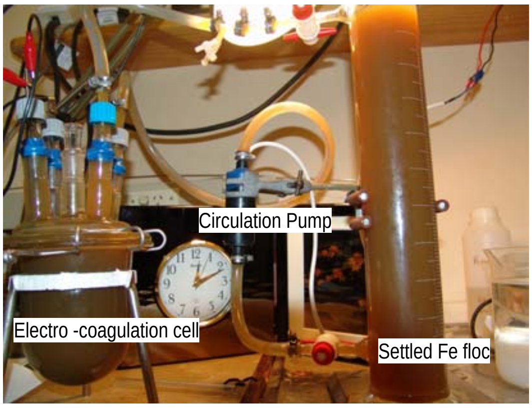

Figure 1. Laboratory EC Apparatus

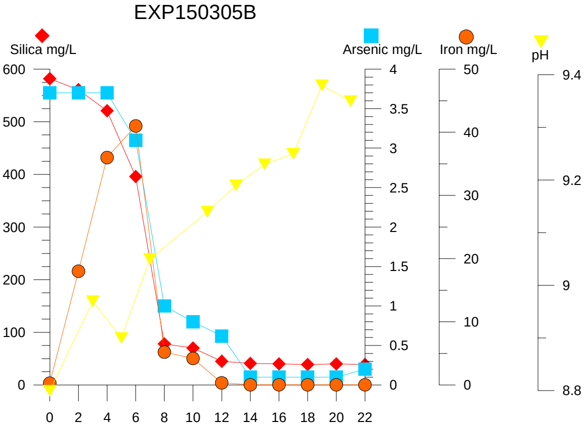

Figure 2: Fe electrodes; typical results

5. Results

Thirty experiments were completed and only a summary is presented here to illustrate the main findings.

1. As reported by Potapov et al. (2002) EC quickly lowers SiO_2 in the geothermal fluids to less than amorphous silica saturation. Typically for cooled aged fluid at ~1.5A and 6-10 V the SiO_2 in the supernatant was reduced to <100 mg/L in ~6 minutes using Al electrodes and ~8 minutes with Fe electrodes; See Figure 2 for typical results.

2. All else being equal the more aged a fluid, the less dissolved Al or Fe was required to coagulate the SiO_2.
3. The time to reduce the concentration of SiO_2 in hot fresh fluid (i.e. little or no polymer or colloid) increased to 14 and 28 minutes for Al and Fe electrodes respectively.
3. Dosing cooled aged brine to pH <5 with hydrochloric acid caused a significant increase in the SiO_2 precipitation rate, down to 2 minutes using Al electrodes and 4 minutes with Fe electrodes.
4. The removal of As was inefficient using Al electrodes; in fluid aged 1-3 days it took between 20 and 26 minutes to remove half of the As (down to 1.5-2 mg/L) while in fluid aged for 3 weeks the As reduced to 0.5 mg/L over a similar time period. Dosing fluid, which had been aged for only a few days, with hydrogen peroxide increased the removal rate to < 0.5 mg/L in 16 minutes.
6. The removal of As with Fe electrodes was significantly faster than with Al and occurred concurrently with the sudden precipitation of the SiO_2; viz. to < 0.5 mg/L in 8 minutes.
7. Preliminary experiments showed that there was considerable extra capacity on the Fe floc to absorb additional As, particularly between pH 4 to 7.
8. In the high flow experiments the floc removal time was typically increased by 1-2 minutes.

6. Discussion

In the aged cooled fluid using either Al or Fe electrodes, the SiO_2 concentration droped precipitously to ~ 100 mg/L after a critical concentration of dissolved Al or Fe was reached. Thereafter the concentration of SiO_2 slowly decreased. This behaviour is interpreted as the sudden precipitation of the colloidal SiO_2 fraction where the colloid and agglomerated particles are destabilized through bridging Al or Fe ions. The subsequent slower removal is of the dissolved (monomer) fraction, a process which may be proceeding stoichiometrically.

Treating hot fluid which contains essentially no colloid, the monomeric SiO_2 concentration (= total SiO_2) slowly decreases, taking about 4 times longer to decrease below 100 mg/L SiO_2 than in the aged fluid.

With Fe electrodes and aged fluids nearly all the arsenic is precipitated concurrently with the colloidal SiO_2 (Figure 2) while in the hot fluid As decreased slowly in concert with the gradual decrease in SiO_2 and Fe concentrations. In contrast, removal efficiency of As using Al electrodes is poor and even where the colloidal SiO_2 completely precipitated there was typically only a minor drop (e.g. 0.5 mg/L) in the dissolved As concentration. Treatment with H_2O_2 or long aging times (>1 week), which presumably allows As(III) to oxidize to As(V), improves the efficiency but it is still considerably less efficient than with Fe electrodes. This suggests only weak adsorption of As(V) as well as As(III) by a silica-aluminium floc compared to an Fe floc. The difference between Fe and Al electrodes may be used to remove the SiO_2 and As as two separate components.

Lowering the pH reduces the repulsion between colloidal SiO_2 particles. Consequently dosing aged fluid with hydrochloric acid to pH < 5 resulted in faster coagulation and removal of the colloidal SiO_2 fraction (less Al or Fe required!). For Al electrodes, a lower pH did not increase the As removal rate. However, with Fe electrodes the colloidal SiO_2 and Fe floc, which adsorbs all the As, precipitates concurrently and halves the removal time from 8 to 4 minutes.

The other effect of lowering the pH is that the capacity of Fe floc to adsorb As increases. (Swedlund and Webster, 1999). Adsorption experiments were conducted that examined differences in As loss with change in pH versus change in floc-to-As concentration ratios. Preliminary results showed significant As(V) adsorption by the Fe floc. The adsorption displayed a strong pH-dependence as found by Swedlund and Webster (1999), increasing towards lower pH values. Little to no adsorption was evident above pH 8, after accounting for As loss observed in blanks. Thus a process where Fe floc is recirculated may considerably reduce power consumption as less floc is required to be generated than would be otherwise in a once through system.

The efficiency of the electrolytic process may be estimated from Faraday's law where the amount of electrogenerated ions produced is proportional of the total amount of electrical charge passed through the cell. The rate of generation could only be approximately estimated from the initial increase in the ion concentration before flocculation. For Al electrodes, the observed generation rate was typically ~ double the theoretical rate while for Fe electrodes the observed generation rates were similar to slightly higher than the theoretical generation rates e.g. given a theoretical generation rate of 6.9 mg/min/L of dissolved Fe the observed rates were 6.8, 8, 7.8 and 6.5 mg/min/L. This suggests that chemical dissolution of the Al electrodes was occurring together with the electrolytic dissolution.

Based on this laboratory work the initial cost estimates of consumables for processing a tonne of Wairakei fluid were $NZ0.05 for power and $NZ0.01 for electrodes. These costs ignore efficiency gains that may be gained in a larger scale process. The use of acid has been found to speed up the flocculation process estimated at $NZ0.01 per tonne, although this has not been optimised. By comparison chemical costs alone for the conventional chemical treatment process were estimated in 2001 to be $NZ0.25 per tonne of Wairakei fluid.

7. Acknowledgements

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