Simultaneous hydrogen sulfide abatement and production of acid for scale control and well stimulation

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Abstract

A process has been developed to flow geothermal vent gas, containing hydrogen sulfide, through a bed of halogen containing oxidizing agent granules. In the absence of significant moisture, hydrogen sulfide reacts with the oxidizing agent to yield elemental sulfur and hydrogen halide gas. The elemental sulfur deposits on the oxidizing agent particles, and the produced hydrogen halide gas is sparged into brine, steam condensate or water. The acid gas dissolves in aqueous solution to yield an inorganic acid solution. The acid may be used to decrease brine pH for silica, carbonate or metal sulfide scale control. The brine pH modification process is especially effective in inhibit,ing silica/silicate scale deposition from flashed, re-injection brine. The acid solution may also be used in well stimulations to dissolved carbonates and metal sulfides that have deposited in tubulars or the reservoir formation. Stimulations can restore productivity or injectivity of wells.

***Keywords**: hydrogen sulfide, abatement, acid production, scale control, well stimulation.*

1 Introduction

Processes by which geothermal brine or steam are used to generate electric power are well known (Barbier, 2002). Regardless of whether brine or steam is used for power generation, spent brine and steam condensate are most commonly re-injected into reservoirs for disposal, replenishing or mining heat from the reservoir, providing pressure support and mitigating subsidence. Geothermal brines and steam generally contain non-condensable gases such as carbon dioxide (CO_2), hydrogen sulfide (H_2S), nitrogen, ammonia, etc. In many areas of the world where oil, natural gas and geothermal fluids are produced from sour reservoirs for subsequent use as energy sources, significant amounts of H_2S may be produced to the surface. This gas may be present in small, nuisance quantities, or in significant concentrations. In the latter case and in many geothermal fields, H_2S emissions may be regulated under environmental law, requiring compliance by abatement. The methods used to achieve such abatement are quite frequently expensive, and may add significantly to the costs of producing and processing geothermal fluids in order to generate electric power. Some of the more common methods of H_2S abatement are caustic scrubbing followed by oxidation, adsorption, and catalytic conversion to elemental sulfur, *i.e.,* Sulfurox, Lo-Cat, Selectox, Stretford, RT-2, SulfaTreat, etc. (Dalrymple, et al., 1989).

Geothermal brines also contain high concentrations of dissolved components, such as silica, metal sulfides and calcium carbonates. The solubility of most dissolved solids in geothermal brines decreases with temperature and pH. Consequently, when a significant reduction in the brine temperature and pressure occurs during flashing of steam, supersaturation and precipitation of a portion of dissolved solids may occur. During the removal of larger amounts of heat from brines, acid gases and flashed steam generally produce significant levels of scale-forming mineral supersaturation and faster precipitation rates. Precipitates can deposit as scale in wellbores, pipelines, and vessels. Scaling of the rock formation in the vicinity of wellbores is also a well-documented occurrence (Messer et al., 1978; Mroczek, et al., 2000).

2 Scale control combined with H_2S abatement

Unocal Corporation pioneered the commercialization of brine acidification (also referred to as pH modification) processes to control scale deposition, particularly siliceous scaling in brine-handling equipment and reinjection wells (Jost and Gallup, 1985). The acids that are commonly utilized in pH modification commercial operations are sulfuric (H_2SO_4) and hydrochloric (HCl). Sulfuric acid may not be compatible with brines containing significant alkaline-earth metals. Under certain conditions, treatment of brine with H_2SO_4 can produce by-product calcium, strontium, and barium and radium sulfate scales. Hydrofluoric and nitric acids are avoided due to by-product CaF_2 scaling and oxidation corrosion, respectively.

In an effort to reduce the costs of scale inhibition or dissolution, several brine acidification processes have been developed that use non-condensable gas as the acid source.

- The EFP process was developed by Kuwada (1982) to control carbonate scaling in production wells. Carbon dioxide (CO_2) gas, collected from turbine exhaust gases, was injected into production wells prone to scale with calcite. The vent gas was injected below the flash point to increase the CO_2 partial pressure and decrease the brine pH by forming carbonic acid.
- Turbine exhaust gas was injected into disposal brine in the Coso Hot Springs, CA geothermal field in the late 1980s (Hibara, et al., 1990) to reduce the pH and slow the kinetics of silica scaling. However, the process resulted in rapid CO_2 gas bubble returns to producing wells that could not be removed efficiently in the power plants. Sulfuric acid is now injected into brine in the Coso Hot Springs field to control silicate scaling.
- Lieffers (1982) oxidized H_2S in turbine exhaust gas with oxygen to form sulfur dioxide, SO_2. The SO_2 gas was injected into disposal brine to control siliceous scaling.
- Hirowatari (1996) developed a biochemical process to generate H_2SO_4 from H_2S in turbine exhaust gas. Bioreactors are used with sulfur-oxidizing bacteria in an aqueous medium to produce acid for brine pH modification.
- A process was developed to reduce operational costs (acid purchase) and improve silica scale inhibition through complexing (Gallup, 1997) by producing sulfurous acid on-site upon burning H_2S in vent gas or elemental sulfur in cooling tower sludge, and then scrubbing the SO_2 in water (Gallup and Kitz, 1997).

These processes that utilize CO_2 or H_2S in turbine exhaust gas sources to control scaling have not been widely used commercially. Some drawbacks to these processes include: (a) large parasitic loads to compress and inject gases into brines, (b) reservoir breakthrough of gas or handling of excess gas, (c) by-product scale formation, and (d) slow biochemical reaction rates requiring large reactors. This paper describes yet another process that has now been developed to simultaneously abate H_2S and produce acid for scale control and dissolution, including well stimulation. This process is similar to that developed by Gallup and Kitz (1997), except that H_2S is converted to hydrogen halide gas to overcome incompatibilities inherent in H_2SO_4 or H_2SO_3 treatment of brines.

3 $H_2S \rightarrow HX$ process (X = Cl or Br)

The new process simultaneously abates H_2S emissions from vent gas and produces acid for brine pH modification or well acidizing (Gallup, 2002). This concept was first developed in the laboratory. Hydrogen sulfide gas was generated in a glass flask by treating a solution of sodium bisulfide, NaHS, with acetic acid, CH_3COOH. The produced H_2S gas was allowed to pass through a horizontal glass column packed with trichloroisocyanuric acid, $C_3N_3O_3Cl_3$, granules at ambient temperature. The reaction produced HCl gas, elemental sulfur and isocyanuric acid, $C_3H_3N_3O_3$, The HCl gas was then allowed to bubble through a glass column filled with water. The pH of the water was initially 7.55. A series of tests was conducted that produced water exhibiting pH values ranging from 1.4 to 1.7 and containing 590 to 1,400 ppm Cl. Gas exiting the water column was monitored for HCl and H_2S using Dräger tube detectors. Less than 3 ppm H_2S was detected in the gas exiting the water column. On the other hand, significant HCl gas escaped the water column. This test proved that HCl gas and acid may be produced by allowing H_2S gas to react with solid Cl-containing oxidizing agent. Other solid halide oxidizing products, such as Ca-hypochlorite, Li-hypochlorite, chloro-bromo hydantoins and Br-hydantoins were tested with nearly identical results.

In the Salak, Indonesia, geothermal field, turbine off-gas is removed through a series of gas ejectors and compressors. The gas is then routed over the top of the cooling tower fan shrouds to dissipate non-condensable gases. Hydrogen sulfide emissions from Salak power plants range from 7 to 12 mg/m^3, which is well below the West Java environmental regulatory limit of 35 mg/m^3. Vent gas at slightly positive pressure exiting the gas removal system was obtained from a side-stream and allowed to pass through columns packed with granules or chips of halide-containing oxidizing agents at a rate of 100 l/min. The concentration of H_2S in the vent gas was ~3,000 ppm. Gas exiting the pilot columns remained below the detection limit of 5 ppm H_2S until breakthrough occurred when the stoichiometric quantity of the halide-oxidizing agent was exceeded. By-product HX gas was trapped in a solution of caustic soda as a safety precaution. During and at the conclusion of the tests, the caustic soda was analyzed for Cl and SO_4. Significant concentrations of Cl were present; only at the conclusions of the tests was SO_4 present. An example of the reaction of vent gas with Ca-hypochlorite granules is:

$$Ca(OCl)_{2(s)} + 2H_2S_{(g)} \rightarrow CaO{\cdot}H_2O + 2S_{(s)} + 2HCl_{(g)} \qquad (1)$$

This reaction is conducted essentially in the absence of water vapor depending on the dryness of gas achieved in the gas removal system. The by-product sulfur and calcium oxide may be used as a fertilizer for soil; when using cyanuric acid or hydantoin, the by-product may be used as a herbicide.

4 Engineering application

Initial pilot testing of the HCl/HBr production process has been proven in laboratory and pilot testing. Additional tests are planned to better quantify efficiencies and economics, and to prepare sufficient HX solution for pilot testing brine and condensate acidification and well stimulation. Process optimization is required to prepare a commercial design and installation of pH modification/H_2S abatement. A simplified schematic of the envisioned process is shown in Figure 1. The process should be relatively cheap, and easy to install and operate. The capital and operating costs of the process are expected to be considerably lower than commercially available H_2S abatement processes that generate elemental sulfur for fertilizer use. Testing conducted to date has verified the technical feasibility of generating acid “on-site” for scale control and well acidizing. Advantages of this process are elimination of the need to purchase and transport acid to a field, and compatibility with brines containing significant alkaline-earth metals. At most geothermal fields there is sufficient H_2S produced in steam to meet scale control and well stimulation requirements. This process is available for license from G. E. Dolbear & Associates, Inc., 23050 Aspen Knoll Dr., Diamond Bar, CA 91765-2545 USA; *http://www.gedolbear.com* .

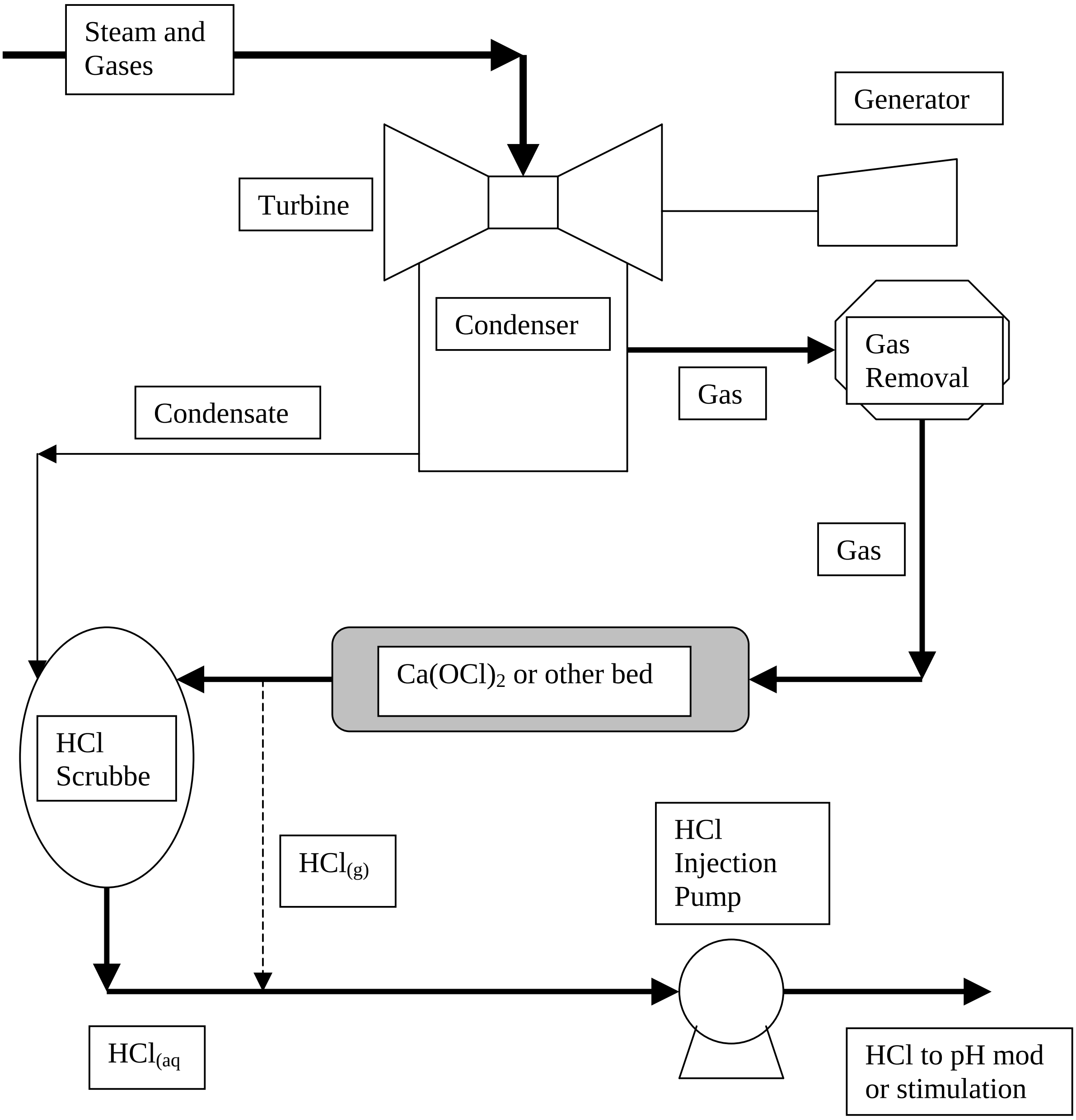

Figure 1: Simplified schematic diagram of $H_2S \rightarrow HCl$ process.

5 Conclusions

By producing HCl gas “on-site,” acidic solutions can be prepared in surface water, steam condensate or cooling tower blowdown for brine pH modification. Dilute hydrochloric acid solution may be used for brine treatment to inhibit siliceous scale deposition, to dissolve existing scale, to “slowly” acid stimulate wells (Gallup, 1999), or to conventionally acidize wells to remove formation damage. Decreasing the pH of brine slows silica polymerization rates, maintains metal sulfides and carbonates in solution, and remediates acid-soluble formation damage (Gallup and Kitz, 1997). The following reactions are examples of uses of HCl generated “on-site” from H_2S:

$$2Si(OH)_{4(aq)} + HCl \neq (OH)_3SiOSi(OH)_{3(s)} + H_2O \text{ (rate dependent on } [OH^-]) \quad (2)$$

$$FeS(s) + 2HCl \rightarrow Fe2+ + 2Cl- + H2S(g) \quad (3)$$

$$CaCO_{3(s)} + 2HCl \rightarrow Ca^{2+} + H_2O + 2Cl^- + CO_{2(g)} \quad (4)$$

The gas may also be directly injected into brine to produce acid and lower pH, but this is typically a more expensive pH modification process and more difficult to control than injecting an acidic solution directly. Decreasing the pH of a brine with HCl solution has also proven to precipitate silver from brine as either the metal or cerargyrite, AgCl (Gallup, 1995). Chlorides of lead, Pb, and mercury, Hg, are quite insoluble. However, these chlorides have not been deposited from brine during pH modification practiced by the author.

The capital cost of vessels to route vent gas through beds of the halide-containing oxidizing agents is anticipated to be low. They will be under almost no pressure. The gases and solids can be handled in plastic or coated piping. Dilute, pH 1 HCl solution can be handled in many plastics. The injection pump for introducing HCl solution into brine should use Hastelloy or Teflon-wetted parts. Injection quills and mixers can be constructed of Teflon in most applications. For well acidizing, service companies can provide necessary corrosion inhibitors.

The major operating cost to produce HCl from vent gas is the halide-containing oxidizing agent. The cyanurates and hydantoins are relative expensive Cl sources. However, the hypochlorites are less expensive. For example, $Ca(OCl)_2$ can be purchased in bulk for less than US$2.00/kg. One kg of HCl produced for scale control or dissolution from H_2S in vent gas based on Reaction 1 completion will cost about US$4.00. This is offset by the sale price of the by-product CaO/S fertilizer (perhaps US$0.50/kg. The delivered cost of 31 wt% HCl to geothermal fields ranges from US$0.44 to 0.88/kg of pure HCl. Although the chemical cost to produce HCl from H_2S “on-site” is 4 to 8 times greater than purchasing and transporting the acid solution to the field, a preliminary capital cost estimate suggests that that the former will be up to 20 times cheaper than the latter.

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