ON-SITE PRODUCTION AND USAGE OF SULFUROUS ACID FOR SCALE INHIBITION

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Abstract

UNOCAL Corporation currently utilizes brine acidification to control scale deposition. Acids utilized in commercial operations include, sulfuric and hydrochloric. A new, patented process has been developed to reduce operational costs and improve inhibition by producing Sulfurous acid on-site upon burning hydrogen sulfide or elemental sulfur. Treatment of brines with sulfurous acid is particularly effective in controlling siliceous scaling by (1) retarding the kinetics of silica polymerization, and (2) forming soluble sulfito-silicate complexes. The advantages of on-site production of sulfurous acid include abatement of hydrogen sulfide, use of sulfur-bearing wastes, reduced corrosion potential, scavenging of oxygen, reduced by-product scale formation potential, and inhibition of silicate, sulfide and carbonate scales. Brine or condensate may be treated with sulfurous acid to control scale deposition, mitigate corrosion and improve gas partitioning in condensers.

1.0 INTRODUCTION

UNOCAL'S patented pH modification process has been proven to make low pressure flash and bottoming cycle heat recovery feasible and economical by inhibiting the formation of silica scale in flash vessels. heat exchangers, and injection pipelines and wells. Now a new process offers even lower operating costs for dual flash plants and binary heat recovery units, improved scale inhibition, and other process advantages. UNOCAL's licensable process for the on-site production of sulfurous acid (H_2SO_3) to control silica, calcite and metal sulfide scales can provide improved profitability in the U.S., Central and South America, Southeast Asia, and Japan (Kitz and Gallup, 1997).

2.0 CHEMICAL CONTROL OF SCALING

UNOCAL Corporation has pioneered the commercial use of brine acidification processes to control scale deposition from geothermal brines. Brine acidification successfully controls silica scaling in both flash and heat recovery plants (Gallup, 1996). Sulfuric acid, H_2SO_4, is the preferred acid for pH modification scale control for most geothermal brines, with the notable exception of alkaline-earth-rich hyper-saline brines, where hydrochloric acid must be used to minimize acid-brine incompatibility. The use of sulfuric acid in brine acidification processes has previously been shown, until now, to be the most economical means of scale inhibition. As shown in Table 1, sulfuric acid is much cheaper than other acids and commercially-available inhibitors.

At the Mak-Ban, Philippines geothermal field, brine utilized in a heat recovery plant is treated with sulfuric acid to control siliceous scale (Gallup, 1997a). The brine pH is reduced from about 6.7 to 5.7 with ~10 ppm H_2SO_4. The kinetics of silica polymerization is slowed by acidifying brine with the acid (Fleming and Crerar, 1982). Acid reduces the concentration of OH^- catalyst in the polymerization Reaction 1, thereby inhibiting silicate scaling. Weak complexation of sulfate with silicic acid via Reaction 2 also appears to improve inhibition (Gallup, 1997b).

$$2\ Si(OH)_4 \xrightarrow{OH^-} Si_2O_7H_6 + H_2O \qquad (1)$$

$$Si(OH)_4 + H_2SO_4 \rightarrow SiO_4H_5SO_4^- + H^+ \qquad (2)$$

Proper treatment with sulfuric acid inhibits scale deposition for sufficient time to transport the brine through low pressure flash separators, heat exchanger tubes, injection piping, injection wells and the near-wellbore formations.

Sulfuric acid	$0.03/kg	Hydrochloric acid	$0.14/kg
Nitric acid	$0.1likg	Hydrofluoric acid	**$0.89/kg**
Acetic acid	$0.77/kg	Formic acid	$0.99/kg
Dispersant “ F	**>$2.00/kg**	Dispersant “G”	**>$2.50/kg**

Table 1. Inhibitor cost comparisons

3.0 OFF-GASES FOR SCALE CONTROL

In an effort to reduce costs of scale inhibition, several brine acidification processes using geothermal gases have been developed. These processes include:

- Carbonate scale control in production wells by the EFP System (Kuwada, 1982). The EFP system consists of injecting CO_2 from turbine exhaust gases into a production well, thereby increasing the CO_2 partial pressure and decreasing the brine pH by carbonic acid formation.
- Silica scale control by injection of turbine exhaust gases into flashed brine upstream of injection wells (Hibara *et al.*, 1990). The brine pH is decreased by carbonic acid generation, and acidification retards the kinetics of silica polymerization reactions (Klein, 1995).
- Treatment of brine with sulfur dioxide gas for control of silicate scaling (Lieffers, 1982). Hydrogen sulfide in turbine exhaust gas is oxidized to SO_2 which is injected into brine upstream of injection wells. The acidic gas reduces the brine pH to inhibit silica scaling.
- Biochemical generation of sulfuric acid from hydrogen sulfide (Hirowatari, 1996). In bioreactors, H_2S from turbine offgas is oxidized to H_2SO_4 by sulfur-oxidizing bacteria in the presence of oxygen.

To-date, these processes have been only partially successful. Problems in practical application include: (1) large energy input for gas compression; (2) the need to remove excess gas from power plant condenses; (3) breakthrough of gas to production wells; (4) by-product scale formation; and (5) slow biochemical reactions requiring large bio-reactor vessels.

4.0 UNOCAL’S $H_2S \rightarrow H_2SO_3$ PROCESS

UNOCAL has developed a patented process to generate H_2SO_3 from H_2S or S for brine acidification (Kitz and Gallup, 1997). This process simultaneously abates H_2S emissions from power plants and generates acid on-site for brine or condensate acidification. Some advantages of our process are:

- Abatement of H_2S and generation of a weaker, less corrosive acid than H_2SO_4.
- Treatment of brine with a reducing acid to inhibit metal silicate scaling, to mitigate pitting corrosion, and to scavenge oxygen corrodent.
- Injection of a liquid into brine at reduced energy consumption compared to gas; no premature gas breakthrough.
- Improved inhibition of silica scaling by stronger complex formation.
- Fast H_2S oxidation reaction kinetics with a lower energy of formation than H_2SO_4.
- Generation of an acid that can inhibit calcite, silica and metal sulfide scales with less potential for forming by-product scales.

- Facilities *to* burn H_2S in **turbine** offgas or S in sludges, and **to** *scrub* SO, using any available waste water stream, **are** inexpensive *to* build and operate.

5.0 "ON-SITE" PRODUCTION OF SULFUROUS ACID

Burning S or H_2S yields SO, (Lund, 1971). Sulfurous acid is readily produced from scrubbing SO_2 into an aqueous solution. The following reactions illustrate the process:

$$S + O_2 \rightarrow SO_2 \qquad (3)$$

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O \qquad (4)$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \qquad (5)$$

Reaction **4** may be accomplished by both thermal and catalytic means. In contrast, H_2SO_4 production requires oxidation of SO_2 to SO_3 followed by scrubbing. This latter process is thermodynamically unfavorable and too slow at low temperatures to be practical. Expensive platinum or vanadia catalysts *are* used to generate H_2SO_4. Thus, for extensive effort and cost, H_2SO_4 may be produced from turbine exhaust *gas* or sulfur waste that is only about ten times stronger than H_2SO_3 (Massey, 1990).

At most geothermal fields, incineration of H_2S or S, followed **by** scrubbing of the **SO,** reaction product with condensate, will **be** the most cost-effective and practical method for producing H_2SO_3. By carefully adjusting the pH of the scrubber water, the bulk of the SO_2 *can* be captured **as** H_2SO_3, while CO_2 and other gases may be vented or collected for beneficial uses. In remote locations where acid supply is limited, **this** $H_2S \rightarrow H_2SO_3$ process is particularly useful. Sufficient H_2S or S is present at most geothermal fields to provide an ample supply of H_2SO_3 for brine and condensate acidification.

6.0 PROOF OF CONCEPT TESTING & DEVELOPMENT

6.1 Laboratory and Field Jar Testing

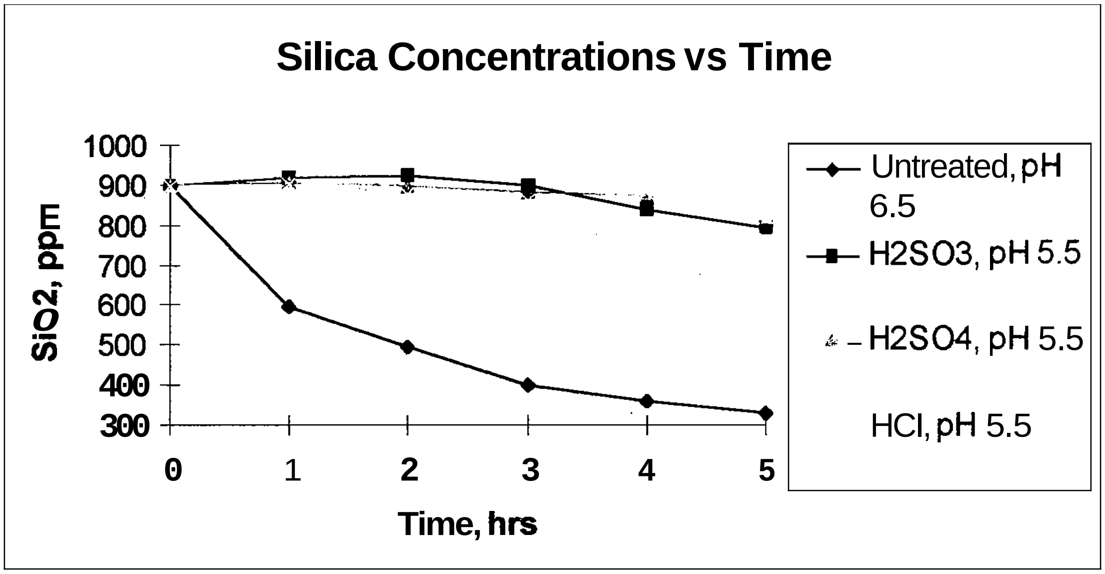
Sulfurous acid **has** been demonstrated to be an acceptable inhibitor for brine silica scaling. Inhibition is achieved by (a) acidifying brine **to** retard silica polymerization kinetics, and (b) complexing with silica to prevent polymerization (Gallup, 1997b). Owing to its weaker acidity, higher concentrations of H_2SO_3 are required to effect the same pH change as H_2SO_4. For example, treatment of Mak-Ban brine with 10 ppm H_2SO_4 reduces the pH to the **5.5 - 6.0** range, a condition that **has** proven to successfully inhibit silica scaling. By contrast, about **26** ppm H_2SO_3 is required to reach this desired pH range.

The efficacy of silica scale control **by** H_2SO_3 is depicted in Tables 2 and 3, and Figures 1 and **2.** (These tables and figures show representative field and laboratory experimental data.) Our studies clearly demonstrate the effectiveness of H_2SO_3 to significantly retard silica polymerization and inhibit silica scaling. Sulfurous acid has proven to be an exceptional silica scale inhibitor and solvent due to formation of soluble bisulfate-silica complexes (Gallup, 1997b).

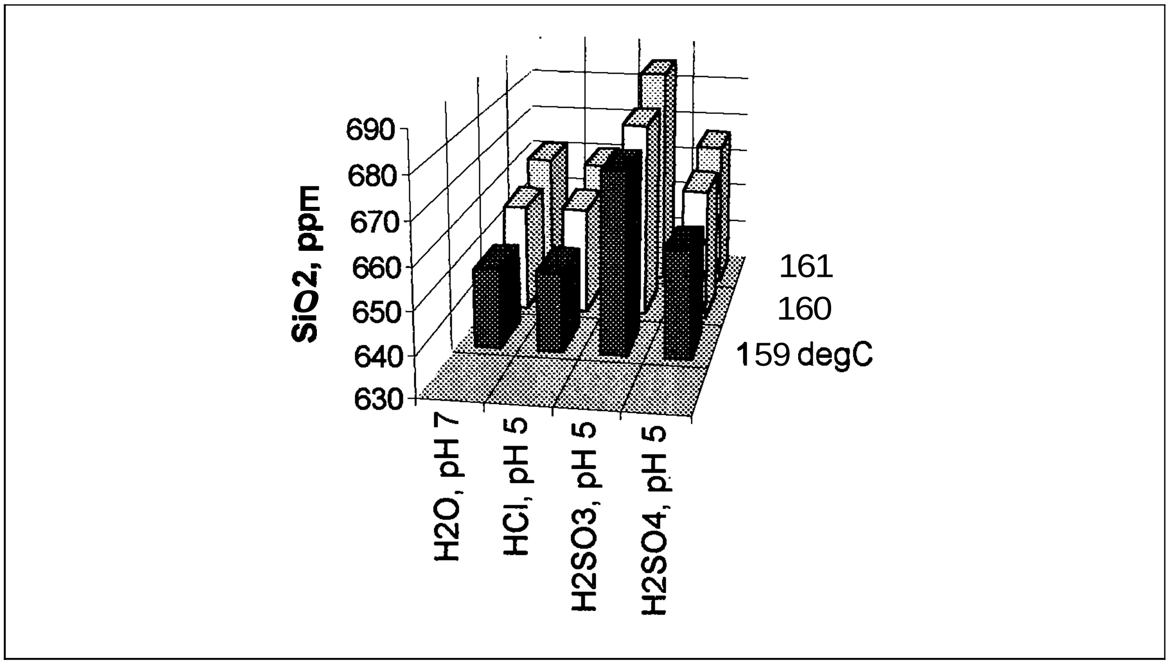
	Silica Concentration, ppm				
Temp, deg C	H2O	0.15m NaCl	0.15m Na2SO3	0.15m NaHSO3	0.15m Na2SO4
25	117	114	130	148	115
100	363	355	390	390	362
150	619	609	659	656	630
200	940	927	992	994	954

Table 2. Amorphous silica solubility in water and salt solutions

	Silica Concentration, ppm			
Time, hrs	pH 6.8	HCl, pH 5	H2SO3, pH 5	H2SO4, pH 5
0	170	180	190	180
2	180	180	210	190
8	170	180	210	190
24	130	150	190	180
48	110	150	190	180
72	105	120	190	160



igure 1. Change in Mak-Ban brine silica concentration with time



Fig

Figure 2. Solubility of amorphous silica in water and acids

6.2 Pilot Testing

Pilot testing of the "on-site" sulfurous acid generation process ($H_2S \rightarrow H_2SO_3$) was conducted during a well flow test at the Mak-Ban, Philippines geothermal field (Gallup and Kitz, 1997). Two-phase brine produced from the well was routed to a test separator operating at 975 kPa. Separated brine was disposed to a sump and subsequently injected into a "cold" brine well. A slipstream of steam and non-condensible gas (containing H_2S) was allowed to flash to atmospheric pressure and then to pass to a collection header. Gas from the header was mixed with liquefied petroleum gas entering a small incinerator. Exhaust gas from the incinerator flowed into a countercurrent gas scrubber. Water was sprayed downflow in the scrubber to form H_2SO_3 solution and to prevent any H_2S or SO_2 emissions. The scrubber water was also disposed into the sump.

The concentration of H_2S in steam sent to the incinerator was only 50 ppm. The theoretical maximum concentration of SO_2 in the exhaust gas was –100 ppm. The concentration of H_2SO_3 in the scrubber water was low. A slight odor of SO_2 was emitted from the scrubber drain. Testing proved the concept of simultaneously abating H_2S and generating H_2SO_3 solution for use in acidification processes; i e., brine scale inhibition, scale dissolution, and condensate pH control.

7.0 ENGINEERING APPLICATION

Initial pilot testing of the H_2SO_3 production process has been proven in concept. Additional tests are planned to quantify efficiencies and prepare sufficient solution for field testing of brine and condensate acidification. Process optimization will allow design and installation of brine and condensate acidification processes while abating H_2S emissions.

The overall process of recovering H_2S as H_2SO_3, inhibiting scales by brine acidification, and abating H_2S from turbine offgas is depicted in Figure 3. This process is relatively easy and inexpensive to operate. The capital cost is essentially the same as or less than other H_2S abatement processes. Testing described herein verifies the technical feasibility of generating acid "on-site" for use at geothermal fields. The process eliminates acid purchase costs and the need to transport acid to remote locations. At most geothermal fields, sufficient H_2S is available to meet all acid requirements.

8.0 SCALE CONTROL

Sulfurous acid complexes with silicic acid to inhibit polymerization (Gallup, 1997b). Sulfurous acid-treated brine maintains higher concentrations of silica in solution than in brine treated with H_2SO_4 or HCl. Considering our complex characterization studies in geothennal applications employing sulfurous acid to control silica scale formation, silica complexes of bisulfite, HSO_3, will be prevalent. Our experiments demonstrate that acidification of brine retards silica polymerization by decreasing the concentration of hydroxide ion catalyst (see Reaction 1). The overall effect of treatment of brine with H_2SO_3 is control of silica scaling by both bisulfite complexation (Reaction 6) and retardation of silica polymerization kinetics.

$$Si(OH)_4 + H_2SO_3 \rightarrow SiO_4H_5SO_3^- + H^+ \qquad (6)$$

Calcite and heavy metal sulfides may also be inhibited by treatment of geothermal brines with low to moderate dosages of H_2SO_3. Calcite scaling may be inhibited in production wells by injecting H_2SO_3 through capillary tubing just below the flash point. Acidification of brine controls the calcite precipitation reaction:

$$CaCO_3 + H_2SO_3 \rightarrow Ca^{2+} + HCO,' + HSO_3^- \qquad (7)$$

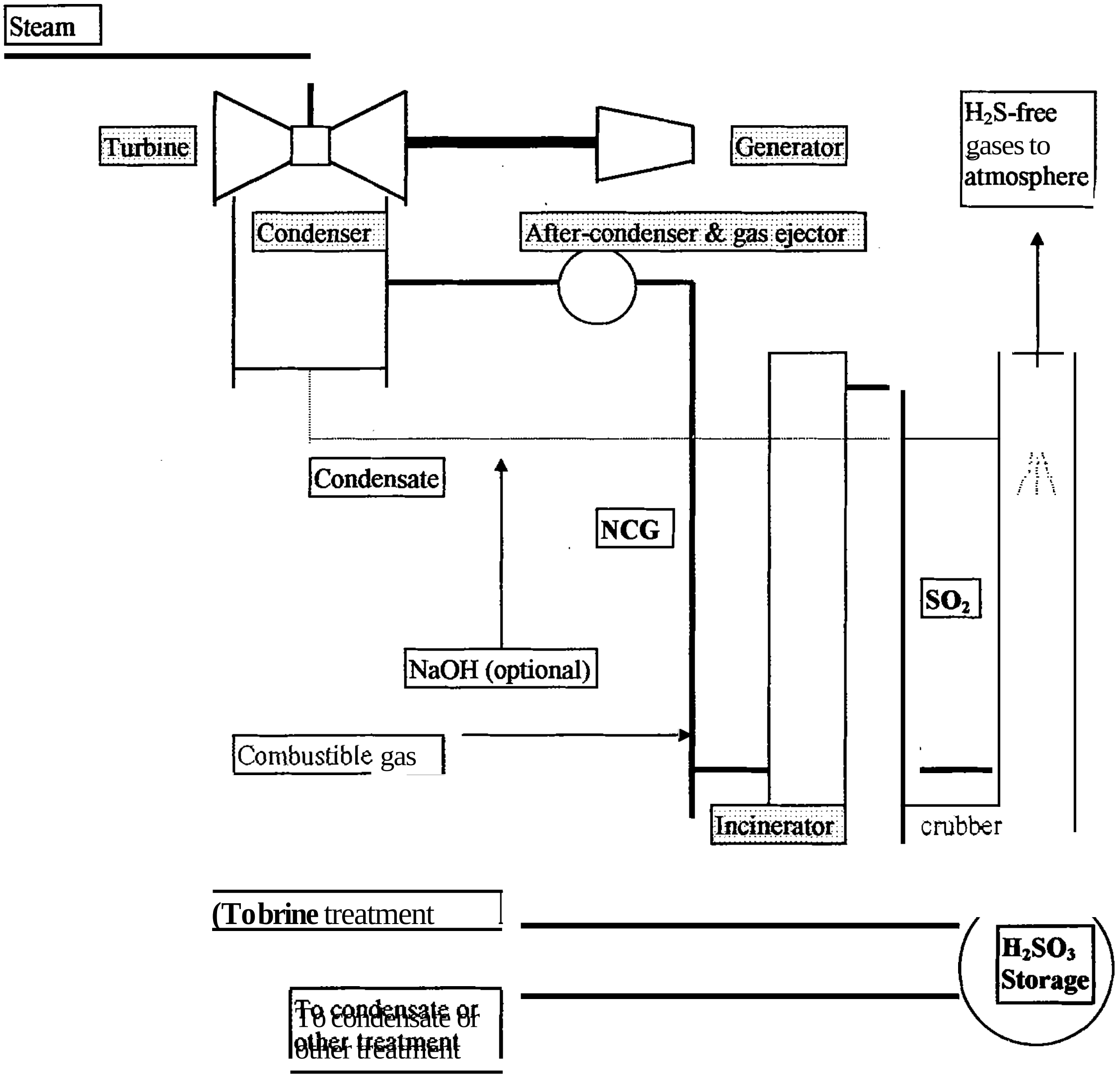
Heavy metal sulfide scales, such as galena, sphalerite and pyrrhotite, are also controlled by acidizing brines (Gallup *et* al., 1990). The inhibition of metal sulfide scaling, especially in production wells by H_2SO_3, is achieved by Reaction S:

$$MS + H_2SO_3 \rightarrow M^{2+} + H_2S + SO_3^{2-} \qquad (8)$$

(where M = Pb, Zn, Fe, etc.). When excess H_2S is removed during flashing, Reaction 8 is thermodynamically favored. Reaction 8 may also continue to proceed further as sulfite species react with **H_2S/sulfides** to form intermediate products such as polythionates and thiosulfates (Lieffers, 1982).

Caution must be exercised in brine acidification processes using sulfuric or sulfurous acids to **minimize** by-product **sulfate/sulfite** scale formation (Gallup et *al.*, 1993). Overdosing with sulfuric acid may precipitate **$CaSO_4$**, **$SrSO_4$** or $BaSO_4$. Sulfites may also precipitate with Ca, Sr and Ba to form scales. However, the solubility of alkaline-earth sulfites increases with decreasing pH and increasing salinity (Lutz and Engelen, 1986a and 1986b). This solubility phenomenon allows most geothermal brines to be treated with significant dosages of *sulfurous* acid without by-product sulfite scale formation.

Figure 3. $H_2S \rightarrow H_2SO_3$ process schematic



Sulfurous acid may be employed not only to inhibit scale deposition, but also to dissolve existing scales or to acidize formations. Acidifying condensate with sulfurous acid generated **by** our process can improve H_2S partitioning **to** the gas phase in power plants. Acidification of cooling tower circulating water improves H_2S partitioning **to** the gas phase in direct contact condensers (Weres, 1988). This reduces secondary H_2S emissions during aeration of the circulating water in the cooling tower, and provides a greater fraction of H_2S in **offgas** for primary abatement and production of H_2SO_3.

9.0 CONCLUSIONS

As a commodity, sulfurous acid is more expensive than some other brine acidifying agents. However, it *can* **be** easily and cheaply produced at geothermal fields by incineration of H_2S or S. A process to generate H_2SO_3 has been developed to simultaneously abate H_2S and produce the reducing, complexing acid for pH modification scale control technology (Gallup and Kitz, 1997). This process eliminates acid purchase costs and the need to transport hazardous acid to remote locations. At most geothermal fields, sufficient H_2S is available to meet all acid requirements for scale inhibition, scale dissolution, condensate conditioning and well stimulation.

Capital investment and operating expenses **are** estimated to be less for an incineration/scrubbing process to generate H_2SO_3 than for most other commercial H_2S abatement systems (Weres, 1988). Incineration and scrubbing generate **H_2SO_3** efficiently. The overall cost to generate acid on-site should **be** small. especially if abatement of H_2S is required at a given field. For example, the total levelized **annual** cost (capital and expense over 30 years at 10% interest) of an incinerator-scrubber at a 100 MWe power plant treating 200 kg/hr of H_2S is estimated to be $800,000. This cost, to produce **–425** kg/hr of H_2SO_3 at 90% abatement efficiency, correlates to a purchase cost ~$0.20/kg. This H_2SO_3 generation cost is quite competitive compared to $0.10 - 0.13/kg for 98 wt.% H_2SO_4 delivered to remote geothermal fields in many third-world countries.

Sulfurous acid has been shown to be an excellent silica scale inhibitor and dissolver. The kinetics of silica polymerization is slowed by acidifying brine with H_2SO_3. The acid reduces the concentration of OH^- catalyst. thereby inhibiting silicate scaling. Complexation of bisulfite/sulfite with silica also enhances inhibition and scale dissolution.

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