Proceedings International Workshop on Mineral Scaling 2011
Manila, Philippines, 25-27 May 2011

pH Modification Scale Control Technology

Darrell L. Gallup

Thermochem, Inc., 3414 Regional Parkway, Ste. A, Santa Rosa, CA 95403

Darrell@thermochem.com

Keywords: silica, scaling, aluminum, iron, inhibition, brine treatment, acid

ABSTRACT

The kinetics of silicic acid polymerization is retarded when the pH of an aqueous solution is decreased. Therefore, a potential method for controlling siliceous scaling from geothermal brine is treatment with acid. Early attempts to control siliceous scaling in geothermal brine-handling equipment by retarding polymerization implied that the pH had to be reduced to <4, which was considered too corrosive for practical use. In 1980, the author and colleagues examined acidification of hyper-saline brine to mitigate ferric silicate scaling. Field studies showed that a compromise between scaling and corrosion could be achieved by reducing the brine pH to no lower than 4.5.

The pH modification process was operated commercially by 1982 at two fields in the Imperial Valley of California, USA. In 1994, this process was installed on a bottoming cycle power plant to control scaling in heat exchangers and injection wells. Today, additional pH modification processes have been deployed at geothermal fields around the world to control amorphous silica and silicate scale deposition. The history and development improvement of pH modification technology will be reviewed.

1. INTRODUCTION

Considerable effort and expense have been made to mitigate silica/silicate scale deposition from geothermal brines during the process of energy extraction. When geothermal brines are flashed to produce steam, chemical constituents in brines are concentrated. The solubility of most species in brine solutions decreases with the concomitant decrease in temperature during flashing. In the case of silica, geothermal brines are initially at or near saturation with respect to quartz and other forms of silica in the reservoir.

$$SiO_{2(q)} + 2H_2O = Si(OH)_4^0 \qquad (1)$$

Dissolution of quartz, $SiO_{2(q)}$, results in the formation of silicic acid, $Si(OH)_4^0$. At elevated pH, silicic acid will dissociate as H^+ and $H_3SiO_4^-$. In the presence of metal ions, certain metal silicate complexes may also form in geothermal brines, such as $MH_3SiO_4^{2+}$ and $M(OH)_3H_3SiO_4^-$, where M = Al and Fe (Salvi et al., 1998). Under certain conditions, silica and silicates may become supersaturated upon flashing (concentration effect) and cooling (solubility effect, see Fig. 1).

Although quartz and other crystalline silica polymorphs exhibit slow precipitation kinetics, amorphous silica/silicates tend to precipitate rapidly as scale deposits via condensation polymerization reactions (Iler, 1979; Gallup, 1998):

$$2\ Si(OH)_4^0 = (OH)_3SiOSi(OH)_3 + H_2O \qquad (2)$$

$$2M(OH)_3^0 + xSi(OH)_4^0 = M_2O_3 \bullet xSiO_2 + (2x + 3)H_2O$$
where M = Al, Fe (3)

Scale inhibition/control methods employed in geothermal fields have generally been specific to brine chemistry and process conditions (Phillips et al., 1980). The most common methods employed for mitigating siliceous scale deposits in geothermal brine-handling systems include: (a) hot brine injection at or near amorphous silica saturation (Henley, 1983), (b) adjustment of brine pH (Rothbaum et al., 1979; Hibara et al., 1990), (c) aging or pond retention (Yanagase et al., 1970), (d) crystallization/clarification (Featherstone and Powell, 1981), (e) removal of silica by controlled precipitation with metals (Rothbaum and Anderton, 1975), (f) controlled precipitation of silica by cationic surfactants (Ueda et al., 2000), (g) dilution with steam condensate or fresh water (Gallup and Featherstone, 1985), (h) evaporation/percolation ponds (Mercado, 1975), (i) reducing agent treatment (Gallup, 1993a), (j) organic inhibitors/dispersants (Harrar et al., 1982; Candelaria et al., 1996), and (k) chelating agents, organic acids, sequestrants and complexing agents (Gallup, 1998). In a few fields, combinations of the above solutions have been deployed (Arnorsson, 2000). Methods have also been developed to remove deposits once they form in equipment, piping and injection wells (Arata et al., 1996; Messer et al., 1978).

2. HISTORY OF PH MODIFICATION

Silica reactions have been studied for over a century. It has been known for a long time that the kinetics of silicic acid polymerization is retarded when the pH of an aqueous solution is decreased, and that silica is prevented from polymerizing when the pH is increased to yield primarily silicate anion, $H_3SiO_4^-$ (Goto, 1956). It is not surprising, therefore, that potential methods for controlling siliceous scaling from geothermal brines and other aqueous solutions include treatment with acid or base. Increasing the pH of brine with caustic has been considered, but rarely practiced due to potential by-product formation of metal carbonates and hydroxides. In almost all cases, increasing the pH of a brine to control silica requires mitigation or controlled precipitation of the by-products (see Fig. 2).

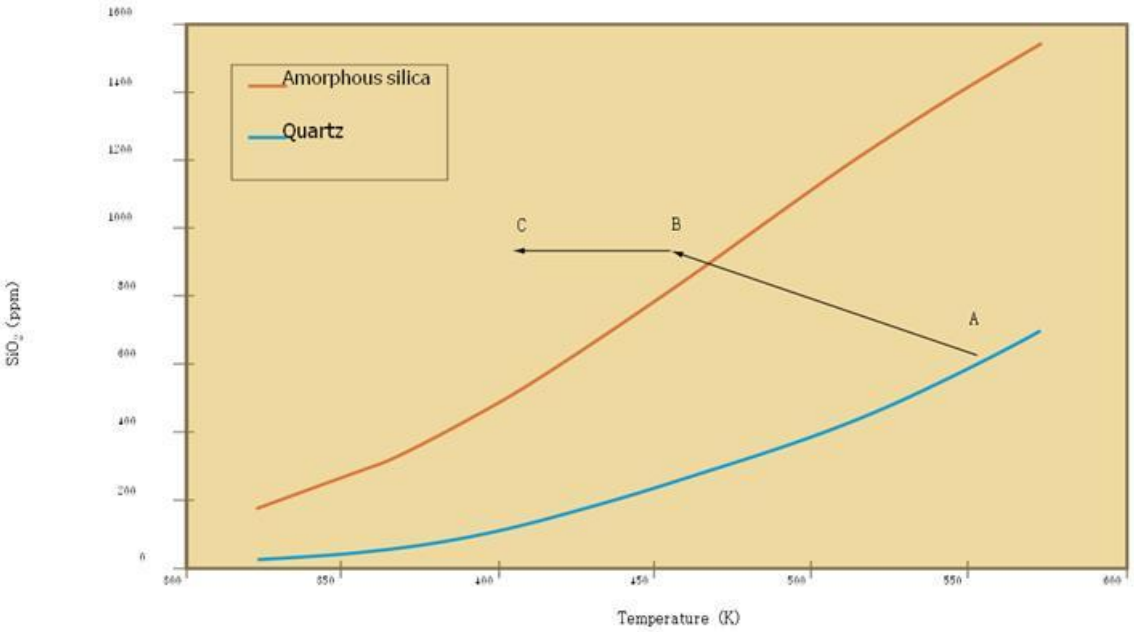


Figure 1: Solubility relationships for quartz and amorphous silica in pure water. A represents the concentration of Si(OH)$_4^0$ from quartz dissolution; B represents the concentration of Si(OH)$_4^0$ in water with respect to amorphous silica solubility upon flashing and cooling; C represents the concentration of Si(OH)$_4^0$ after convectively cooling the flashed solution, *e.g.*, bottoming cycle heat recovery.

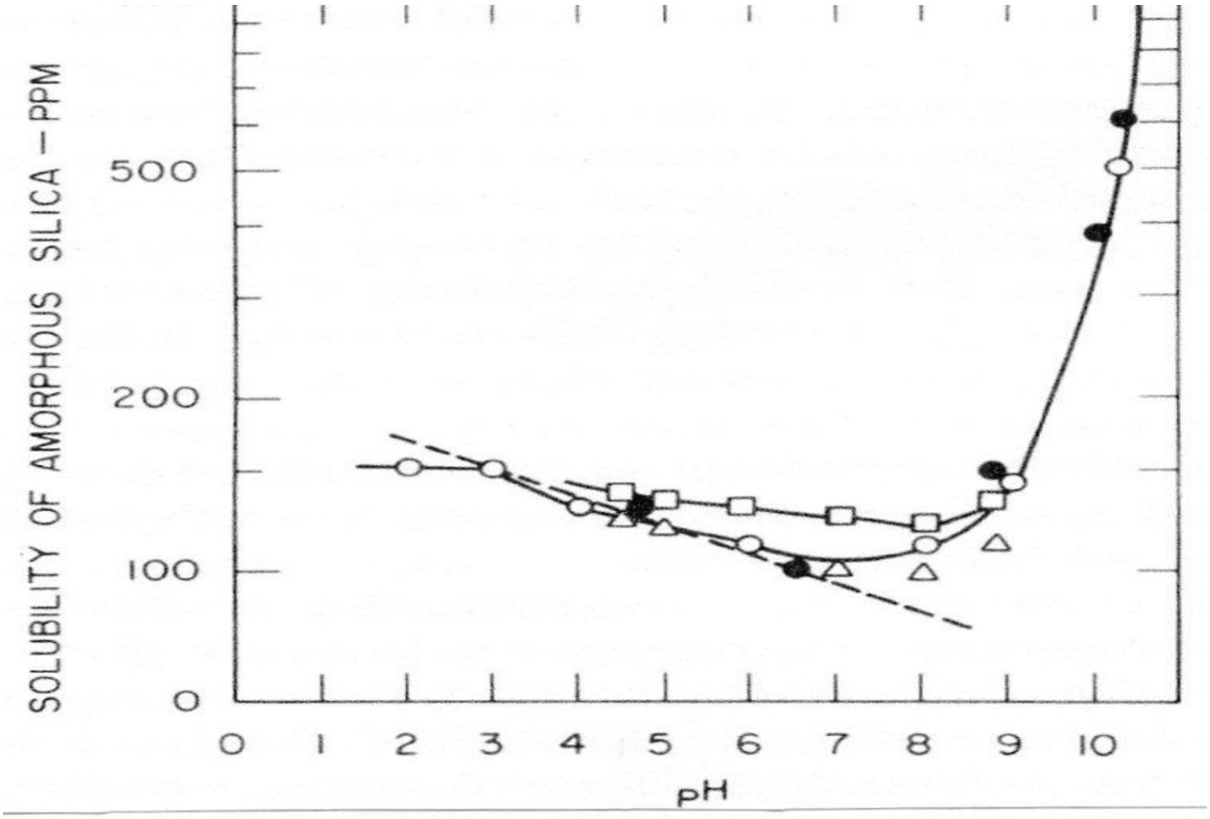


Figure 2: The solubility of amorphous silica vs. pH at ~25°C (Iler, 1979)

Early attempts to control siliceous scaling in geothermal brine-handling equipment by retarding polymerization implied that the pH had to be reduced to <4.5, which was considered too corrosive for practical use (Owen, 1975). At the Salton Sea and Brawley geothermal fields of southern California, USA, attempts to control siliceous scaling by hot brine injection at silica saturation indice practical use (Owen, 1975). At the Salton Sea and Brawley geothermal fields of southern California USA, attempts to control siliceous scaling by hot brine injection at silica saturation indices (SSI) of ≤ 1.0 failed. The failure of hot brine injection was attributed to the deposition of an iron-rich amorphous silica scale, which precipitated at temperatures as high as 50°C above that predicted for pure amorphous silica (see Figure 3).

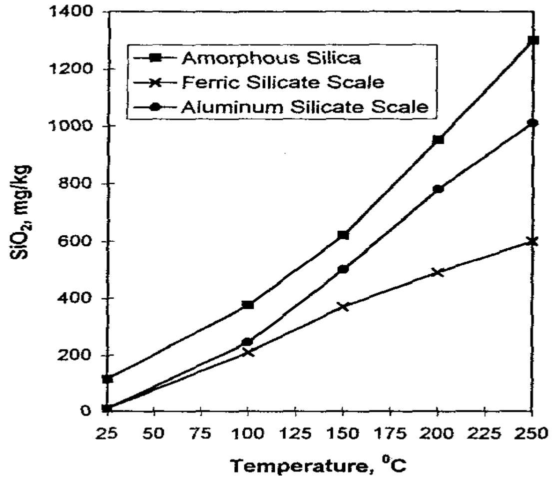


Figure 3: The solubility of amorphous silica, Al-rich amorphous silica and Fe-rich amorphous silica between 25 and 250°C.

In 1980, the author and colleagues examined acidification of the hyper-saline brines at Salton Sea and Brawley to mitigate the ferric silicate scale deposition in surface equipment, piping and injection wells. Field pilot and demonstration studies showed that a compromise between scaling and corrosion could be achieved by reducing the brine pH to no lower than 4.5. In some instances, the pH of the brines was reduced by only 0.1 to 0.5 units (measured at 25°C). Using this "pH modification" process, ferric silicate scaling was reduced from > 30 cm/year to < 1 cm/year without severely corroding surface piping and injection well tubulars. Hydrochloric acid, HCl, was employed in these fields to reduce the pH slightly because other acids were incompatible with brine constituents. The discovery that the pH of brine only needed to be reduced slightly to control the ferric silicate scaling formed the basis of Unocal's patented scale control technology (Jost and Gallup, 1985; Gallup and Jost, 1985; Gallup, 1996a).

The pH modification process was operated commercially by Unocal as early as 1982 at the Salton Sea and Brawley geothermal fields. Numerous process improvements were made which allowed the Brawley 10MWe plant to operate successfully until 1987. The Brawley plant was dismantled and removed in 1987 by the operators due to the inability to mitigate heavy metal sulfide scaling in production wells. The Brawley equipment was eventually moved to the Salton Sea field. Commencement of operation of Salton Sea Unit 2 using the Brawley equipment and pH modification scale control technology began in 1990 (Hoyer et al., 1992). In 1993, Unocal sold its operations (Units 1 – 3) to Magma Power Co. Units 1 and 3 utilized crystallizer reactor-clarifier technology to control iron silicate scaling (Featherstone et al., 1995). CalEnergy Operating Corp. later purchased the Magma Power assets, and combined pH modification in high temperature locations of production facilities with crystallizer reactor-clarifier in low temperature and injection operations. This combination continues to operate in Salton Sea Region 1 today. To control corrosion by HCl, Hastelloy C275 quills and mixers are used in conjunction with cement-lined and duplex stainless steel piping. Injection wells disposing of the pH modified brine were worked over a little more often than those disposing of clarifier brine.

In 1994, at the Mak-Ban, Philippines field, Unocal installed another pH modification process as part of a bottoming cycle power plant addition to the field (Gallup et al., 1993). Prior to National Power Corporation's addition of the bottoming cycle power plants at Mak-Ban, silica scaling was controlled by hot brine injection (SSI ≤ 1.1; Al-rich SSI ≤ 1.3). (Scale deposited from Mak-Ban brine was originally assumed to be pure amorphous silica, but subsequent studies showed that the scale was an Al-rich silicate with a composition approaching $Al_2O_3{\bullet}10SiO_2$.) To control scaling in heat exchanger tubes and injection wells, pH modification processes were installed. Brine sent to the bottoming cycle plant was cooled from 175 to 135°C, which increased the SSI and Al-rich SSI to ~2.0. Cheaper and easier to handle sulfuric acid, H_2SO_4, was injected into brine upstream of the bottoming cycle plant to decrease the pH from ~6.5 to ~5.7 (Gallup, 1996b). Carpenter 20 injection quills were utilized with stainless steel mixers. A proprietary silica/silicate scaling model was used to target the acid dosage and pH necessary to control $Al_2O_3{\bullet}10SiO_2$ deposition (Gallup et al., 1993). The pH modification process operated successfully for 10 years. Brine injectivity was relatively constant during this period and similar to hot brine injection performance.

Delivery of 98% H_2SO_4 to the Mak-Ban field was by tank truck that passed through vehicle and pedestrian congestion. As a result of safety concerns, Kitz and Gallup (1996) examined methods to generate H_2SO_3 and H_2SO_4 at the field using H_2S in vent gas. A pilot burner-scrubber was tested for this application. At about the same time, Kiyota et al. (2000) described a bioreactor to convert H_2S to H_2SO_4 for use in pH modification processes in geothermal fields of Japan. Commercial operation of the bioreactor was achieved by 1998 to reduce the pH of brine at a field on the island of Kyushu. Hydrogen sulfide in vent gas may also generate HCl under certain reaction conditions to not only acidify brine, but also to stimulate wells (Gallup, 2003).

At the Coso geothermal in central California, Al-rich silica scaling was deposited in surface equipment and injection wells, attributed to setting the hot brine injection temperature at SSI of ~1. Since Al-rich amorphous silica is less soluble than pure amorphous silica, pH modification was conducted by injecting acid-rich vent gases into spent brine in an effort to minimize CO_2/H_2S emissions into air. Although the vent gas injection was successful in controlling scale deposition, increasing gas returns in production wells began to overwhelm the gas removal system of the turbine-condensers. This operation was discontinued. By 1999, twelve pH modification (H_2SO_4 injection) stations were installed at the field. At the injection temperature of 110 - 120°C, the SSI approached 2.3 in 44 injection wells. (The author believes that the Al-rich SSI was about 2.5.) Prior to institution of pH modification technology at the field the annual injectivity decline rate averaged 6%. Post pH modification deployment (pH 4.5 – 5.0), the annual injectivity decline rate averaged 0.75% (8X increase in injection well life). The use of pH modification at Coso has declined due to difficulty in maintaining the equipment and reduction in produced brine from the wells.

In 2007, the Blundell, Utah Unit 2 plant was fitted with a bottoming cycle heat recovery system. Similar to the Mak-Ban experience, the SSI increased to ~2.4 due to convective cooling of the brine. A pH modification system was installed to control scaling in the heat exchangers, piping and injection wells. And, like Mak-Ban, no injectivity losses due to scaling have been observed. A Hastelloy C-276 quill and small piping used to pre-mix the acid initially installed at Blundell failed, and has since been replaced with Teflon®-lined components.

3. DEVELOPMENT & IMPROVEMENTS

Today, additional pH modification processes have been deployed at geothermal fields in the United States, Iceland and New Zealand to control amorphous silica and silicate scale deposition. (Hoyer et al., 2008; Sigfusson and Gunnarsson, 2011). The success or failure of pH modification scale control technology is dependent on the kinetics of silica polymerization. The reactions responsible for scale deposition must be slowed for a time sufficient to allow brine to migrate deep into injection formations before significant polymerization occurs. Engineering solutions have been implemented to mitigate most corrosion and operational issues, but an understanding of the chemistry of siliceous scale control continues to develop.

When considering pH modification scale control technology it is important to obtain a complete brine analysis with pH being measured in the field and laboratory. Redox potential measured in a closed system is also useful. If iron is detected, the oxidation state should be determined. Titration of brine with acid in the field will not only help understand acid requirements and buffering capacities, but also to measure alkalinity. From the brine analysis, one may calculate (a) geothermometers to compare with temperature and pressure measurements, (b) Pourbaix (Eh-pH) diagrams of speciation and mineral stabilities, (c) the tendencies for silica scaling under various temperature and pressure regimes, and (d) the scaling rate (Thermochem, Inc. proprietary kinetic model adjusted to field conditions). The brine analyses may also be used to predict pure amorphous silica scaling vs. metal silicates, and to select a compatible acid for reducing the pH.

A useful test is to place geothermal brine into a temperature-controlled hold-up vessel (HUV). Over a period of time, aliquots of brine are removed from the HUV, and total and monomeric silica concentrations are measured. The loss of total, filterable and monomeric silica from brine over a period of time may be used to understand the kinetics of polymerization. By adjusting the pH of the brine in the HUV, one may estimate the time it takes for the onset of polymerization to occur as a function of acid addition. The brine temperature and pressure may also be adjusted to determine an optimal final flashing temperature and pressure for the pH modification process. This allows one to determine the pH and acid dosing requirement when flashing to low pressure or when cooling brine in a bottoming cycle plant. An example of this type of testing is shown in Fig. 4. Featherstone et al. (1995) expressed concern about the inability of pH modification to allow low pressure flashing (cooler brine injection) compared to crystallizer reactor-clarifier technology, which preferably flashes brine to atmospheric pressure. This is a concern at the Salton Sea and other hyper-saline or Fe-rich brine fields, but not elsewhere.

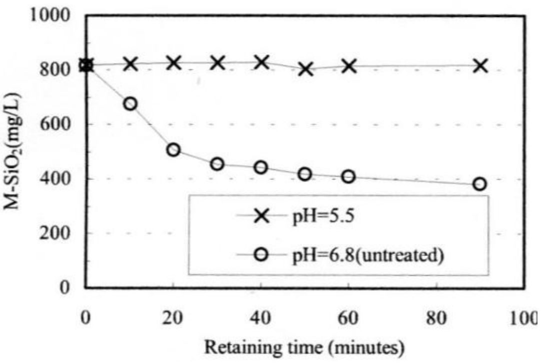
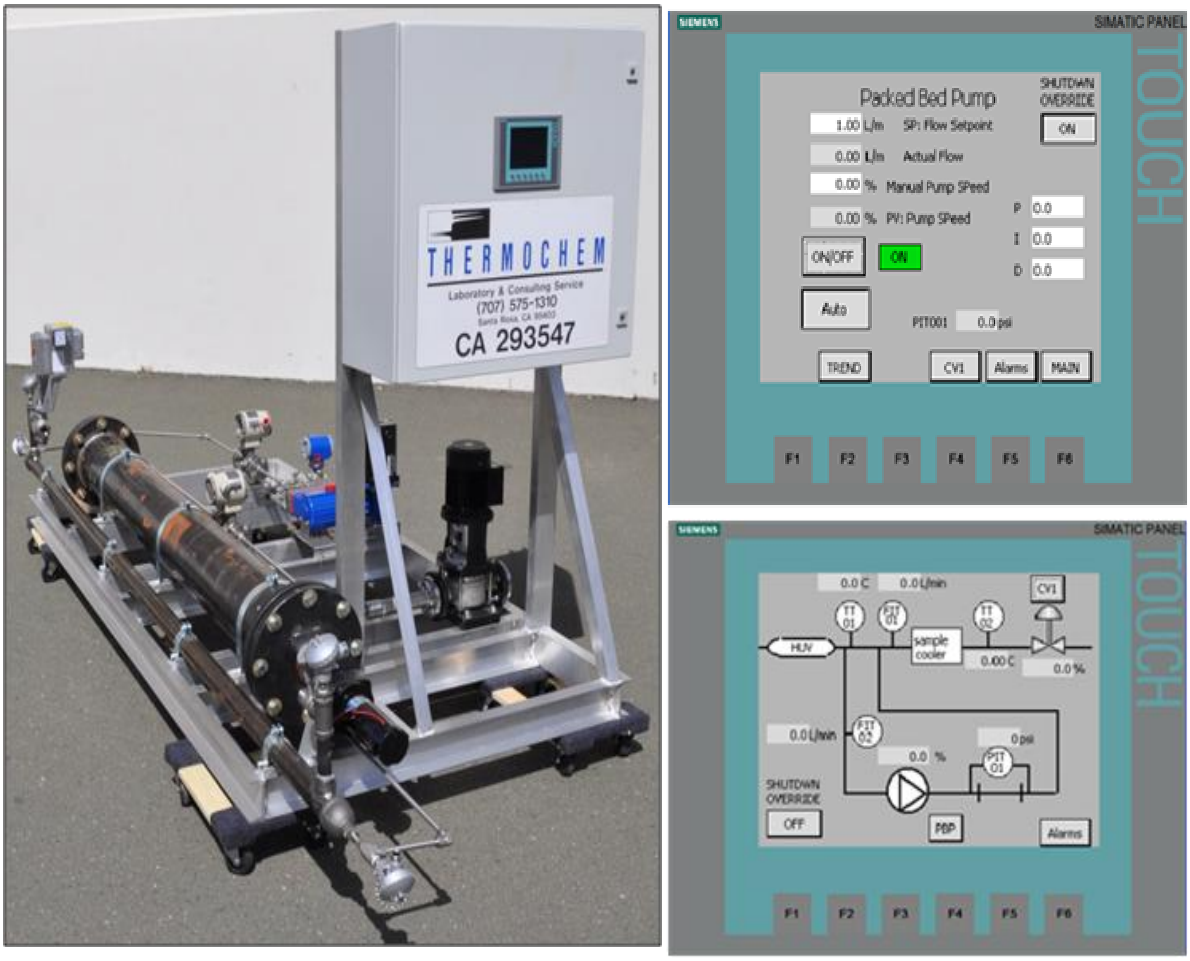


Figure 4: Monomeric silica in solution with increasing holdup time. pH 5.5 maintains monomeric silica constant in solution for 90 minutes compared with immediate polymerization at pH 6.8 (from Kiyota et al., 2000).



1.00 L/m SP: Flow Setpoint
0.00 L/m Actual Flow
0.00 % Manual Pump SPeed
0.00 % PV: Pump SPeed
P 0.0
I 0.0
D 0.0
PIT001 0.0 psi

0.0 C
0.0 L/min
0.00 C
0.0 %
0.0 L/min
0.0 %
0 psi

Figure 5: HUV – Packed Bed Test Skid and control screen

Another recommended test consists of passing brine through a packed bed of injection formation rocks. Scaling in the bed or in a slim-tube (tube blocking test) is monitored over a pH range. Pressure differential and changes in brine chemistry across the bed (at different hold-up times) is monitored to determine the optimal pH for scale control. The packed bed materials may also be examined to determine the effect of pH modified brine on the rock mineralogy. Injection formation rocks containing significant calcite ($CaCO_3$) or other acid neutralizing minerals may increase the pH of brine sufficient to prematurely trigger silica polymerization. If such a reaction occurs in the near wellbore formation, brine injectivity may suffer. Therefore, it is also important to know the mineralogy of the formation into which pH modified brine is injected. In combination with an HUV, the kinetics of silica polymerization may be monitored as a function of brine pH. While the effects of rock-brine interactions and simulation of injection of pH modified brine may not be determined absolutely, the relative trends in HUV packed bed testers can shed light on the efficacy of the technology to control scaling and near well-bore formation damage (see Fig. 5).

Especially when flashing brine to low pressure conditions, the loss of brine buffers may lead to very steep titration curves in the desired pH range. As shown in Fig. 6, a small change in acid pump rate can lead to highly scaling or corrosive conditions. This situation may be improved by installing multiple acid injection units. Dual and triple acid injection points have proven to overcome this obstacle. This is achieved by (a) injecting less acid at upstream, higher temperature and pressure conditions sufficient to retard silica polymerization and reduce corrosion at those locations, and (b) injecting enough acid at downstream, lower temperature and pressure conditions to reach the final pH target. With more buffering capacity remaining at the downstream location, the second or third acid injection unit uses a smaller pump that is less prone to under- or over-dosing.

In some pH modification applications, the acid dosage may be rather small (a few ten's of ppm). We have found that direct acid injection into brine may be feasible. On the other hand, when the acid dosing requirement to achieve the target pH is significant, pre-dilution of acid with hot, non-aerated brine is advantageous. Pre-dilution minimizes corrosion of quills and primary acid-brine static mixers of fin, vane or auger design.

Treatment of brines with reducing agents has proven to not only inhibit ferric and manganic

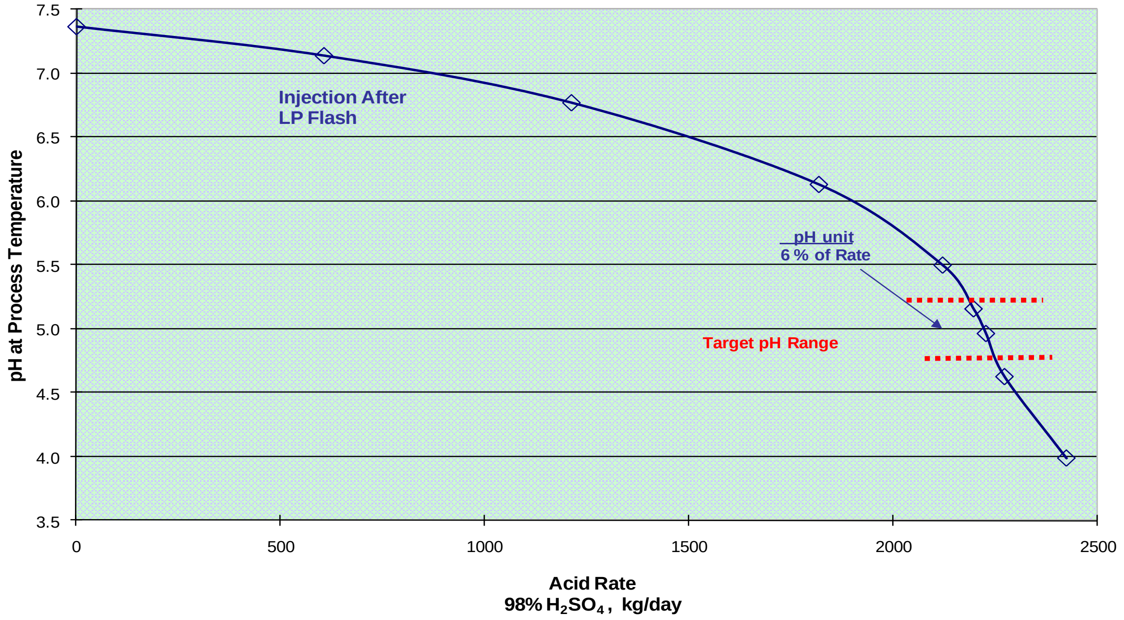


Figure 6: The effect of acid dosing dual-flashed brine, which is not well buffered

Table 1: Comparison of mild steel corrosion in pH modification tests with and without added sodium formate

	Acid Treatment		Acid and Reducing Agent Treatment	
Test	General Corrosion, mil/yr	Pitting, mil/yr	General Corrosion, mil/yr	Pitting, mil/yr
pH 4.0	1326	7709		
pH 4.5	306	4524	254	1099
pH 5.0	258	2385	224	554

silicates, but also to decrease corrosion. Ferrous and manganous-rich amorphous silicas exhibit a higher solubility in aqueous solution than their higher oxidation state counterparts (Gallup, 1993b). For example, in pilot testing of acid injection and reducing agent plus acid injection, general and especially pitting corrosion were decreased by the mixture (see Table). Reducing acids have also been shown to control both ferric silicate scaling and corrosion. A preferred reducing acid is formic, HCOOH, because it is strong enough to acidify brines at reasonable dosages, and the by-product of reaction is benign CO_2. Oxygen scavengers are also acceptable reducing agents in this application. Precaution must be taken to ensure that by-products of oxygen scavenging and metal ion reduction agents are compatible with other brine constituents. The reducing agents are known to precipitate silver, gold, antimony and arsenic from geothermal brines, which may or may not be desirable (Gallup et al., 1995).

As mentioned above, pH modification may be combined with other scale control methods. We have found that mixing warm or cold steam condensate or fresh waters with brine, whilst designed to dilute silica to below saturation (SSI or M-rich SSI < 1), may still result in scaling. To alleviate incompatibility with respect to silica, we often adjust the pH of heated condensate or fresh water to match that of the brine. When cold condensate or fresh water is mixed with brine to dilute silica/silicate, we often recommend reducing the pH to < the brine pH. These pH adjustments are designed to mitigate silica, silicate, carbonate, sulfide, hydroxide and other acid soluble mineral incompatibilities. When dilution waters are incompatible with brine to form sulfates, fluorides and other non-acid soluble species, other inhibitors are deployed with or without acid (Gallup and Featherstone, 1985; Gallup and Featherstone, 1995a; 1995b).

4. CONCLUSIONS

pH modification technology continues to develop as a solution to controlling siliceous scaling from geothermal brines. Prior to 1980, acidification of brine was considered as a scale control process, but ultimately deemed too risky corrosion-wise for practical use. Eventually, it was discovered that the very low pH values that were believed necessary to control scale deposition were unwarranted. By acidifying brines to pH ≥ 4.5 (measured at ambient conditions), both scaling and corrosion were minimized. In some cases, a little scaling (< 1 mm/yr) was found to be beneficial in providing a protective layer on steel that resisted acid attack. With time, pH modification technology not only improved with chemical and engineering solutions, but also became more acceptable as a scale control process.

The original process was applied to dual and triple flash plants, but required relatively hot brine injection due to the lower solubility of metal silicates compared to pure amorphous silica. Process improvements led to the use of the technology to control scaling in low pressure flash and bottoming cycle heat recovery plants. As the technology gained more historical success, it received more consideration as a practical and cost-effective method to control siliceous scaling. Currently, a number of fields are using pH modification technology to control scale deposition. When applied carefully and using process improvements, the technology may control scaling in equipment, injection piping, injection wells and injection formations. Retardation of silica/silicate polymerization reactions may reduce injectivity decline rates (increase injection well life) caused by near wellbore formation damage and “skin” effects.

The technology may be used in combination with other scale control processes. It offers an advantage over some of the processes used in the industry – cheap, effective inhibitor, relatively small footprint, moderately expensive equipment requirement, reduced waste disposal, no ponding, no surface disposal of brine, opportunities for continued improvements, etc.

ACKNOWLEDGEMENTS

I thank my many Unocal Corporation and Chevron Corporation colleagues for their support in development of pH modification technology, and Thermochem, Inc. management for permission to publish this paper.

REFERENCES

Arata, E., Erich, R., Paradis, R., 1996. Recent innovations in pigging technology for the removal of hard scales from geothermal pipelines. Geotherm. Resour. Council Trans. 20, 723-727.

Arnórsson, S., 2000. Injection of waste geothermal fluids: chemical aspects. Proc. World Geotherm. Congress 2000, 3021-3026.

Candelaria, M.N.R., Garcia, S.E., Baltazar Jr., A.D.J., Solis, R.P., Cabel Jr., A.C., Nogara, J.B., Reyes, R.L., Jordan, O.T., 1996. Methods of coping with silica deposition – the PNOC experience. Geotherm. Resour. Council Trans. 20, 661-672.

Featherstone, J.L., Powell, D.R., 1981. Stabilization of highly saline geothermal brines. J. Petrol. Technol., 33, 727-734.

Featherstone, J. Butler, S., Bonham, E., 1995. Comparison of crystallizer reactor clarifier and pH mod process technologies used at Salton Sea geothermal field. Proc. World Geotherm. Congress 1995, 2391-2396.

Gallup, D.L., 1993a. The use of reducing agents for control of ferric silicate scale deposition, Geothermics, 22, 39-48.

Gallup, D. L., 1993b. The influence of iron on the solubility of amorphous silica in hyper-saline geothermal brines. Proc. EPRI 1991 Symp. on Chem. in High Temp. Aq. Solns., F6f1-15.

Gallup, D. L., 1996a. Brine pH modification scale control technology. Geotherm. Resour. Council Trans., 20, 749-755.

Gallup, D. L., 1996b. Combination flash - bottoming cycle geothermal power generation facility: a case history. Geotherm. Resour. Council Bulletin, 25, 264-270.

Gallup, D.L., 1998. Aluminum silicate scale formation and inhibition (2): scale solubilities and laboratory and field inhibition tests. Geothermics, 27, 485-501.

Gallup, D. L., 2003. Simultaneous hydrogen sulfide abatement and production of acid for scale control and well stimulation. Proc. Intern. Geotherm. Conf. – Reykjavik 2003, pp. 5.

Gallup, D.L., Barnes, M.L., Cope, D., Kolimlim, Q.S., Leong, J.K., 1993. Brine heat exchanger treatment method. US Patent 5,190,664.

Gallup, D.L., Featherstone, J.L., 1985. Acidification of steam condensate for incompatibility control during mixing with geothermal brine. US Patent 4,522,728.

Gallup, D. L., Featherstone, J. L., 1995a. Control of NORM deposition from Salton Sea geothermal brines. Geotherm. Sci. and Technol., 4, 215-226.

Gallup, D.L., Featherstone, J.L., 1995b. Use of added water to achieve 100% injection weight in geothermal operations. US Patent 5,413,718.

Gallup, D. L., Featherstone, J. L., Reverente, J. P., Messer, P. H., 1995. Line Mine: A process for mitigating injection well damage at the Salton Sea, California (USA) geothermal field. Proc. World Geothermal Congress 1995, 2406-2412.

Gallup, D.L., Jost, J.W., 1985. Control of metal-containing scale deposition from high temperature brine. US Patent 4,537,684.

Gallup, D. L., Kitz, K., 1998. On-site production and usage of sulfurous acid for scale inhibition. Proc. 19th PNOC-EDC Geotherm. Conf., 191-198.

Goto, K., 1956. Effect of pH on polymerization of silicic acid. J. Phys. Chem., 60, 1007-1008.

Harrar, J.E., Locke, F.E., Otto Jr., C.H., Lorsensen, L.E., Monaco, S.B., Frey, W.P., 1982. Field tests of organic additives for scale control at the Salton Sea geothermal field. Soc. Petrol. Engin. J., Feb., 17-27.

Henley, R.W., 1983. pH and silica scale control in geothermal field development. Geothermics, 12, 307-321.

Hibara, Y., Tazaki, S., Kuragasaki, M., 1990. Advanced H_2S gas treatment system for geothermal power plant – "geothermal gas injection technology." Geotherm. Sci. Technol., 2, 161-171.

Hoyer, D. P., Kitz, K. R., Gallup, D. L., 1997. Salton Sea Unit 2: innovations and successes. Geotherm. Sci. & Technol., 5, 155-169.

Hoyer, D., Spinks, K., Powell, T., 2008. Mighty River Power's geothermal development program in the Taupo Volcanic Zone of New Zealand. Geotherm. Resour. Council Trans., 32, 365-368.

Iler, R.K., 1979. The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry. Wiley-Interscience, New York, pp. 78-83.

Kiyota, Y., Hirowatari, K., Tokita, H., Haruguchi, K., Uogata, K., 2000. Evaluation on geothermal injection treatment by pH modification. Proc. World Geotherm. Congress 2000, 3077-3082.

Mercado, S., 1975. Cerro Prieto geothermoelectric project: pollution and basic protection. Geothermics, 2, 1394-1398.

Mroczek, E., 2010. pH Modification Pilot Plant Trials. Proc. World Geotherm. Congress 2010,

Jost, J.W., Gallup, D.L., 1985. Inhibiting scale precipitation from high temperature brine. US Patent 4,500,434.

Messer, P.H., Pye, D.S., Gallus, J.P., Injectivity restoration of a hot-brine geothermal injection well. J. Petrol. Technol., 30, 1125-1130.
``

Owen, L.B., 1975. Precipitation of amorphous silica from high-temperature hypersaline geothermal brines. Lawrence Livermore Laboratory report UCRL-51866, pp. 20.

Phillips, S.L., Mathur, A.K., Garrison, W., 1980. Treatment methods for geothermal brines. In: Caspe, L.A., Pinchback, T.R. (Eds.), Geothermal Scaling and Corrosion. ASTM Special Technical Publication 717. ASTM, Philadelphia, PA, pp. 207-224.

Rothbaum, H.P., Anderton, B.H., 1975. Removal of silica and arsenic from geothermal discharge waters by precipitation of useful calcium silicates. Geothermics, 2, 1417-1425.

Rothbaum, H.P., Anderton, B.H., Harrison, R.F., Rohde, A.G., Slatter, A., 1979. Effect of silica polymerization and pH on geothermal scaling. Geothermics, 8, 1- 20.

Salvi, S., Pokrovski, G.S., Schott, J. Experimental investigation of aluminum-silica aqueous complexing at 300°C. Chemical Geology, 151, 51-67.

Sigfusson, B., Gunnarsson, I. 2011. Scaling prevention experiments in the Hellisheidi power plant, Iceland. Proc. 36th Stanford Workshop on Geotherm. Reserv. Engin., pp. 5.

Ueda, A., Kato, K., Abe, K., Furukawa, T., Mogi, K., Ishimi, K., 2000. Recovery of silica from the Sumikawa geothermal fluids by addition of cationic reagents. J. Geotherm. Res. Soc. Jpn, 22, 249-258.

von Hirtz, P.N., 2011. Advancements in pH-Modification Process Control. Proc. IGA-WPRB Scaling Workshop.

Yanagase, T., Suginohara, Y., Yanagase, K., 1970. The properties of scales and methods to prevent them. Geothermics, 2, 1619-1623.