UNUSUAL ARSENIC SULFIDE SCALING IN A BINARY TEST PLANT

Kevin Brown[1,2],Jenny Webster-Brown[1,2], Maja Rasmussen[2] and Simon Addison[3]

[1]GEOKEM, PO Box 30-125, Barrington, Christchurch, 8422, NZ

[2]University of Canterbury, Private Bag 4800, Christchurch 8140, NZ

[3]Mighty River Power, PO Box 245, Rotorua 3040, NZ

kevin@geokem.co.nz

Keywords:*Arsenic sulfide, scaling, binary plants, geochemical thermodynamics.*

ABSTRACT

During the planning period for the Ngatamariki geothermal power station, a pilot plant was constructed by Mighty River Power to investigate options for the design of the final production plant.

During the binary plant testing at lower temperatures, a deposit appeared at 85ºC in the test section after the retention tank. This deposit was not present during a similar test at 90ºC. The deposit was orange-brown in colour, very porous and had deposited a significant thickness (~0.15mm) during the 18 days of the test. SEM investigation of the deposit showed that it was composed of mainly arsenic and sulphur with iron and antimony as minor constituents.

Geochemical thermodynamic modelling indicated that the fluid was significantly undersaturated with respect to amorphous orpiment (As_2S_3), at 85°C, but was possibly saturated with respect to arsenopyrite (FeAsS). SEM-EDS analysis of the deposit indicated that the atomic ratio of As:S was approximately 1:1, more akin to the ratio in arsenopyrite than the 1:1.5 that would be expected for As_2S_3, but the Fe:As ratio was only 0.11:1. This could be the first recorded occurrence of an (Fe-depleted) arsenopyrite depositing in surface geothermal plant. Due to the formation of this scale, the reinjection temperature at Ngatamariki was designed to be always at or above 90ºC.

1.0 INTRODUCTION

During the planning period for the Ngatamariki geothermal power station, a pilot plant was constructed by Mighty River Power to investigate options for the design of the final production plant. The pilot plant was designed to be able to test a variety of dual flash and binary options for development. The test plant also included a retention system to simulate fluid residence time in reinjection pipelines and reinjection wells. Removable pipe sections throughout the test plant were included in the pilot plant to investigate scaling and corrosion for the conditions tested.

2.0 PILOT PLANT

Only the binary section of the pilot plant is described here. A full description of the pilot plant is given in Addison and Brown (2012). A diagram of the binary section of the test plant is shown in Figure 1. Separated brine and steam were supplied to the pilot plant from an adjacent well (NM7) and separator. The steam was passed through a heat exchanger and exsolved gases were vented to the atmosphere. The condensed steam, less the vented gases, was added to the brine and then passed through a further heat exchanger. The steam heat exchanger is normally only designed to remove the latent heat of the steam with a very small decrease in temperature of the condensate. The condensate normally has a low pH due to the residual dissolved gases and when added to the brine lowers the pH of the brine. This assists in reducing the likelihood of silica polymerisation as the pH is reduced before the silica saturation index is exceeded. However this reduction in pH increases the likelihood of antimony and arsenic sulphides (Brown, 2011) depositing within the preheater, reducing efficiency of the unit as deposition occurs.

The combined brine and condensate was then fed to a hold up vessel which provided a ~55 minute retention time to simulate the time spent in reinjection pipelines and reinjection wells.

Removable pipe sections labelled as “test sections” in Figure 1, were located at strategic positions to enable scaling and corrosion to be investigated for different operating conditions. After each different test condition, the test sections were removed, and the internal surfaces investigated by optical microscopy and SEM, The SEM analysis also included EDX analysis of the elemental composition of any scale deposited.

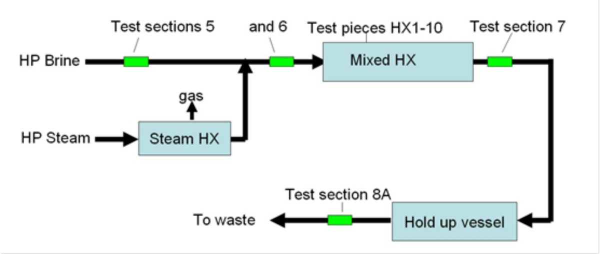

Figure 1: Diagram of the binary section of the pilot plant

2.1 Conditions tested

Three trials were conducted on the binary test rig. Steam and brine from NM7 were separated at 13 barg (195ºC). Steam flow of 0.4 t/hr was condensed in the heat exchanger and gases were exsolved at a pressure of 12.5 barg. The condensate exit temperature was 180 – 185 ºC. The condensate was then mixed with a brine flow of 1.6 t/hr and the combined brine and condensate (2.0 t/hr) had a temperature of 185 – 190 ºC. The exit temperature of the mixed heat exchanger was 95ºC, 85ºC and 90 ºC in the first, second and third tests respectively.

2.2 Results of the pilot testing

The first test (exit temperature = 95ºC) ran for 11 days and the other two tests ran for 18days each.

The pH_{25} of the brine and condensate mixture was measured as 5.6 in the brine exiting the mixed heat exchanger. In the three tests, the deposits observed in the test sections 5 and 6 were identical in all three tests, as the conditions at these positions were the same.

2.2.1 Test position 5

At this position in the test plant, the brine is undersaturated with respect to amorphous silica (SSI = 0.76). The deposit on the test pipe section was black, and very thin. A cut section of the pipe is shown in Figure 2.

Figure 2: Test point 5 pipe sample

SEM EDX analysis of the deposit showed that it was composed of amorphous silica colloids, with small amounts of iron sulfide. The colloidal silica contained significant amounts of aluminium with Si/Al ~ 17%. The colloids were small (~ 5μm) as shown in Figure 3.

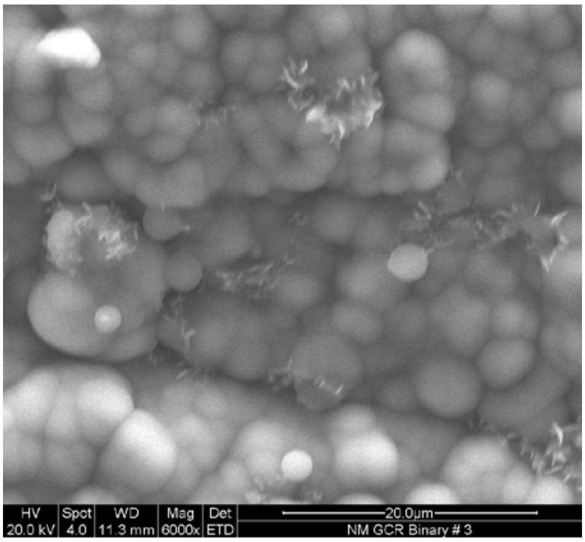

Figure 3: SEM of test position 5 deposit showing silica colloids and small amounts of iron sulfide.

Since the fluid is grossly undersaturated with respect to amorphous silica at this point, the deposit was taken to be formed during the shut down of the plant where the temperature was dropped to ambient as the plant was drained. The small amount of iron sulfide present may have been deposited on the surface as a backwash from the inlet of the condensate which was positioned close to the test pipe position.

2.2.2 Test position 6

Immediately after the condensate is added to the brine, the temperature is ~ 185 ºC and the SSI = 0.78. The deposit on the test section is black coloured, thin, soft and easily removed. A cut section of the pipe is shown in Figure 4.

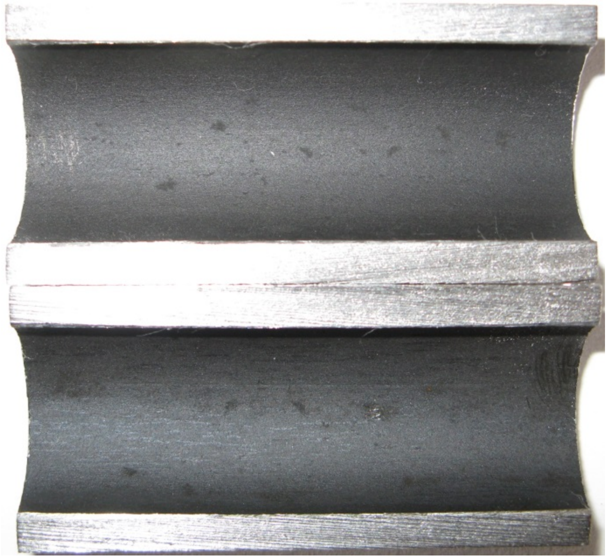

Figure 4 Test point 6 pipe sample.

SEM EDX analysis showed that it was composed almost entirely of iron sulfide in a 1:1 atomic ratio. This was present as small plate-like crystals as shown in Figure 5. There were very small amounts of arsenic, zinc, copper and silver which were also probably present as sulfides.

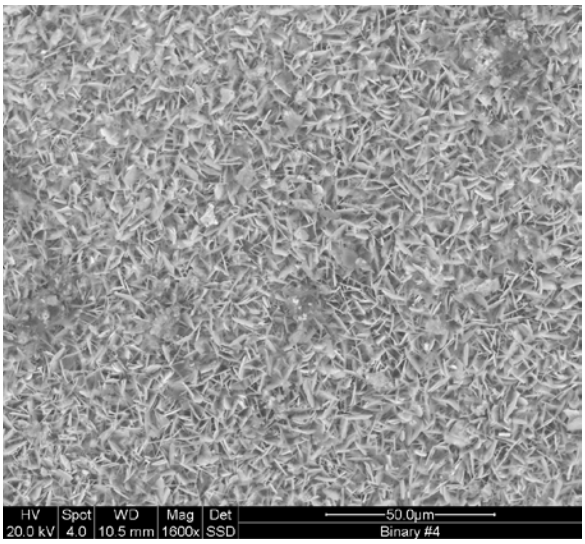

Figure 5: SEM image of test position 6 deposit showing iron sulphide.

2.2.3 Test position 7

This position is directly downstream of the heat exchanger where the temperature of the brine and condensate mixture was cooled to 95ºC, 85ºC and 90ºC in the three tests. The SSI was 1.87, 2.16 and 2.04 respectively in the three tests. In general, the deposits on the test pipes in this position were all very similar in the three tests. The deposit on the pipe sections were purple in colour (Figure 6), relatively thin, soft and easy to remove. The deposits were colloidal

(Figure 7) and consisted of mainly antimony sulfide with increasing arsenic sulfide as the temperature decreased. Very small amounts of silica were also deposited, but these may have been deposited as the plant was shut down.

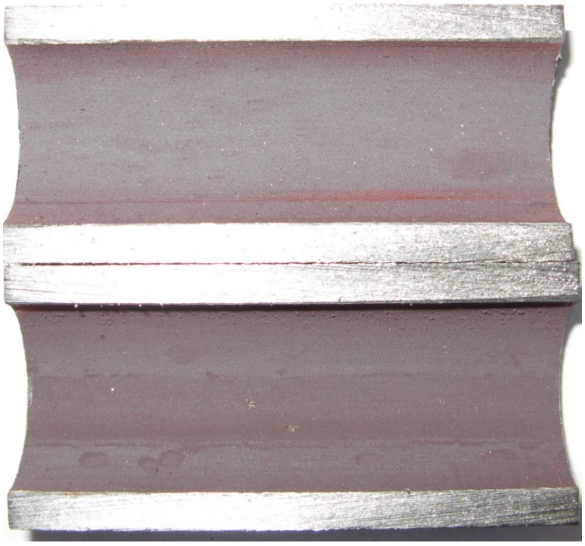

Figure 6: Test point 7 pipe sample

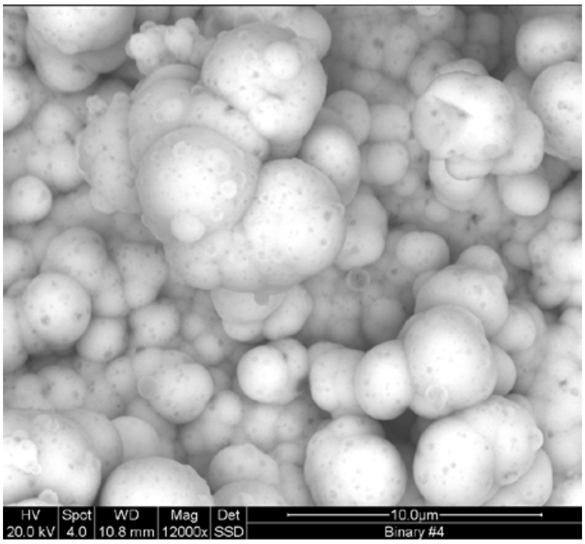

Figure 7 : SEM image of test position 7 deposit showing predominantly antimony sulphide colloids.

The deposits were analysed by EDX on the SEM and the results are shown in Table 1. As can be seen, the deposit is mainly antimony sulfide, but there are significant concentrations of arsenic sulfide. Iron is also deposited, with less iron as the temperature is decreased.

	Test 1	Test 2	Test 3
Temp ºC	95	85	90
S (wt%)	24.3	29.6	27.8
Sb (wt%)	46.8	48.9	54.3
Fe (wt%)	12.4	2.3	6
As (wt%)	10.6	19.3	11.9

Table 1 : Analyses of deposits at sample point 7

2.2.4 Test position 8

This position is after an average retention time of 55 minutes. There was minimal temperature loss during the retention, so the SSI etc is the same as at sample point 7. The deposits at this sample point displayed a large variation in analysis and morphology.

The deposits at the two higher temperature samples at 95ºC and 90ºC were similar in morphology and colour.They consisted mainly of antimony sulfide, were coloured dark purple//black (Figure 8) and were spherical colloids when viewed under the SEM (Figure 9).

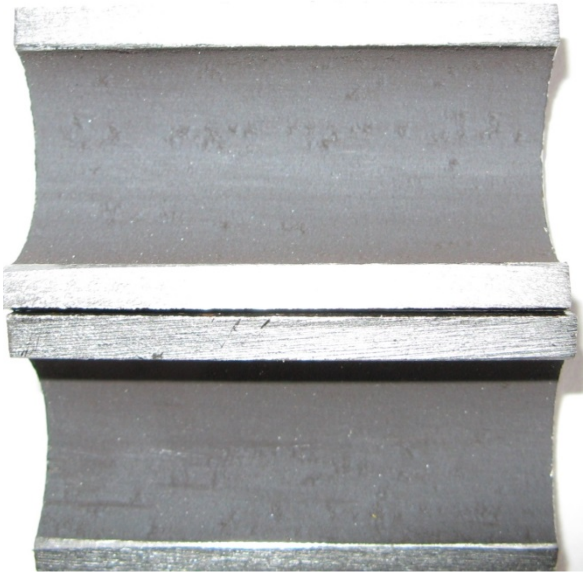

Figure 8: Test point 8 pipe sample from the 90ºC test

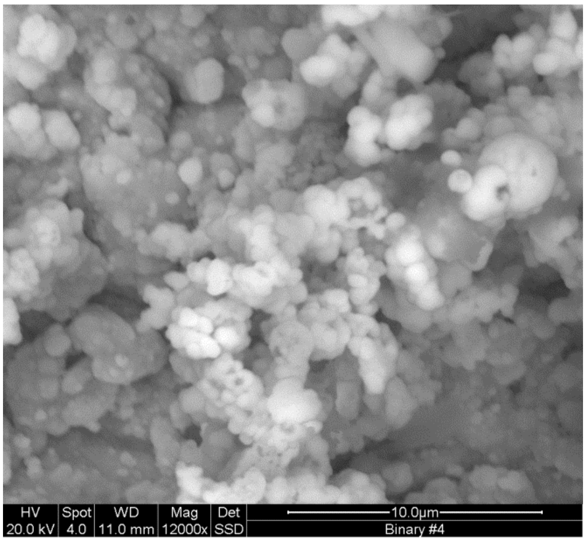

Figure 9: SEM image of deposit from test point 8 of the90ºC test, showing fine, colloidal antimony sulphide

The difference between these two deposits and that deposited at the lower temperature of 85ºC is shown in Table 2, which is the elemental concentrations of the deposits from test point 8 for the three tests. It can be seen that there is a much higher concentration of arsenic sulfide in the 85^{o}C test sample.

	Test 1	Test 2	Test 3
Temp ºC	95	85	90
S (wt%)	20.7	22.5	23.7
Sb (wt%)	24.7	3.2	37.8
Fe (wt%)	36.1	4.0	20.9
As (wt%)	11.3	62.0	12

Table 2: Analyses of deposits at sample point 8

As well, the deposit from the low temperature sample was a different colour (Figure 10). The colour was an orange-brown hue that had not been seen previously in the binary tests.

Figure 10: Test point 8 sample from the 85ºC test

When viewed under the SEM, the morphology of the 85ºC deposit was also very different, consisting of rods with a circular cross section and a diameter of 0.2 – 2.0 μm and lengths of 5 – 20 μm as shown in Figure 11.

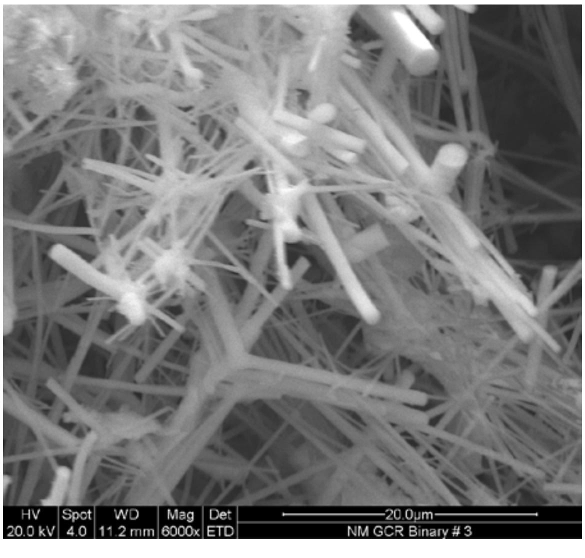

Figure 11: SEM image of the 85ºC deposit at test point 8.

This deposit had not been seen at the test point 7 in this test, and so must have required a retention time to form. This deposit was also much thicker than the deposits from the higher temperature tests. The consequence of this testing was that the reinjection temperature for the Ngatamariki plant was set at 90ºC rather than 85 ºC, in order to avoid the formation of the more voluminous arsenic sulfide deposit.

3.0 GEOCHEMICAL MODELLING

At the time, the deposit at test section 8 of the 85ºC test was assumed to be an unusual polymorph of the amorphous arsenic sulfide ie amorphous orpiment. This would have the formula As_2S_3. The system is reducing, and so the arsenic would be in the +3 rather than the +5 oxidation state. The formula As_2S_3 requires the atomic ratios to be 1:1.5 for As:S. However, the As:S atomic ratio proved to be closer to 1:1 in a series of EDX analyses. This difference is outside the error normally accepted for EDX analyses.

After the Ngatamariki power plant had been built, brine and condensate analyses became available from the plant and it was pertinent to confirm the deposition of arsenic sulfide by modelling the geochemistry. The brine and condensate analyses were combined in the ratio of the steam fraction, and the final "reinjection" brine was calculated to have the concentrations given in Table 3.

pH	5.86	NH_3	3.76
pH temp	22ºC	HCO_3	345
Li	6.72	SiO_2	598
Na	520	B	15
K	113.6	H_2S	22
Ca	2	Sb	0.096
Cl	914	As	2.15
SO_4	5.04		

Table 3: Calculated concentrations (ppm) of the chemicals in the reinjection brine

The concentrations in Table 3 were input into the geochemical code PHREEQC (Parkhurst and Appelo, 1999). The WATEQ4F geochemical database was used as this included geochemical data for amorphous orpiment. The temperature was raised to 90ºC and the saturation index calculated for amorphous orpiment. The log of the saturation index for amorphous orpiment at 90ºC was ~ -8.0 indicating that it was grossly undersaturated. It was thought that the pH of the condensate may have been high due to the loss of dissolved gases when sampling, and so a pH of 4.6 was substituted. The temperature was then raised to 90ºC and a further saturation index calculated for amorphous orpiment. Again it was calculated to be grossly undersaturated. The saturation index was then calculated as a function of temperature to indicate the temperature at which orpiment might be expected to deposit. Using PHREEQC, it was found that orpiment only reached saturation at ~ 25ºC.

At this stage, as a check, the calculation was repeated with the SOLVEQ geochemical code (Spycher and Reed, 1998), which also had geochemical thermodynamic data for amorphous orpiment. Orpiment saturation was reached at ~10ºC (Figure 12). Therefore, as found with PHREEQC, orpiment was grossly undersaturated at 90ºC

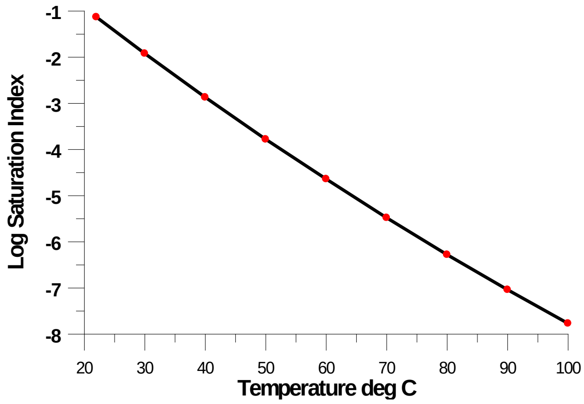

Figure 12: SOLVEQ calculated saturation index of orpiment with temperature, for the reinjection brine.

Further calculations using more extreme values for the various parameters, to try to create orpiment saturation at 90ºC, were unsuccessful. From these calculations, together with the ratio of analysed arsenic to sulfur, it is apparent that the compound responsible for the deposit in the pilot plant at 85ºC after the retention tank cannot be orpiment.

The As:S ratio of 1:1 in this deposit is, however, consistent with that of arsenopyrite (FeAsS). Initial SOLVEQ modelling indicated that the fluid would not precipitate arsenopyrite, as it was calculated to be undersaturated. However, the thermodynamic formational free energy data for arsenopyrite has recently been revised (Pokrovski et al, 2002), and the solubility constant for arsenopyrite calculated from this revised free energy is almost 6 orders of magnitude less than that used in SOLVEQ. Assuming a similar log K - temperature relationship to that used in SOLVEQ, and using the same reaction to describe arsenopyrite solubility;

$AsFeS + 1.5H_2O + 0.375H^+ + 0.375SO_4^{-2} = H_2AsO_3^- + Fe^{2+} + 1.375\ HS^-$

revised log K for arsenopyrite solubility were calculated (Table 4). Using this new solubility data, the reinjection brine was remodeled, using PHREEQC to determine the concentrations of each of the reactive ions in the arsenopyrite dissolution reaction given above, and the ion product (Q). Redox conditions were controlled by the $H_2S:SO_4$ redox couple, and were reducing in the range of pe = -3.3 to -3.5. The log saturation index (SI) was then calculated as log Q/log K. When SI > 0, saturation with respect to arsenopyrite has occurred (Table 4).

Temp (°C)	logK	SI
60	-19.25	0.324
70	-19.08	0.201
80	-18.93	0.128
85	-18.87	0.097
90	-18.81	0.064
95	-18.76	0.032

Table 4. Revised log K and modelled saturation indices (SI) for arsenopyrite solubility in the reinjection brine.

Arsenopyrite is predicted to be stable within modelling error and at equilibrium with the reinjection brine (i.e., SI ~0) at all of the temperatures used in the pilot plant studies (80, 90 and 95oC). It is predicted to become increasingly oversaturated as the temperature decreases. Therefore its presence in the pilot plant “reinjection” pipe is (thermodynamically) possible.

Sensitivity analysis of the modelling shows extreme sensitivity of the SI to minor changes in redox conditions and pH. The redox and pH conditions in the reinjection brine are currently poorly constrained, and so it must be acknowledged that the modelling outcome is highly dependent on assumptions made to generate the chemistry of the final reinjection brine (Table 3). Minor changes in the brine chemistry, or further slight revision of the thermodynamic data for arsenopyrite, could conceivably lead to modeled undersaturation switching to saturation or oversaturation with respect to arsenopyrite, over the temperature interval of interest (90 to 85°C).

However, the atomic ratio of Fe:As in the 85°C deposit was not typical of arsenopyrite, being too low in Fe (Fe:As 0.11:1 instead of 1:1). There is no known solid solution between arsenopyrite and orpiment, that would allow for a variable Fe content in an arsenic sulphide phase. However, this could be the first recorded occurrence of an Fe-depleted arsenopyrite mineral.

SUMMARY

This is the first instance of an arsenopyrite-like phase depositing in the surface infrastructure of a geothermal plant. While the orange deposit did not have the correct stoichiometry for arsenopyrite, being depleted in Fe, recently published thermodynamic data for arsenopyrite does indicate that this mineral could form in the reinjection line. It is postulated that this could be an As-Fe-S phase, with a composition intermediate to that of orpiment and arsenopyrite.

The precipitation of this phase constrains the reinjection temperature art Ngatamariki to greater than 90°C, unless some other means of inhibiting scale formation can be devised.

ACKNOWLEDGEMENTS

We thank Mighty River Power for permission to publish this data.

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