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FACTORS CONTROLLING pH AND OPTIMUM CORROSION MITIGATION IN CHLORIDE- BEARING GEOTHERMAL STEAM AT THE GEYSERS

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ABSTRACT

A chloride (Cl) scrubbing water and sodium hydroxide (NaOH) injection system has been tested for corrosion mitigation of superheated, Cl-bearing geothermal steam (38-94 ppmw) in the northwest portion of The Geysers in California. Corrosion has been successfully mitigated by maintaining a pH of 8 to 9 in the liquid phase. The liquid is removed along with greater than 90% of the Cl by a vertical separator. The dissociation of the major soluble gaseous constituents of geothermal steam; carbon dioxide (CO2), hydrogen sulfide (H2S), ammonia (NH3) and possibly boric acid (H2BO3) buffer the pH in the liquid phase and should be considered for optimizing corrosion mitigation. Modeling CO2, H₂S and NH₃, with a chemical computer modeling program, ONEBOX, demonstrates that these gases compete with NaOH in the liquid phase to determine the pH of the system. Preliminary results indicate that this modeling technique may help to develop process parameters for optimizing NaOH injection for corrosion mitigation in steam wells with varying chemistry.

INTRODUCTION

Corrosion of well casing and the steam gathering system has become a major operational problem in some parts of The Geysers in northern California as well as at other geothermal facilities In superheated steam such as is worldwide. produced in the Coldwater Creek Steam Field in the Northwest Geysers, this corrosion correlates with Cl ion concentration in the steam. The presence of Clas HCl in superheated steam and related corrosion has been discussed previously for The Geysers (Haizlip and Truesdell, 1988; Bell, 1989), Larderello (Allegrini and Benvenutti, 1974; D'Amore et al., 1990) and other geothermal systems producing superheated steam (e.g., Truesdell et al., 1988). Corrosion is believed to be related to the partitioning of HCl into any liquid present and the subsequent dissociation into Cl⁻ and hydrogen ions (H⁺).

Under certain physical conditions in the steam gathering systems and sometimes in cased portions of geothermal wells, HCl is virtually totally soluble and dissociates completely (Haizlip and Truesdell, 1988). Although the concentration of Cl is usually not high in dry or superheated geothermal steam (e.g., <1 to 150 ppmw Cl⁻ in the Northwest Geysers), it can become highly concentrated when small amounts of condensed steam are present. Condensation of steam under superheated conditions is negligible; heat sinks such as sampling ports and pipeline supports or other uninsulated sections of pipeline as well as flow dynamics localize condensate. Chloride concentrations in condensate drains and knock-out pots along the steam gathering system can be as much as 600 times the concentrations in steam.

The dissociation of HCl in liquid produces a two pronged attack on carbon steel, i.e., both H⁺ and Cl⁻ can cause corrosion. Both acid (H⁺) and Cl⁻ can accelerate many types of corrosion (e.g. stress corrosion cracking, pitting) by electrochemical reactions (combining compositional and electrical potential effects; Pickering, 1985). In New Zealand, Giggenbach (1979) first described the cathodic reaction by which acid attacks carbon steel in geothermal systems as: $Fe^{+2} + 2H^+ = Fe^{+2} + H_2$. When Cl⁻ interacts with metal in water, metalhydroxide and H⁺ result. This reaction causes local pH to drop as low as <1 and causes severe pitting (e.g., Fontana and Greene, 1978).

Both theory (e.g., Pickering, 1985) and field observations in geothermal gathering systems and well casings suggest that corrosion rates are accelerated by the presence of both acidic conditions and high Cl⁻ concentrations relative to one parameter. Acidic condensates generated by dissolved gases such as H₂S, and CO₂, though corrosive (Giggenbach, 1979), have been generated in steam gathering pipelines and geothermal well casing throughout The Geysers for many years

without catastrophic corrosion (Dodd, et al., 1975). In many geothermal fields throughout the world, brine gathering systems carry very saline fluids without significant trouble until concentrations and temperatures similar to those of the Salton Sea Geothermal System (>25wt%TDS,>300°C) are approached. However, corrosion rates based on metal loss in the steam gathering system at Coldwater Creek Steam Field have been documented as high as 100 mpy (inch/year X 10⁻³). It appears that the simultaneous attack of H⁺ and C1⁻ is particularly damaging and therefore a successful corrosion mitigation scheme must neutralize the acid and remove the C1⁻

In order to mitigate the double attack of H⁺ and Cl⁻ on the pipe at Coldwater Creek Steam Field, a steam scrubbing system using water and sodium hydroxide (NaOH) was designed and tested. The Coldwater Creek Steam Field, in the northwest portion of The Geysers of northern California, was operated by GEO Operator Corporation during the definition of the corrosion problem and development of the mitigation program and by Coldwater Creek Operator Corporation during the implementation and testing of the mitigation system; both are wholly owned subsidiaries of Geothermal Resources International, Inc. Steam scrubbing has been used previously in The Geysers and in many power industries. The addition of chemicals to neutralize geothermal steam for the purposes of corrosion mitigation has been utilized for many years in Italy at Larderello (Allegrini and Benvenutti, 1974: Ing. Giovanni Allegrini, Dr. Bruno Tarquini, pers. comm., Oct., 1989), has been operated using water/NaOH in The Geysers (Bell, 1989) and tested in New Zealand (Soylemezoglu-et al., 1980); all have been successful at reducing corrosion to acceptable levels.

A water/NaOH steam scrubbing test station was installed and tested on two adjacent wells in the Coldwater Creek steam field (Figure 1). Previous work provided some basic design constraints and operational parameters such as maintaining the pH between 8 and 9 (Ing. Giovanni Allegrini, Dr. Bruno Tarquini, pers. comm., Oct., 1989; P. Hirtz pers. comm., Sept., 1989). Therefore, the purpose of the present test program was to determine the best parameters by which the system could be operated and corrosion monitored in this specific application. Test results would allow the system to be tailored to other wells with different Cl⁻ concentrations and levels of superheat, evaluate the basic design of water and chemical injection and removal and, if possible, determine the minimum water and chemical requirements for successful corrosion mitigation.

The NaOH and water solution is injected into a complex superheated steam and noncondensible gas solution. The two operational variables of the system are the NaOH and water injection rates. The two main, easily measured process parameters which determine the effectiveness of the system at removing Cl⁻ and neutralizing pH, are the water removal rate and pH. The complexity of the system is reflected in the relationship between these operational variables and process parameters. Direct correlations between corrosion rates and water/Clremoval rates and pH validated these process parameters. However, more complex analysis including computer modeling was required to analyze the relationship between the operational variables and process parameters. The physical (pressure, temperature and enthalpy) and chemical (noncondensible gas including HCl) nature of the steam precludes direct correlations.



FIGURE 1: Basic design of Coldwater Creek Cl⁻ scrubbing system with sample and corrosion port locations, (abbreviations are defined in text).

The results of evaluating the complex chemical process of steam scrubbing and neutralization with NaOH are presented in this paper. The emphasis is on the relationship between the process parameters of pH and water (therefore Cl⁻) removal, and the mitigation of corrosion and the operation of the system. Because the water injection and water removal rates are connected by simple mass and enthalpy balance equations, most of the emphasis is on the pH of the water. Because the pH of the water correlates strongly with corrosion rate, it is a very important process parameter, but because it does not correlate directly with NaOH injection, it is a complex parameter. Because NaOH injection is also used to scrub acid gas (H₂S abatement) in The Geysers, it seemed reasonable to look first at the effect of the noncondensible gases in the steam on liquid pH. As this process has yet to be optimized in the particular conditions of the Coldwater Creek Steam Field, the results below are preliminary. However, a better understanding of the effect of noncondensible gases on the liquid pH may allow for quicker optimization of new systems set up on other wells in the steam field with different gas chemistry.

METHODOLOGY

A dual well scrubbing station (Figure 1) has been designed to desuperheat steam, neutralize pH and separate out a liquid containing Cl⁻. Water mixed with a 25% solution of NaOH is injected downstream from each well through atomizing nozzles. A vertical, cyclone separator installed approximately 75 meters from the injection ports removes the concentrated liquid (water plus condensate) with at least 99% efficiency.

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Water injection rates were set by applying an energy and mass balance equation with steam flowrate, steam superheat, pressure, and temperature of injection fluid to obtain a specific liquid flow of 1% by weight. NaOH rates were then set by measuring the Cl⁻ concentration in the steam directly, and by back calculating the Cl⁻ produced from the Cl⁻ concentrations in the separator assuming 100% solubility and 100% removal at the separator. Initially, NaOH was injected at a 1:1 mole ratio of Na:Cl but was then increased slowly until a pH of 8 to 8.5 was obtained at the separator. An average NaOH:HCl mole ratio of 1.7 to 1 proved effective in obtaining the required pH.

A two-tiered sampling program was designed to help control the injection system and determine the Cl⁻ balance, i.e., production minus removal. The pH and water removal rate at the separator and other physical parameters; steam flow rate, pressure and temperature, were monitored along with operational variables twice every 12 hours. Other process parameters such as geochemical and total particulate samples were collected after every change in injection rates and once a week after conditions stabilized.

Sampling locations (Table 1) were chosen to monitor all phases of the system. Sampling ports are located along the bottom (USBLS) and the side (USP) of the steam gathering pipeline upstream of the separator, and along the vertical rise (DSP) and the bottom of the pipeline (DSBLS) downstream of the separator (Figure 1). USBLS and DSBLS designate liquid samples collected during mitigation before separation (USBLS) and after separation (DSBLS). These samples are collected from the liquid side of a Weber mini-separator. USP and DSP



designate samples collected isokinetically using a curved probe inserted into the steam flow upstream (USP) and downstream (DSP) of the separator. These are gas and steam condensate samples of superheated, unmitigated steam and scrubbed steam, respectively. In addition liquid samples are collected at the drains of each well before their junction (DRAIN), at the separator (SEP), and from a drop pot downstream of the separator (DP2).

Analyses of Cl⁻, particulate, sodium (Na⁺), H₂S and total noncondensible gases were performed in an on-site laboratory. Selected condensate samples were analyzed by the University of Utah Research Institute (UURI) and Thermochem, Inc. and noncondensible gases were analyzed by Thermochem, Inc.

Interpretation of analytical results and physical measurements was facilitated by a spreadsheet which used energy and mass balance equations to calculate the water present after mixing the superheated steam and injection water. For the completely soluble components such as Cl⁻, concentration in steam could be determined from the Cl⁻ removed at the separator or the Cl⁻ concentration in the water using the calculated flow rate. These calculations provided an evaluation of the effectiveness of the process. Furthermore, they could be used throughout the test to optimize the system.

Retractable corrosometer probes (Rorhbach Cossasco) were used to monitor corrosion rates. A port is provided along the bottom of each well loop and downstream of the separator along the bottom of the steam gathering pipeline (Figure 1). Corrosometers have been used extensively for monitoring corrosion of carbon steel in the geothermal fields of New Zealand (Soylemezoglu et al., 1980). They provide continuous and almost instantaneous corrosion rates. A sensing element

TABLE 1: Liquid and steam condensate chemistry of mitigated steam (1). Steam condensate and gas chemistry of dry (superheated) steam (2).

Sample	Na	CI	В	NH4	HCO3	CC3	SO4	S	SiO2	Fe	TDS	pН
Location	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	
WELL 1 $^{ m 1}$												
USBLS	10209	12700	1682	76	3484	nd	432	143	156	0.58	26974	8
SEP	9541	12350	2938	126	4620	nd	580	189	153	1.47	28227	8
DSP	3.39	2.3	37.8	na	2180	nd	7.8	89	nd	0.18	1927	6.7
DSBLS	12.6	12.6	42.2	640	2249	nd	10	92	3.2	0.21	1826	6.6
DP2	4133	9135	1531	1240	_1	nd	144	0.04	89	214	16660	6.3
WELL 2 ¹						1. 1 1. 14					ب	
DRAIN	3144	2340	2203	55	2110	844	90	168	54 02	24	9937 9	8 /
USBLS	3163	2350	2232	52	2630	630	94	182	54 08	1 25	10353	8.6
SEP	2989	2200	2116	68	3050	324	84	222	55.25	3.32	9711.2	8.6
DSP	2.08	0.625	21.24	na	na	na	na	na	nd	0.19	44.01	6.4
DSBLS	22.25	41.9	59.22	475	1280	nd	67	195	5.78	1.81	1508	6.4
DP2	1520	4640	1138	800	nd	nd	22	nd	44.9	1164	9890	6.2
WELL 1-2 ¹			· .								÷	
									<i>i</i>	•		
1/DRAIN	6838	8325	2170	290	4060	nd	121	202	69.32	nd	20013	8.2
2/DRAIN	4724	2180	2251	52	3690	2350	20	559	53.92	0.61	14005	9
USBLS	6237	5340	2168	70	4040	9770	1	366	64.29	1.11	17210	8.6
SEP	5819	4860	2275	77	4230	925	1	104	69.67	0.8	16226	8.6
DSP	2.2	2.5	22.87	na	na	na	na	na	nd	0.95	51.12	6.5
DSBLS	65.25	52	53.97	600	1710	nd	38	191	5.59	0.22	1846.8	6.5
DP2	2390	2675	937	100	2080	nd	46	134	167	0.62	7472	7.8
DRY STEAM	² CI	В	CO2	H2S	NH3	N2	CH4	H2	Total NCG			
	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw			
WELL 1	94	59.2	30700	1300	699	380	1820	303	35250			
WELL 2	38.4	68.4	7820	712	447	90.4	350	116	9540			
WELL 1-2	34.2	63.05	16500	981	544	202	888	195	19300			

in the corrosometer measures the difference between the conductivity of a metal and the corrosion product (metal-oxide). The electrical resistance of the exposed sensing element is increased as its cross-sectional area is reduced by corrosion and this can be translated into metal loss in mils per year (mpy).

RESULTS/INTERPRETATION

The success of this scrubbing process can be demonstrated by high Cl⁻ removal rates and decreased corrosion rates. Corrosion rates in the steam pipeline decreased to less than 5 mpy following the installation and stabilization of the scrubbing stations. Corrosion is directly mitigated by neutralizing the liquid pH. During the test, increased corrosion rates directly coincided with a pH of less than 8 at the separator reflecting the absolute necessity of maintaining above neutral pH while removing chlorides. However, a complex relationship exists between the gas chemistry, the operational variables (specifically NaOH injection) and pH. This is indicated by the fact that there is no direct relationship between NaOH:HCl mole ratio and pH.

Chloride concentrations in the dry steam (Table 1; dry steam is without mitigation) are an average of steam samples collected over the two month test period. From the start-up of Well 1

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(after a prolonged shut-in period) to the completion of the test, superheat increased from 10 to 30 degrees C. Chemical measurements were made over this time period and Cl⁻ increased 10 ppmw. This correlation has been observed in other geothermal wells at The Geysers (Haizlip and Truesdell, 1989). Once maximum superheat and steam flowrate stabilized, Cl⁻ concentration fluctuated little. Well 1, Well 2 and both wells combined contain 94 \pm 7, 38 and 40 \pm 9 ppmw Cl⁻ respectively ("dry steam", Table 1). Only one opportunity was available to sample Well 2.

The difference between the mass of Clremoved at the separator and the total mass of Clmeasured in the dry steam determines the scrubbing efficiency; $95 \pm 10\%$ Cl⁻ at Well 1, $65 \pm 8\%$ at Well 2 and 86 \pm 28% for both wells combined. The total mass of Cl⁻ removed at the separator is calculated by multiplying the Cl⁻ concentration in the separator water by the separator fill rate. The total mass of Clproduced from the well is determined by multiplying the Cl⁻ concentration in the steam by the steam flow rate. Higher than 100% removal rates may reflect start-up conditions when excess Clis being removed from the pipewalls. Lower removal rates are associated with water injection rates resulting in water flows to the separator of < Probe samples of the scrubbed steam 1%. downstream of the separator contain an average of $1.6 \pm .8$ ppmw Cl⁻, indicating that greater than 98% of the Cl⁻ is being removed by scrubbing.



FIGURE 2: Measured HCO₃- in the liquid vs pH for Well 1 (\blacksquare), Well 2 (\Box) and Well 1-2 (\blacktriangle). Calculated values vs pH from the steam chemistry of Well 1 (O) and Well 2 (\bigcirc) assume equilibrium conditions.(See Text).

The main soluble gases, CO₂, H₂S and NH₃ correlate linearly with pH in the liquid. In general, measured bicarbonate (HCO3-) increases with increasing pH in the liquid (Figure 2) but falls above the calculated values determined assuming equilibrium distribution between liquid and steam. Gas distribution coefficients (Giggenbach, 1980) were applied to known partial pressures (P(CO₂), P(H₂S) and P(NH3)) in the dry steam, with HCO3-, ammonia ion (NH4⁺⁾ and sulfide (HS⁻) calculated as a function of pH from gas dissolved in liquid dissociated to equilibrium at line temperature (176 deg C) (e.g., Figure 2). The downstream liquid samples (DSBLS) show the greatest disequilibrium and may reflect incomplete separation during sampling. Measured HS⁻ also correlates positively with pH and approaches calculated values. NH4⁺ correlates negatively with pH, as expected, although measured values are considerably lower than expected for equilibrium conditions. The system contains more dissolved acidic gases and less NH4+ than predicted in simple two-phase, one-component equilibrium systems. It is clear from this simple comparison that each gas plays an intricate role.

DISCUSSION

As presented above, successful corrosion mitigation includes removing Cl⁻ and neutralizing acid. The correlation between pH and corrosion rates has been clearly demonstrated with corrosion probes. Because Cl⁻ removal was successful during most of the test, it has not been directly correlated with corrosion rates, except for the obvious comparison between pre-mitigation versus mitigation. The pH of liquid downstream of the separator is similar to non-Cl⁻ bearing steam condensate at The Geysers in that it is not being buffered. However, low corrosion rates downstream of the separator are consistent with the importance of the absence of Cl- in keeping low corrosion rates after the buffering solution has been removed.

Both field experience at The Geysers and empirical studies support the role of noncondensible gases in buffering pH. Chloridefree steam condensate has a pH of about 6.5 to 7. NaOH injection is used as a method of removing acidic H₂S from the steam. As would be expected, a system with HCl as the sole component achieves a pH of 12.5 by adding a mole ratio of 1 to 1.15 NaOH to HCl in solution (R. McCartney, pers. comm., 1990). In the complex geothermal steam at The Geysers a mole ratio of up to 2:1 is required to achieve a pH of eight at the separator during corrosion mitigation, evidence that the major soluble gases such as CO₂, H₂S, NH₄ and possibly H₂BO₃ play a large role in buffering pH.

To better understand the gas chemistry, we used the modeling program ONEBOX (Weres, 1983; adapted for GEO by Thermochem in 1985) on a few sample sets. ONEBOX determines pH and steamwater distribution and speciation for a given fluid chemistry (at least the major components of geothermal steam) and enthalpy. The scrubbing process was modeled by inputting appropriate proportions of the initial components (the injection fluid (including NaOH) and the dry steam) based on the steam flow rates, temperature and chemistry of the steam, water injection rates, temperature and chemistry of injected water, and pressure. The resulting liquid and steam proportions and chemical composition (calculated; Table 2) were then compared with actual steam quality and liquid chemistry after mixing the steam and injection water in the pipeline (measured; Table 2). Initial runs used non-equilibrium partitioning of CO2 into the liquid phase and various residence times for contact between the liquid and the steam. ONEBOX does not accommodate for HCl gas at present, hence our initial model did not include HCl as a factor in controlling pH. In later runs, assuming the Cl⁻ was originally HCl, the role of HCl was approximated by removing from the input a molar equivalent of NaOH required to neutralize the H⁺ associated with the Cl⁻ measured in the liquid sample.

The results of modeling were consistent with actual values (Table 2). Actual steam quality, determined from measured and calculated removal rates at the separator, compared well, varying less than 7%. When not accounting for HCl, the predicted pH was between 9.1 and 9.2, considerably higher than actual values. However, when a 1:1 mole equivalent of Cl⁻ was removed from the NaOH, modeled pH's approached the actual pH to within 2% error for Well 1 and the two wells combined. Measured distributions of HCO3⁻, NH4⁺ and HS⁻ in the liquid phase; following HCl normalization, are of the same order of magnitude but diverge from those predicted by ONEBOX.

Measured HS⁻ (120-240 mg/L; 190±40) is similar to predicted (140-360 mg/L; 250±150), except for two drain samples. Deviations may reflect loss of H₂S during the collection process, precipitation of pyrite (FeS₂) which is a known by-product of corrosion, or oxidation to and reduction of sulfate. NH₄⁺ most closely parallels the conditions of the model, agreeing to within 10%. NH₃ gas partitions the most readily into the liquid phase and may have reached equilibrium.

Although the partitioning of CO₂ into water

	MEAS 1	CALC ² 1 SEC	HC1 NORM ³ 1 SEC	MEAS	CALC 1 SEC	HC1 NORM 1 SEC	HC1 NORM 5 SEC		
	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw	ppmw		
	1-2/SEP 12/	/21/89							
Water (%)	0.01	0.013	0.013	0.01	0.009	0.009			
H2S	180.2	1951.1	345.5	591.6	1740.8	186.6			
NH4	74.9	70.2	71.0	51.8	58.9	59.2			
FIX CO2	3590.4	8224.6	1326.5	2662.0	48.5	458.0			
SiO2	28.5	57.2	57.7	1.6	6.5	6.5			
H2SO4	247.0	125.9	126.9	20.4	139.5	139.5			
NaOH	3414.3	11415.4	1814.0	248.1	778.0	80.8			
рH	8.5	9.15	, 8.5	9	9.25	8.39			
	1/DRAIN 12	/21/89			(Equil) ⁴				
Water (%)	0.007	0.009	0.009	0.01	0.015	0.015	0.015		
H2S	74.2	3435.4	311.2	196.9	2036.6	200.4	222.6		
NH4	41.6	87.5	88.0	125.6	1051.2	105.9	105.9		
FIX CO2	1278.6	18983.1	1521.2	3330.8	10648.0	1083.3	1148.5		
SiO2	23.6	94.9	94.9	32.4	63.6	63.7	63.7		
H2SO4	38.4	209.1	209.2	591.9	140.1	140.0	140		
NaOH	3955.8	25433.3	1984.8	3512.5	13600.0	1396.5	1396.5		
рН	8.3	9.18	8.29	8	9	8.16	8.16		
	1-2/SEP 1/8	8/89		2/SEP 1/10/90					
Water (%)	0.016	0.015	0.015	0.017	0.022	0.022	0.022		
H2S	110.2	1980.0	287.4	235.3	1285.2	143.3	143.2		
NH4	76.9	70.2	70.5	67.9	64.7	59.7	59.7		
FIX CO2	3049.2	8390.0	1097.3	2200.0	3432.0	347.7	347.9		
SiO2	257.8	52.4	52.4	25.9	35.1	32.2	32.2		
H2SO4	10.2	116.0	115.8	85.7	76.9	70.6	70.6		
NaOH	3749.1	11600.0	1505.5	2442.8	5400.0	580.1	580.1		
рH	8.6	9.12	8.43	8.6	9.11	8.28	8.28		
	1/DRAIN 1/8	8/90		2/DRAIN 1/10/90					
Water (%)	0.013	0.014	0.014	0.017	0.022	0.022	0.022		
H2S	214.2	2780.5	358.1	178.2	1168.4	143.3	143.2		
NH4	289.8	87.3	87.8	54.7	58.8	59.7	59.7		
FIX CO2	2926.0	15005.5	1756.5	1522.4	3120.0	347.7	347.9		
SiO2	17.5	71.0	71.1	25.3	31.9	32.2	32.2		
H2SO4	123.5	156.8	156.9	91.8	69.9	70.6	70.6		
NaOH	3013.7	19684.4	2222.5	2574.4	4909.1	580,1	580.1		
pН	8.2	9.11	8.35	8.4	9.11	8.28	8.28		

TABLE 2: Modeled vs measured pH and gas distribution

Notes:

1: Measured in liquid; 2: Calculated assuming non-equilibrium partitioning of CO₂ into the liquid and a 1 second residence time between liquid and steam; 3: Same as 2 except NaOH normalized by

molar equivalent of HCl in liquid; 4: Equilibrium partitioning of CO2 in the liquid.

is relatively slow, the reaction:

 $CO_2(aq) + OH^- ----> HCO_3^-$ (1)

is almost instantaneous (Michels, 1981). This suggests that the partitioning or scrubbing of CO₂ into the liquid is pH and kinetically controlled. The steam-liquid interaction time of one second used in the modeling may be insufficient but increasing the residence time to five seconds and assuming equilibrium conditions (Table 2), effected neither the predicted HCO₃- or pH. Measured HCO₃concentrations are 2-3 times higher than predicted with NaOH correction by ONEBOX and 0.3-0.5 times predicted without the NaOH correction. This deviation is greatest in Well 2 which contains lower HCl and P(CO₂) and higher P(NH₃) and P(H₂S). What appears to be a simple pH change affects the gas solubility much more strongly (decreasing solubility by an order of magnitude) in ONEBOX, than field measurements suggest. Several factors may be affecting the input parameters for ONEBOX, one being the actual strength of the NaOH solution. In periodic checks of NaOH injection rates, more NaOH was measured at the separator than was assumed to be injected. This would underestimate the OH⁻ input thereby lowering the HCO₃⁻ predicted by ONEBOX relative to measured values. Furthermore, the relationship between CO₂ hydration and pH may be more complex than this preliminary model allows.

CONCLUSIONS

The results of testing of steam scrubbing with NaOH at the Coldwater Creek Steam Field show that corrosion can be successfully mitigated by controlling the operational variables; water and NaOH injection rate, using two main process parameters; pH and water removal rate. Simple mass balance and enthalpy equations connect the water injection and removal. Assuming 100% solubility of HCl, mass balance equations can provide Cl⁻ removal rates. However, the relationship between NaOH, HCl, noncondensible gases and pH is complex and precludes simple correlations.

A computer model using the major soluble gases can recreate the measured pH at the separator provided a correction for HCl neutralized by NaOH is made. Modeling results indicate that HS⁻, HCO3⁻ and NH4⁺ are competing with the NaOH in determining the pH of the system. This computer modeling could be an important tool in determining the NaOH required to obtain a specific pH in scrub water provided the gas composition of the steam and physical conditions of the system are known. These are preliminary results and further work is need to refine the gas chemistry and account for other soluble species in the corrosion mitigation system. However, application of this modeling technique to geothermal wells with varying chemistry may help to develop other process parameters for optimizing NaOH injection for corrosion mitigation. Finally, these field tests provide interesting data to verify computer models of two-phase water chemistry.

ACKNOWLEDGEMENTS

The authors appreciate the release of this data by Coldwater Creek Operator Corp., a wholly owned subsidiary of Geothermal Resources International, Inc. We thank Jim Combs, Mark Walters and Ross McCartney for reviewing the manuscript and Linda Johnson for its preparation.

BIBLIOGRAPHY

Allegrini, G. and Benvenuti, G., 1970, Corrosion Characteristics and Geothermal Power Plant Protection (Collateral Processes of Abrasion, Erosion and Scaling), Geothermics, v. 2, Part 1, p. 865-881.

- Bell, D., 1989, Description of an Operational Desuperheating and Chloride Scrub System, Geothermal Resources Council Trans. v. 13, p. 303-307.
- D'Amore, F., Truesdell, A.H. and Haizlip, J.R., 1990, Production of HCl by Mineral Reactions in High-Temperature Geothermal Systems, Proceedings, 15th Workshop on Geothermal Reservoir Eng., Stanford, CA., in press.
- Dodd, F.J., Ham, W.C., Johnson, A.E., 1975, Material and Corrosion Tests at The Geysers, U.N. Symposium on Geothermal Energy, 1975, v. 3, p. 1959-1963.
- Fontana, M.G. and Greene, N.D., 1978, "Corrosion Engineering", 2nd Ed., MacGraw- Hill, 465pp.
- Giggenbach, W.F., 1979, The Application of Mineral Phase Diagrams to Geothermal Corrosion, Proceedings of New Zealand Geothermal Workshop 1979, Part I, p. 217-226.
- Giggenbach, W.F., 1980, Geothermal Gas Equilibria, Geochim. Cosmochim. Acta, v. 44, p. 2021-2032.
- Haizlip, J.R. and Truesdell, A.H., 1988, Hydrogen Chloride in Superheated Steam and Chloride in Deep Brine at the Geysers Geothermal Field, CA., Proceedings, 13th Workshop on Geothermal Reservoir Eng., Stanford, CA., p. 93-100.
- Michels, D.E., 1981, CO₂ and Carbonate Chemistry Applied to Geothermal Engineering, Special Report; LBL-11509, GREMP-15 UC-66a, Lawrence Berkeley Laboratory, Berkeley, CA, 27pp.
- Pickering, H.W., 1986, On the roles of Corrosion Products in Local Cell Processes, National Association of Corrosion Engineers, 1986, v. 42, no. 3, p. 125-140.
- Soylemezoglu, S., Lichti, K.A. and Bijnen, H., 1985, Geothermal Corrosion Case Studies of the Wairakai and Broadlands Geothermal Fields using the 'Corrosometer'Method, Proceedings, New Zealand Geothermal Workshop, 1980, Aukland, N.Z., p. 27-32.
- Truesdell, A.H., Haizlip, J.R., Armannsson, H. and D'Amore, F., 1989, Origin and Transport of Chloride in Superheated Geothermal Steam, Geothermics, v. 18, no. 1/2, p. 295-304.
- Weres, O., 1983, Documentation for Computer Program CNDSR, LBID-622, Lawrence Berkeley Laboratory, Berkeley, CA., 129pp.