

# COMBINATION FLASH - BOTTOMING CYCLE GEOTHERMAL POWER GENERATION: SCALE INHIBITION AT BULALO FIELD

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## Abstract

*Binary cycle units comprising 16 MWe were installed at the Bulalo, Philippines geothermal field utilizing flashed waste brine that was previously injected directly to the reservoir. In this bottoming cycle, the brine temperature is reduced from 177°C to 135°C across heat exchangers. Over-saturation of silica during conductive cooling of the brine increases to >100%. As a result, silica scaling rates in heat exchanger tubes and brine disposal systems are predicted to increase thirty-fold from 0.1 to >3 mm/yr. Silica scaling in heat exchanger tubes and downstream injection piping must be controlled to maintain optimum heat transfer and to prevent injection piping and well scaling.*

*Siliceous scaling in heat exchangers, cooled injection brine piping, injection wells and near-wellbore formation is inhibited by UNOCAL's patented pH modification process. This process consists of acidification of brine entering the binary plant heat exchangers. Brine pH is reduced from about 6.5 to 5.5 by treatment with only 10 mg concentrated sulfuric acid per kg of brine. The pH modification process has successfully controlled silica scaling in heat exchangers and injection brine piping for over two years. Silica scaling, as a result of flashing and cooling brine, has been reduced to less than 1 mm/yr at a relatively low operating cost.*

## 1.0 INTRODUCTION

General processes by which geothermal brine can be used to generate electric power are well known (DiPippo, 1980). High enthalpy (>0.8 kJ/g; >160°C) geothermal brines are usually flashed to a reduced pressure to generate steam. Steam produced from flashing operations is generally used in conventional steam turbine-type power generators to generate electricity. Lower enthalpy brines are often utilized in binary cycle power systems consisting of heat exchangers. In binary cycles, brine vaporizes a low-boiling point, secondary liquid, such as hydrocarbons. The organic vapor is utilized in a gas turbine-generator to generate electricity (Campbell and Harvey, 1991).

Cooled brine from both flash and binary power plants is typically reinjected into the geothermal reservoir to replenish the aquifer, maintain reservoir pressure and to protect the environment. Steam flashing concentrates brines with respect to dissolved solids. Most dissolved species present in flashed brines exhibit prograde solubility. Thus, if the dissolved species are at or near their saturation concentration in brine, a significant reduction in the temperature of the system may result in supersaturation and precipitation of scale deposits (Wahl, 1977). In low-enthalpy, binary cycle systems, that utilize heat transfer media of lower boiling point than water, scaling components in brine rarely exceed saturation. Furthermore, the limited temperature reduction possible for low enthalpy brines generally produces little or no fouling of heat exchangers or injection wells.

## 2.0 SILICA SCALING

An especially troublesome dissolved solid component of high-enthalpy geothermal brine is silica, found at or near saturation concentrations in the form of silicic acid oligomers. Silica tends to precipitate from geothermal brine as hydrous, amorphous opal or as metal silicate at almost every stage of brine processing as the temperature is reduced (Manceau *et al.*, 1995). Silica scale deposition in flash plants and brine reinjection systems is commonly controlled by disposing of brine at temperatures above which silica/silicate is saturated or only slightly over-saturated. However, a significant amount of heat remains in high temperature injection brine that may otherwise be extracted in a binary bottoming cycle.

Silica scaling results from polymerization of silicic acid (Reaction 1).



Methods utilized to control siliceous scaling in commercial flash plants include reaction/clarification/flocculation, brine acidification (Featherstone *et al.*, 1995) and high temperature injection (Benavidez *et al.*, 1988). In the high temperature injection mode, brine is maintained at sufficiently high temperature so that dissolved silica remains near- or under-saturated with respect to amorphous silica. Slow precipitation kinetics of amorphous silica in low enthalpy brines usually minimizes siliceous fouling of heat exchangers (Chen *et al.*, 1988).

High temperature injection brine heat may be recovered in bottoming binary cycles by flowing brine through heat exchangers (Wigley and Stevens, 1993). At the Kawerau, New Zealand geothermal field, heat recovery is practiced by passing 180°C flashed brine through energy converters. Heat recovery at Kawerau results in decreasing the injection brine temperature to approximately 120°C. The heat extracted brine, exhibiting a pH of 8, is injected into a shallow (140 m) well or discharged into the Tarawera River. Surprisingly, no silica scaling has been reported to form in the heat exchangers or the injection well. Silica deposition rates from this brine are expected to exceed 0.5 mm/yr, however (Gallup, 1996).

### 3.0 MAK-BAN FLASH - BINARY PROCESS

- A second combination flash-bottoming cycle heat recovery process is now operated at the Bulalo geothermal field, located 70 km southeast of Manila on the island of Luzon, Philippines. The Bulalo field produces from a high-enthalpy, liquid-dominated reservoir (Figure 1) to supply 426 MWe installed generating capacity, including the 16 MWe of bottoming-cycle capacity. A single flash, single-entry turbine process was initially installed at the field. The average reservoir temperature is 280°C and the brine is flashed to ~1,200 kPa. Commercial scale geothermal brine injection in the Philippines was pioneered at the Bulalo field. From the start of geothermal operations in 1974, including flow tests of exploration wells, all produced brine has been reinjected into the reservoir (Sta. Maria *et al.*, 1995). Reinjection of flashed brine at ~177°C minimized the deposition of siliceous scales. A representative flashed brine composition is provided in Table 1. Predicted and measured silica deposition rates approach ~0.1 and 2 mm/yr, respectively (Gallup, 1996).

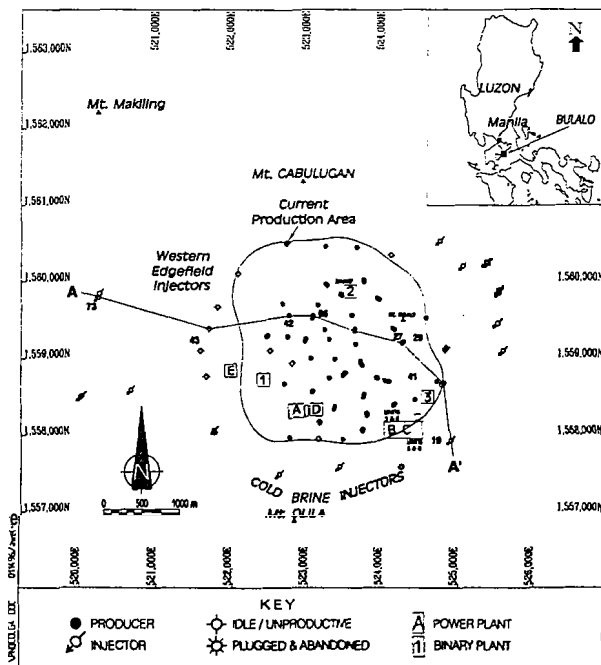


Figure 1. Map of Bulalo field showing production and injection wells. Inset shows field location. Power plants shown are A-C (existing), D-E (planned), and 1-3 (binary).

Analyte	Value
pH (unit, 25 <sup>0</sup> C)	6.5
NCG (wt%)	0.89
B (all ppm)	120
Ca	33
Fe	0.4
K	530
Mg	0.1
Na	2340
SiO <sub>2</sub>	895
Cl	4190
HCO <sub>3</sub>	15
SO <sub>4</sub>	21
TDS	8111

In 1994, binary cycle units, comprising 16 MWe, were installed at the field utilizing high temperature waste brine that was previously injected directly to the reservoir. The binary bottoming cycle consists of six Ormat energy converters which are complete, self-contained, modular power units. The converters utilize a turbine-generator skid with dual, low speed organic vapor turbines each directly connected to opposite ends of an air-cooled generator. Each unit employs an air-cooled condenser for condensing the turbine exhaust, and shell and tube-type organic fluid preheater and vaporizers. The injection brine thermal energy is transferred within shell-and-tube heat exchangers to a pentane working fluid. Pentane vapor powers the condensing turbine-generator. The brine temperature is reduced across the heat exchangers from  $-177^{\circ}\text{C}$  to  $-132^{\circ}\text{C}$  ( $-350^{\circ}\text{F}$  to  $\sim 280^{\circ}\text{F}$ ). Figure 2 is a diagram of the combined flash - bottoming cycle facility.

During the heat recovery process, over-saturation of silica in the injection brine increases from an average of 10% to as much as 100%, and scaling rates are predicted to increase thirty-fold from 0.1 to 3 mm/yr (Klein, 1995; Gallup, 1996). Figure 3 depicts the path of amorphous silica saturation as brine is flashed and cooled in the production system. Point A represents the approximate solubility of quartz in Bulalo brine. The concentration of dissolved silica in brine increases from about 660 ppm to about 925 ppm upon flashing to  $177^{\circ}\text{C}$  and 1,200 kPa at Point B. The solubility of amorphous silica is exceeded at Point B by about 100 ppm (or 12% supersaturation). At this level of supersaturation, very minor silica scaling ( $< 3$  mm/yr) is observed in brine-handling equipment. In the absence of scaling, the concentration of dissolved silica remains constant as the brine is cooled to  $132^{\circ}\text{C}$  through the heat recovery process (Point C). Silica is supersaturated by nearly 100% at Point C, where the solubility of amorphous silica approaches 500 ppm. This degree of supersaturation is conducive to precipitation of silica scale.

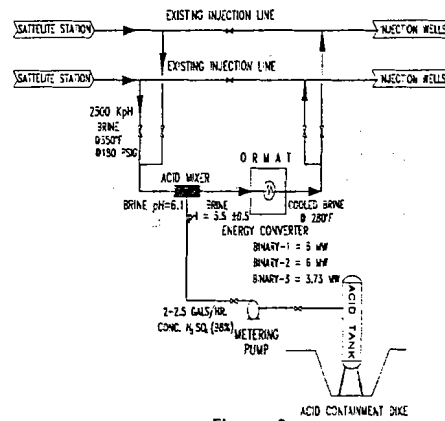
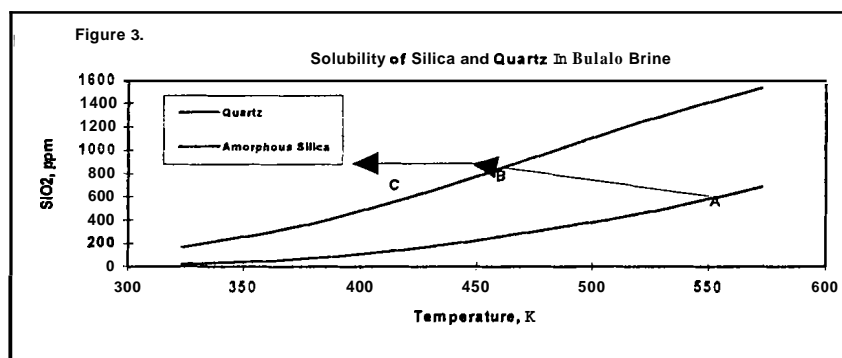


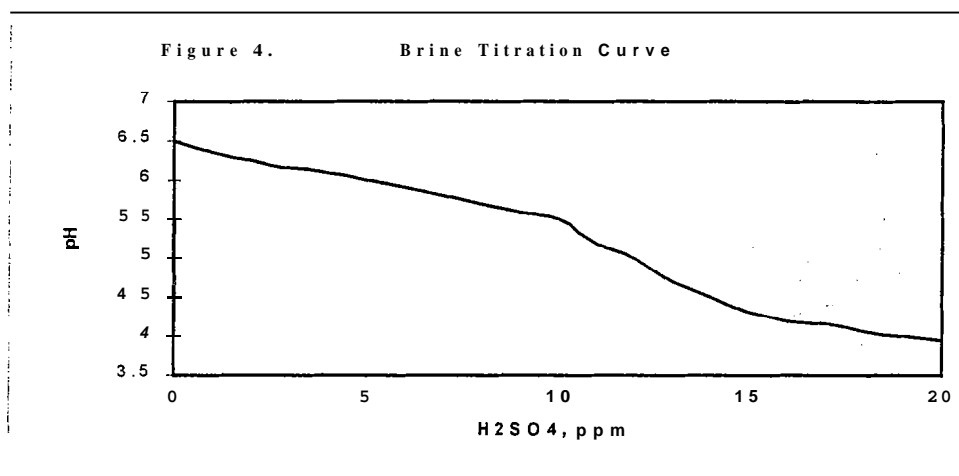
Figure 2  
SIMPLIFIED FLOW DIAGRAM  
pH MODIFICATION FACILITIES  
MAK-BAN 15.73 MW BINARY PROJECT



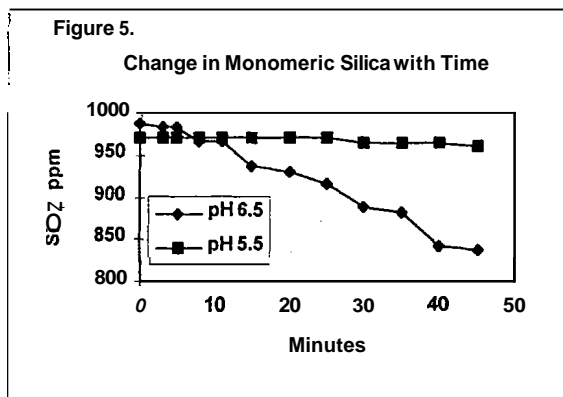
The flow of brine through a given binary plant typically ranges from 10 - 20 m<sup>3</sup>/min. The residence times of brine in the heat exchangers, injection piping and injection wells are estimated to be about 0.5, 60 and 30 minutes, respectively. Sufficient induction time in the brine injection system exists for silica polymerization to initiate (Fleming and Crerar, 1982). Owing to the potential for silica scaling in the heat exchangers and downstream injection system at pH 6.5, the bottoming cycle at Bulalo was conservatively designed and constructed. At the Kawerau, New Zealand field, where heat recovery is successfully practiced in the absence of scale control (pH8), the residence time of brine in the injection system is believed to be much less than that present at Bulalo. Cooled brine at Kawerau is injected at a depth of only 120m, while cooled brine at Bulalo is injected at depths exceeding 2000 m. The residence time of brine in Bulalo wellbores is likely to be an order of magnitude greater than in Kawerau wellbores (Wigley and Stevens, 1993). To control silica/silicate scaling, the heat exchanger outlet temperature was set at 132°C, and a silica scale inhibition process was installed (Gallup, et al., 1993).

#### 4.0 SCALE INHIBITION

Siliceous scaling in heat exchangers, cooled injection brine piping, injection wells and near-wellbore formation at the Bulalo field is inhibited by acidification of brine sent to the binary plants. Pilot scale testing demonstrated that silica scaling was efficiently controlled by reducing the brine pH by about one unit with concentrated sulfuric acid, H<sub>2</sub>SO<sub>4</sub>. Figure 4 presents a representative Bulalo brine titration curve. The brine pH may be reduced from 6.5 to the 5.5 - 6.0 range by treatment with 5 - 10 ppm 98 wt% H<sub>2</sub>SO<sub>4</sub> (2 - 2.5 gal/hr per 5500 kph). An equivalence point in the titration is reached upon treatment with ~10 ppm H<sub>2</sub>SO<sub>4</sub>. The buffering capacity of the brine is lost at pH <5.5, and addition of > 11 ppm H<sub>2</sub>SO<sub>4</sub> reduces the pH below 5. Overdosing with acid can result in relatively corrosive conditions below pH 4.5.



Brine incubation tests performed at the field confirm that silica polymerization may occur at 132°C and pH 6.5 after only 5 minutes of induction time. Up to 20 ppm monomeric silica may disappear in brine after only ~8 minutes residence time in brine-handling equipment. There is essentially no induction period before the onset of silica polymerization in some brines (see Figure 5). Silica scale deposition is expected to occur especially downstream of the heat exchangers in the injection piping and injection wells. Injection wells are located up to 2900 m from the heat exchangers. At pH 5.5, the concentration of monomeric silica in brine remains relatively constant after 45 minutes of incubation. Actual concentrations of dissolved and monomeric silica in pH 6.3 brine decrease slightly from the heat exchanger outlet to the injection wellhead as shown in Table 2.



**Table 2.** Brine Silica Analyses

Sample Location/Conditions	pH	Total Silica, ppm	Monomeric Silica ppm
Acidification:			
Downstream of Heat Exchanger	5.5	ND*	731
Injection Wellhead A	5.5	ND	746
Injection Wellhead B	5.5	ND	743
No Acid Injection:			
Downstream of Heat Exchanger	6.3	766	769
Injection Wellhead A	6.3	748	753
Injection Wellhead B	6.2	766	759

By contrast, the concentration of monomeric silica appears to increase across the injection piping when the brine is acidified to pH 5.5. This apparent increase in monomeric silica may be due to scale dissolution and silica-sulfate complex formation. This silicate specie may be decomposed by the strongly acidic molybdate reagent employed in the silica analysis that liberates additional active silica appearing as monomer (Iler, 1979).

Flash separator brine (177°C and 1,200 kPa) is acidified just upstream of the heat exchangers by pressurizing, injecting and carefully mixing 98 wt% sulfuric acid. The acid-handling system consists of a rubber-line storage tank with a capacity of 8 m<sup>3</sup>, and acid pumps and delivery piping are constructed of Alloy 20. Acid is introduced into the brine through an injection quill at a rate of about 0.15 L/min. During initial startup of the process, a 1.5 m long, 41 cm diameter, carbon steel static mixer with six finned mixing elements lined with Teflon was employed to bring the brine-acid mixture to homogeneity. This design apparently failed due to "cold flow" of the Teflon coating at high pressure resulting in a significant pressure drop across the mixer. Eventually, an unlined carbon steel mixer was employed that does not suffer serious acid corrosion due to high turbulence of brine at the mixing location just downstream of a pipe elbow. The pH at the Bulalo heat recovery plants is typically reduced from about 6.5 to 5.5 by treatment with only 10 mg concentrated sulfuric acid per kg of brine to slow the kinetics of Reaction 1. The rate of silica polymerization is decreased by an order of magnitude upon reducing the brine pH by 0.3 - 1 unit. Acidification of brine can also reduce iron and manganese silicate scaling.

Caution is exercised during sulfuric acid treatment of brine to limit corrosion and alkaline-earth sulfate precipitation (Reaction 2).



(where M = Ca, Sr, Ba, and Ra). Sulfate ions added to brine in the pH modification process enhance silica solubility by forming a weak silica-sulfate complex (Marshall and Chen, 1982). When the potential for sulfate scaling in brine is present, hydrochloric or other acids may be utilized, or the brine may be treated with a sulfate scale inhibitor (Gallup and Featherstone, 1995).

## 5.0 PROCESS OPERATION

The heat recovery process, incorporating silica scale control by brine pH modification, has been successfully operated at the Bulalo geothermal field for over two years. This is the first bottoming cycle to generate electrical power using flashed, injected brine that is highly super-saturated in silica, and that requires scale control. The cost to treat Bulalo injection brine with sulfuric acid is -0.0012¢ (US) per kW-hr of total generation (flash plus binary), owing to the low dosage of acid required to reduce the pH from 6.5 to the 5.5 - 6.0 range. Corrosion of brine-handling equipment attributable to acid injection has been minimal (< 0.1 mm/yr).

Silica scaling, resulting from flashing processes and conductive cooling of brine across heat exchangers, has been reduced to less than 1 mm/yr. Inspections have shown that very little silica scaling occurs in heat exchanger tubes. This is consistent with incubation tests that showed silica polymerization occurs after about 5 minutes of residence time in the cooled brine piping. Considering silica polymerization induction times, brine flow rates, and brine residence times, silica scaling is predicted to form >350 m downstream of the heat exchangers. Therefore, it may be possible to treat brine with acid both upstream and downstream of the heat exchangers to control siliceous scaling in injection piping, wellbores and near wellbore formation. The potential for corrosion may be further reduced by injecting some acid into brine at temperatures below 132°C.

The potential for scaling in the heat recovery process is monitored by brine silica analyses and by injection well tests. Total and monomeric silica concentrations are determined in brines sampled upstream and downstream of the heat exchangers and at injection wellheads. Figures 6 and 7 graphically depict how total and monomeric silica, respectively, are maintained in solution across the heat recovery system by brine acidification. (Changes in concentrations from the different trials are due to different wells with changing compositions being produced to the process.) Injectivity indices (II) for wells disposing of heat recovery brines are obtained periodically. Table 3 indicates that minor decreases in IIs have occurred in wells disposing of pH modified, heat recovery brines during the past two years of operation. These decreases in II are similar to those observed for wells disposing untreated, high temperature brines.

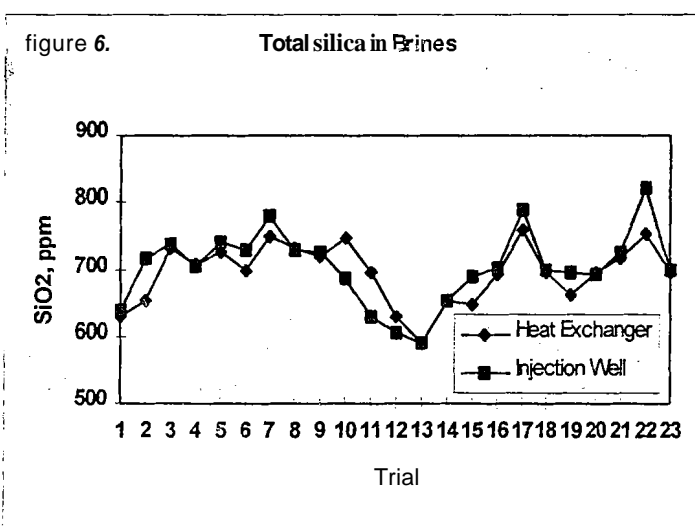


Table 3. **Change in Injectivity Indices**

Well	Utilization	Injectivity Index Decrease, %
A	Heat Recovery, acidified	17
B	Heat Recovery, acidified	0
C	Heat Recovery, acidified	17
D	Heat Recovery, acidified	20
E	High Temperature, untreated	10
F	High Temperature, untreated	0
G	High Temperature, untreated	0
H	High Temperature, untreated	11
I	High Temperature, untreated	40
J	High Temperature, untreated	7

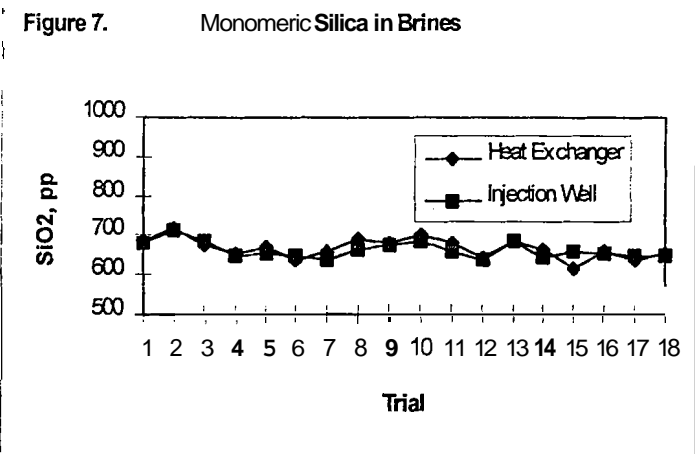


Table 4 presents analyses of scales collected around the heat recovery system. The scales are typically <0.2 mm thick and consist primarily of amorphous silica resembling A-opal. Minor amounts of formation minerals (quartz, clays, feldspar, and pyrite) are co-deposited in the silica matrix. The scale deposits also contain some magnetite corrosion product. Not unexpectedly, at the acid injection point, the fraction of magnetite increases, the sample also contains a trace of wuestite, FeO, and crystalline silica, but the corrosion rate remains relatively low (< 20 mils/yr.). Small amounts of scales deposited downstream of the heat exchangers consist primarily of molecularly-deposited amorphous silica. No sulfate precipitates have been detected in samples due to injection of low dosages of sulfuric acid into brine. Models (Weres, et al., 1982; Gallup, 1996) predict that very little silica or sulfate scales should form in this process employing pH modification scale control technology.

Table 4. Scale Analyses	Upstream of Acid Injection; pH 6.5	Upstream of Heat Exchanger; pH 5.5	Downstream of Heat Exchanger; pH 5.5
X-Ray Diffraction:			
Major	Amorphous	Amorphous	Amorphous
Moderate		Magnetite	
Minor	Quartz, Chlorite, Illite, Magnetite, Pyrite	Quartz, Cristobalite, Pyrite, Wuestite	Quartz, Plagioclase, Pyrite
Bulk Chemical Analyses of Major Elements (wt%):			
SiO2	78.86	71.69	80.11
Al2O3	7.51	2.83	6.67
Fe3O4	2.69	19.21	2.42
Fe(OH)3-SiO2	0	3.76	0
FeS2	0.55	0.85	0.56
CaO	0.89	0.29	0.84
K2O	2.34	0.85	2.26
Na2O	1.62	0.62	1.38
MgO	0.5	0.14	0.41
+H2O	4.2	0.78	4.33
TOTAL	99.16	101.02	98.98

Condensate and cold brine may also be combined with hot brine at the field provided the pH of the individual fluids or the mixture is maintained in the 5 - 6 range (Gallup and Featherstone, 1985; Jost and Gallup, 1985). Although injection of acidic turbine offgases into brine (Schoonmaker, 1989) could effect the required pH change to control scale in this combined flash-bottoming cycle plant, no attempt has been made to do so. Gases potentially cycle back to the production wells causing an overload of gas extraction systems in the steam power plant. Improvements in flash-bottoming cycle geothermal power plants are under development, including reducing the heat exchanger outlet brine temperature further.

## 6.0 CONCLUSION

A combination flash-bottoming cycle geothermal power generation facility has been successfully operated at the Bulalo, Philippines geothermal field. A brine acidification process is utilized to minimize silica scale formation in injection facilities. Injecting a controlled amount of concentrated sulfuric acid into brine allows re-injection of the cooled brine after it has been processed through the heat exchangers of a binary cycle heat recovery plant. A slight decrease in brine pH inhibits silica scaling, and simultaneously minimizes corrosion attack on carbon steel pipelines and wells. The combined flash-bottoming cycle facility affords a 4% increase in power generation at the field. No sulfate scaling has been observed as a result of treating brine with sulfuric acid. The cost to treat the injection brine with sulfuric acid is approximately 0.0012¢ (US) per kW-hr of total generation (flash plus binary). The capital cost of the acid injection system is about US\$ 500,000. Improvements in the flash - bottoming cycle geothermal power plants are in progress.

## 7.0 ACKNOWLEDGMENT

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## 8.0 REFERENCES

- Benevidez, P. J., Mosby, M. D., Leong, J. K., and Navarro, V. C. (1988) Development and performance of the Bulalo geothermal field. *Proc. 10th NZ Geotherm. Workshop*, 55-60.
- Campbell, R. G. and Harvey, C. (1991) Expanding the Mammoth geothermal project. *Geo. Res. Council, Trans.*, 15,349-353.
- Chen, S. H., Rau, H., DeBellis, C., and Neusen, K. F. (1988) Silica fouling of heat transfer equipment - experiments and model. *J. Heat Transfer*, 110,841-849.
- DiPippo, R. (1980) Geothermal energy as a source of electricity. Report RA 28320-1, U.S. Dept. of Energy, 1-26.
- Featherstone, J., Butler, S., and Bonham, E. (1995) Comparison of crystallizer reactor clarifier and pH mod process technologies at the Salton Sea geothermal field. *Proc. World Geotherm. Congress*, 2391-2396.
- Fleming, B. A. and Crerar, D. A. (1982) Silicic acid ionization and calculation of silica solubility at elevated temperature and pH: application to geothermal fluid processing and reinjection. *Geothermics*, 11, 15-29.
- Gallup, D. L. (1996) Brine pH modification scale control technology. *Geo. Res. Council, Trans.*, 20, 749-755.
- Gallup, D. L. and Featherstone, J. L. (1985) Acidification of steam condensate for incompatibility control during mixing with geothermal brine. *US. Patent* 4,522,728.
- Gallup, D. L. and Featherstone, J. L. (1995) Control of NORM deposition from Salton Sea geothermal brines. *Geotherm. Sci. & Tech.*, 4,2 15-226.
- Gallup, D. L., Barnes, M. L., Cope, D., Kolimlim, Q. S., and Leong, J. K. (1993) Brine heat exchanger treatment method. *U.S. Patent* 5,190,664 and *Philippine Patent* 27,868.
- Iler, R. K. (1979) *The Chemism of Silica*, (John Wiley & Sons, New York), Chapter 3.
- Jost, J. W. and Gallup, D. L. (1985) Inhibiting scale precipitation from high temperature brine. *US. Patent* 4,500,434.
- Klein, C. W. (1995) Management of fluid injection in geothermal wells to avoid silica scaling at low levels of silica oversaturation. *Geo. Res. Council, Trans.*, 19, 503-511.
- Manceau, A., Ildephonse, Ph., Hazemann, J.-L., Flank, A.-M. and Gallup, D. (1995) Crystal chemistry of hydrous iron silicate scale deposits at the Salton Sea geothermal field. *Clays & Clay Miner.*, 43,304-317.
- Marshall, W. L. and Chen, C.-T. A. (1982) Amorphous silica solubilities-VI. Postulated sulfate-silicic acid solution complex. *Geochim. Cosmochim. Acta*, 46, 367-370.
- Schoonmaker, J. L. (1989) The Coso geothermal power projects. *Geo. Res. Council, Trans.*, 13, 645-651.
- Sta. Maria, R. B., Villadolid-Abrigo, M. F., Sussman, D. and Mogen, P. G. (1995) Development strategy for the Bulalo geothermal field, Philippines. *Proc. World Geotherm. Congress*, 1803-1805.
- Wahl, E. F. (1977) *Geothermal Energy Utilization*, (John Wiley & Sons, New York), Chapter 5.
- Weres, O., Yee, A., and Tsao, L. (1982) Equations and type curves for predicting the polymerization of amorphous silica in geothermal brine. *Soc. Pet. Eng. J.*, 22, 9-16.
- Wigley, D. M. and Stevens, L. (1993) Developments in Kawerau geothermal field. *Proc. 15th NZ Geotherm. Workshop*, 47-53.