Scaling – From Production to Reinjection
3rd GNS Science - JOGMEC Workshop

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Tokyo
10 December 2018
Outline

- The New Zealand geothermal reservoir
- Rotokawa reservoir
- ECC cement grout
- Deep Acidity Examples and Management
- Silica Scaling
- Calcite Scaling
- Anhydrite Scaling
- Iron sulphides
- Antimony sulphide (stibnite)
- Silica and Calcite Scaling Management
The New Zealand Geothermal Reservoir

- **Boiling**
  - injects CO$_2$ & H$_2$S in the shallow reservoir
  - Mixing with oxygenated fluids
  - Very corrosive

- **Vapour Dominated**
  - Cl in superheated vapour
    - transported as HCl
  - concentration
    - Cl in the brine
    - temperature of separation

- **Deep Acidity - Magmatic Fluids**
  - $4\text{SO}_2 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4 + 3\text{H}_2\text{SO}_4$
  - HCl

\[300 \text{ Co} \quad 200 \text{ Co} \quad \text{mixing} \quad \text{recharge} \]

\[387 \quad \text{mixing} \quad \text{recharge} \]

\[604 \quad \text{piezometric surface} \]

\[444 \quad \text{condensate} \quad \text{pot} \quad \text{cold gas seep} \]

\[546 \quad \text{boiling} \quad \text{cap} \quad \text{hanging aquifer} \]

\[551 \quad \text{envelope} \quad \text{aquiclude} \quad \text{condensation} \]

\[552 \quad \text{steam cap} \quad \text{boiling-point fumarolic discharge} \]

\[543 \quad \text{discharge} \quad \text{condensation} \quad \text{boiling point fumarolic} \]

\[444 \quad \text{condensate} \quad \text{pot} \quad \text{cold gas seep} \]

\[526 \quad \text{boiling} \quad \text{in vapor} \quad \text{envelope} \]

\[539 \quad \text{recharge} \quad \text{recharge} \]

\[575 \quad \text{mixing} \quad \text{conducting} \]
The New Zealand Geothermal Acid Features

Rotorua

Rotokawa

Middle Earth

GNS Science
The New Zealand Geothermal Reservoir

B. Christenson (GNS)
New Zealand Rotokawa Reservoir
highly corrosive acidic $\text{SO}_4\text{-Cl}$ rich fluids

1. Deep upwelling reservoir fluids; rise to shallow levels [5]
2. Clay Cap (weekly developed)
3. Central Field Fault
4. Lake Rotokawa extensive area of acid-$\text{SO}_4\text{-Cl}$ fluids
6. Drain back downward to generate advanced argillic alteration in RK4/RK2
7. Boiled fluids inject large quantities of $\text{CO}_2$ and $\text{H}_2\text{S}$ into steam condensates
8. Mix with oxygenated fluids

- Rotokawa Cross Section  Winick et al, 2009. NZGW
External Casing Corrosion of Cement Grouts

- Ohaaki well Br23
  - 0.4 mol/kg $\text{H}_2\text{CO}_3$
  - pH 5 @150°C
- 10 months exposure
  - fully carbonated all samples and cause severe corrosion
  - Added quartz sample
    - lost over 60% of its volume
  - Pure cement
    - 35% of its volume lost
Deep Acidity
Common in Many Volcanic Geothermal Fields

Not all acid is created equal!

$\text{HSO}_4/\text{SO}_4 \ & \ \text{CO}_2/\text{HCO}_3$ Buffers

- $\text{SO}_4/\text{HSO}_4/ \ & \ \text{CO}_2/\text{HCO}_3$ Buffers
  - pH at depth is neutral
  - Acidity increases markedly at shallow depth
  - Well bore corrosion

- HCl
  - Completely dissociated
  - Low pH in reservoir and at shallow depths

Lichti et al; NZGW 1998
Deep Acidity – GNS reviews

- Mt Apo; Philippines
  - pH 3.2-5.5
  - Cl-Na-K relative proportions
  - No excess Cl
  - Acidity due to SO$_4$
  - Silica
    - 1000 mg/L
    - No deleterious scaling
    - Little pipe corrosion
    - Amorphous silica protects from corrosion

Nogara et al. 27 Workshop on Geothermal Reservoir Engineering, 2002
Deep Acidity – Philippines

- Mt Apo;
  - Now lower pH 2.5
  - Corrosion observed
  - pH too low for Am Silica protection
  - NaOH injection trial
    - pH to 4.5
    - Not successful
- Mahanagdong
  - pH 2.87 - 4.05
  - NaOH solution through a 1” Incoloy 825 tubing at 20 m depth
  - Thinning rate decline
    - 1.05 to 0.21 mm day$^{-1}$
  - corrosion control pH of 4.5

Tamboboy et al. 2015; WGC
Deep Acidity – Philippines

- Tiwi
  - The production liner was removed and the corrosive zones isolated
  - Injection of 4 wt.% NaOH at a depth of 1070 m (12.7 mm capillary tubing of Inconel 625).
  - The pH is controlled at 4.5–5.0.
  - Overdosing with NaOH (pH > 6) is found to exacerbate silica scaling
  - Dissolved iron concentrations in the fluid have been reduced by 80%

NaOH Steam Scrubbing

- Italy, Larderello.
  - downhole using a capillary and at the wellhead using corrosion-resistant wellheads,
- USA, The Geysers, California.
  - Superheated to wellhead
  - NaOH has been used similarly
  - trials successful with dry steam scrubbing using calcite packed beds and amines which avoids the reduction in steam utilization efficiency


Silica Scaling in New Zealand

- Major & difficult problem – given the large volumes of brine disposed
  - Above surface piping
  - Reinjection Wells
New Zealand “Unnatural” Acidity – pH Mod

- Control of silica scaling
  - $\text{H}_2\text{SO}_4$ dosing
  - 3 NZ Geothermal fields
    - Including Rotokawa!
  - Difficult process to control
    - Adding acid
    - Corrosion pH 5.5 (@25°C)
    - Heavy metal (Sb & As) causing corrosion on Fe pipes (Quest Integrity GNS sponsored research (Lichti et al; WGC 2015)
- Water rock reaction of acidic fluids
- Operational and Infrastructural
  - Acid delivery, storage, handling, cost
Experimental Chemistry - Laboratory Studies
Private Companies (NZ & International)
NEDO - GNS Corrosion studies

High Temp./Press. Apparatus
400°C & 500 bar

“real world”

“simulated world”
Scaling – Experiments and Modelling

With silica deposition rate data we can calculate the effect of scaling in the reinjection aquifer!

Injection into 130°C Fluid into a Reservoir at 80°C at 50 kg/s for 10 years
Assumptions about the geometry of the porosity of the aquifer required

Calcite Scaling Thermodynamics

Calcite Deposition – Production Problem

\[ \text{Ca}^{++} + \text{CO}_3^\equiv \leftrightarrow \text{CaCO}_3 \]

Most \( \text{CO}_3^\equiv \) present as \( \text{HCO}_3^- \) or \( \text{H}_2\text{CO}_3 \)

On boiling

\[ \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 \uparrow + \text{H}_2\text{O} \]

\[ 2\text{HCO}_3^- \rightarrow \text{CO}_3^\equiv + \text{CO}_2 \uparrow + \text{H}_2\text{O} \]

Overall

\[ 2\text{HCO}_3^- + \text{Ca}^{++} \rightarrow \text{CaCO}_3 + \text{CO}_2(g) + \text{H}_2\text{O} \]

RETROGRADE SOLUBILITY
Calcite Scaling Kinetics

- Deposition Kinetics - Rapid (heterogeneous nucleation – seed available)
- Occurs within wellbore just above flash point
- Scaling calibrated for the field
  - Some wells predicted to scale but don’t
  - Depends on how the boiling occurs and rapidity of depressurization
- Severe scaling can result out in the formation
  - Cannot remediate easily
- Surface Pipes
  - Mixing of incompatible fluids (high HCO$_3$ and high Ca)
  - Degassing due to depressurization
Anhydrite Scaling

- \( \text{Ca}^{2+} + \text{SO}_4^{=} = \text{CaSO}_4 \)
- Caused by mixing Ca and SO\(_4\) fluids
- Independent of pH
- Retrograde solubility
- Not common in production wells
- Mainly volcanic geothermal environments
  - But often shallow acid-sulphate zone present
- Antiscalant (like for calcite) effective
- Often self limiting
- Treat during well drilling (case off or injecting calcium salts can work)

After Mubarok & Zarrouk, 2017
Iron Sulphides

Pyrite FeS$_2$; Pyrrhotite Fe$_{(1-x)}$S ($x = 0$ to $0.2$)

- Acid fluid can carry a lot of iron from corrosion/erosion
- Precipitates in response to boiling & cooling
  - sensitive to pH and H$_2$S & H$_2$ gas fugacity (redox)
- Severe problem can occur
  - when mixing incompatible fluids (low and high pH, high iron, gas, differing enthalpy)

Jamero et al. 2018 Geothermics
Antimony (& Arsenic) Sulphides

\[ 2H_3SbO_3 + 3H_2S = Sb_2S_3 + 6H_2O \]

- Particular problem in NZ Geothermal Fields (Brown, 2011)
  - Now reported elsewhere
  - Binary Plants
  - pH mod for silica inhibition
- Low pH and cool temperatures required
- Highly insoluble under these conditions
- e.g. pH 5 & 15 mg/l H_2S 150°C 3.34 mg/l; 100°C 0.008 mg/l
- Caustic dissolves (anion H_2SbO_3^-)
- Antiscalants show promise (Gill, 2013)
NZ Calcite Scaling Management

- Keep the scaling in the wellbore
- Maintain WHP and control output

0.1 mg/l Ca
0.25 g/tonne CaCO$_3$

1 Step Flash

Log Q/K

Casing depth/m

NZ Calcite Scaling Management

- Antiscalant injection
  - Highly effective
  - Below boiling point
  - Many commercially available
  - Need to choose appropriate one (lab and field testing)
  - Not out in the formation
NZ Scaling Management – calcite & silica

• Periodic Well Workovers
  • Reaming
  • Acidizing (implications for well integrity!) – HCl & HF
  • High pressure water blasting
  • Broaching
  • Novel Chemical treatment (Alkali, EDTA)

What is more expensive: Avoidance or workovers?
Geo40 (New Zealand) 
Manufacture of colloidal silica 

Ohaaki Commercial Demonstration Plant (in co-operation with Contact Energy Ltd and Ngati Tahu Tribal Lands)
Conclusions

Scaling occurs from Production to Reinjection. It cannot be totally avoided.

However thorough chemical understanding of the influent and effluent composition and chemistry, good power station design, monitoring of the reservoir response to production and knowledge on how to deal with the problem all work to minimizes the potential for disaster.
Acknowledgements

GNS Science
Contact Energy Ltd
Mercury Energy Ltd
Wairakei Prawn park
New Zealand Government Research Funding