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## **Mixing of Tikitere Geothermal Discharges with Sewage**

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## SUMMARY

- amorphous silica deposition directly from the Tikitere geothermal fluid is unlikely to occur;
- amorphous silica deposition may occur as a scale due to splash and evaporation of Tikitere geothermal fluid;
- geothermal fluids and steam contain negligible quantities of heavy metals (except for mercury) so collection of samples for analysis of heavy metals is not recommended;
- increasing the pH to near neutral (e.g. through reaction of the fluids with concrete) of Tikitere geothermal fluid would not cause deposition of the anhydrite or gypsum;
- deposition of sulphate scale would occur as a scale due to splash and evaporation of Tikitere geothermal fluid;
- ammonia in the Tikitere geothermal fluid is likely to be stable if the Tikitere flow is contained and pH is kept low;
- scaling of silica and sulphate minerals is unlikely to occur after Tikitere geothermal fluid is mixed with untreated sewage;
- wastewater flows will provide some dilution of Tikitere geothermal fluids; this dilution will increase over time as wastewater flows increase over time.

## 1.0 INTRODUCTION

As an outcome of discussing the “Evaluation of Geothermal Water Treatability” report (referred to here as “The Report”) by AWT at the Lake Rotorua Technical Advisory Group Meeting held on 15<sup>th</sup> Feb 2006 the Group requested comments on the tendency of the Tikitere geothermal fluids for

- a) silica deposition
- b) sulphite deposition
- c) chemical and physical conditions controlling ammonium to nitrate transformations

## 2.0 TIKITERE GEOTHERMAL FLUID

The fluid compositions show that they are condensed steam which has mixed in various proportions with aerated groundwaters. Very little, if any, deep chloride rich geothermal water reaches the surface. The condensed steam containing hydrogen sulphide (H<sub>2</sub>S) is oxidized to sulphur (S) which is then oxidized to sulphate (SO<sub>4</sub>), essentially sulphuric acid. Oxidation of H<sub>2</sub>S to S by oxygen is rapid but the subsequent oxidation to sulphate only occurs rapidly in the presence of bacteria (some of which are also likely to be able to oxidize H<sub>2</sub>S directly to SO<sub>4</sub>). Consequently many features at Tikitere discharge very acidic fluids (e.g. pH 2.5) with high sulphate concentrations (e.g. 51 to 2100 mg/kg). Typically the acid fluids also have low total sulphide (total as H<sub>2</sub>S <0.2 mg/L) as the form of the sulphide present at low pH is as a dissolved but volatile gas which is easily lost from solution; similarly the acid fluids have low total carbonate concentrations due to the volatility of CO<sub>2</sub>.

In other features the high acidity is neutralized by ammonia giving rise to near neutral fluids at about pH 6 but which also contain high concentrations of ammonia present as ammonium NH<sub>4</sub><sup>+</sup> (e.g. 640 mg/L as NH<sub>3</sub> in Ruahine). These fluids can also contain more dissolved sulphide. The most recent analyses of a few of the “high ammonia” springs have total H<sub>2</sub>S typically < 15 mg/L (at pH 6 about 10 percent of the total sulphide is present as HS<sup>-</sup>).

The composition of the condensates varies naturally (e.g., depending on steam supply, condensation, etc.) and as the geothermal fluid mixes further with a variable amount of runoff (etc) results in the compositional changes observed in the RDC monitoring results.

The low fluid pH, composition and sediment load needs to be taken into account when material selection and specification for pipes and pumps.

We assume in this analysis that the “hydrology” of drainage from the geothermal springs is stable and unlikely to be naturally altered in say a major flood, hydrothermal eruption and the like.

It is possible the field could be developed for geothermal power which may affect the steam supply to the springs; either increasing due to the stimulation of boiling at depth or perhaps even quenching as the steam is redirected. This possibility should be taken into account in the risk assessment.

### **3.0 SILICA**

The silica content of the discharges vary considerably and it appears that many are undersaturated with respect to amorphous silica (AM) but some are closer to equilibrium (e.g., mini cook pot with a silica content of 274 mg/L indicates an equilibrium temperature of about 78° C whereas the measured spring temperature was 68° C). As the fluids cools the potential exists for the AM solubility to be exceeded as at 25° C the equilibrium solubility is ~120 mg/L. The silica values given in "The Report" show however that in the culvert all the silica is essentially soluble (i.e. no colloids) and furthermore the silica is undersaturated with respect to AM. Even if the silica was significantly oversaturated amorphous silica deposition (or polymerization to form colloids) would be negligible due to the low pH, which dramatically slows the deposition kinetics.

Although AM silica deposition per se will not be a problem, scaling due to splash and evaporation is possible but if allowed for may not be a significant problem.

### **4.0 HEAVY METALS**

Geothermal fluids and steam contain negligible quantities of heavy metals so collection of samples for analysis of heavy metals is not recommended. It follows that heavy metal sulphide scaling will not be a problem. The exception is mercury and we expect the analytical results for this element to be highly variable. Mercury is transported in geothermal steam as elemental and will mostly be oxidized close to the surface and scavenged by particulates of which S would be most efficient.

### **5.0 SULPHIDE**

Although sulphide scaling will not occur "The Report" mentions that H<sub>2</sub>S could be detrimental to the bioreactor operation. Since the pH of the fluids in the culverts is below 4, the total H<sub>2</sub>S concentration will be low and indeed a culvert sample collected in 2003 had a total H<sub>2</sub>S < 0.2 mg/L. It is suggested any samples collected for sulphide preferably be analysed on site or preserved (e.g. with zinc or cadmium acetate) for analysis soon thereafter to limit oxidation by bacteria. As discussed above some Tikitere features contain considerably more H<sub>2</sub>S and it depends on which fluids are predominant in the mixture.

### **6.0 SULPHATE SCALING**

Unlike sulphide scaling deposition of anhydrite (or perhaps gypsum at less than 50° C) may be more likely due to the high sulphate content and calcium in solution. Preliminary calculations show that the high sulphate features are undersaturated with respect to anhydrite (at temperature). The solubility of this mineral is pH independent and also has retrograde solubility. This means that the solubility increases on cooling and mixing with fresh water drainage and runoff undersaturates the mineral even further. One analysis at the culvert gives a sulphate concentration of the order of 380 mg/L with calcium of 9 mg/L. A preliminary calculation shows that increasing the pH would not cause deposition of the anhydrite or gypsum.

However splash and evaporation would lead to the deposition of sulphate scale.

## **7.0 AMMONIA TO NITRATE TRANSFORMATION.**

Williamson and Cooke (1982) comprehensively investigated the nitrogen transformation in the Waiohewa Stream. They concluded that nitrification in the Tikitere discharges is suppressed by the low pH of these discharges (~ pH 3). In contrast the lower Waiohewa “provides conditions where large amounts of the geothermal nitrogen is converted to nitrate” which laboratory experiments seemed to show were sediment related. The experiments conducted by Williamson and Cooke (1982) were not particularly sophisticated or controlled (from a microbiological point of view) and can be repeated if required. However their data suggests that if the Tikitere flow is contained and pH is kept low the ammonia will be stable. Data off the “Net” suggests maximum nitrification occurs at about pH 7.2 and reducing the pH to 6 decreases the rate to 10% of the maximum (Matthew Stott, Pers. Comm.)

## **8.0 MIXING TIKITERE GEOTHERMAL DISCHARGES WITH SEWAGE**

Some qualitative observations are made of likely effects because the chemical process is too complex to model. First, the discharges will be diluted which further decreases the undersaturation of both the silica and sulphate minerals (sewage contains ~ 30 mg/L  $\text{SO}_4$ ) Furthermore, it is likely that carboxylic acids and other organic compounds in the sewage will effectively sequester calcium and magnesium, suggesting that scaling will not be an issue after mixing. The pH will increase but given the low BOD and perhaps even reducing conditions we would not expect an increase in the nitrification of the ammonia.

We have no data on the sediment load in the geothermal discharges nor can predict the effect on the sewage or eventual treatment. Williamson and Cooke (1982) analysed the sediment with XRF and showed it to be 48% S and 50% Si. It is possible the mercury content of the sulphur will be tens of milligrams per kilogram of sulphur and the low BOD will limit oxidization of the sulphur by the sulphur oxidizing bacteria after mixing with the sewage.

The data on constituents present in Tikitere geothermal fluids provided in the “The Report” and in a spreadsheet labelled “Flows and their constituents from Tikitere geothermal field” is limited and primarily considers conventional pollutants such as nutrients and suspended solids. Pertinent analytical data presented consists of average values for boron, calcium, and silica concentrations from three samples taken in 2004. These show silica levels of approximately 90 mg/L. Concentrations of this level are below the solubility of amorphous silica at environmental temperatures.

In reviewing the available flow data, Peter Dine has indicated that the flow rate of Tikitere geothermal fluids is typically approximately 17 L/sec. This is a combination of flows at the “bottom culvert” and the “middle culvert” minus clean water from the “upper culvert”. Clean water flowing through the “upper culvert” is not from the Tikitere geothermal field and therefore this water will not be added to the sewerage main (Peter Dine pers. comm.).

Estimates of eastern trunk sewer main flow (upstream of Eastgate and the airport) are in the

range 1.1 L/sec (dry weather flow) to 4.6 L/sec (wet weather flow). The dry weather flow is expected to ultimately increase to 4.3 L/sec when at 100 percent of design.

Rotorua District Council (Greg Manzano, pers. comm.) has no data on calcium, silica, or sulphate likely to be in this flow or in raw sewage influent to the treatment plant but influent typically has a pH in the range of 7.6 to 7.8 units. Levels of calcium, silica, and sulphate in raw sewage are likely to be primarily related to the source drinking water with some degree of input possible during water use. Levels of calcium may be somewhat higher than the values of around 8 mg/L reported as an average for the three Tikitere samples noted above since there are many possible sources of calcium. However, it is unlikely that silica levels would be as high as those in Tikitere geothermal fluids. With regard to sulphate, a concentration of 30 mg/L would be typical of the composition of medium strength domestic wastewater (United Nations. 2003. Wastewater Treatment Technologies: A General Review. New York, 11 September).

Wastewater flows can be expected to have lower concentrations of silica and sulphate minerals (e.g., calcium sulphate in the form of either gypsum or anhydrite) than Tikitere geothermal fluids. Therefore wastewater flows will provide some dilution of Tikitere geothermal fluids; this dilution will increase over time as wastewater flows increase.