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The Generation of HCl in the System NaCl–KCl–H_2O–Quartz at 600°C: Implications Regarding HCl in Natural Systems at Lower Temperatures

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ABSTRACT

In experiments at 600°C in the system NaCl–KCl–H_2O, within the analytical uncertainty, stoichiometric quantities of Cl and total alkali metals (Na+K) appear to dissolve in steam coexisting with chloride-rich brine at high pressures in the absence of solid salt. In contrast, at lower pressures, where steam coexists with precipitated salts, significant excess chloride as associated hydrogen chloride (HCl°) dissolves in steam. The HCl° appears to be generated by the reaction of solid NaCl(*s*) (halite) with steam, producing solid NaOH(*s*) that diffuses into halite, forming a solid solution. Where HCl° is present highly associated NaOH° as well as associated NaCl° appear to dissolve in steam, and the solubility of each is increased as the mole fraction of NaOH(*s*) in halite increases. In our quasi-static experiments, compared to dynamic flow-through experiments of others, higher initial ratios of H_2O/NaCl have resulted in higher mole fractions of NaOH(*s*) in solid solution in halite and, accordingly, higher solubilities of NaCl° and NaOH° dissolved in steam. Addition of quartz to the system NaCl–KCl–H_2O results in the formation of sodium disilicate by reaction of silica with NaOH(*s*) and an order of magnitude increase in the concentration of HCl° dissolved in steam.

In natural hydrothermal systems at lower temperatures where brine or brine plus steam are present in the absence of precipitated salt, the pH of the brine is controlled mainly by base exchange reactions involving a variety of silicates that fix Na^+/H^+ and K^+/H^+ activity ratios. Where feldspars are present pH values generally are near neutral. Where mica, but no feldspar is present pH values may become only moderately acid. High acidity in salt-absent brine systems occurs only where all feldspars and mica have been altered to other minerals (generally pyrophyllite/kaolinite or alunite). The situation changes significantly when salt precipitates. Hydrolysis produces HCl° by the reaction of water with NaCl when halite is present. The NaOH(*s*) that is produced as a byproduct is likely to react with quartz plus various alumino-silicates, producing a variety of alteration products and allowing steam to become greatly enriched in HCl° compared to the composition of steam that is attained in the simple system NaCl–KCl–H_2O with halite present. Also, when a natural high-temperature hydrothermal system changes from one in which the pore fluid is brine to one in which the pore fluid is dry steam there is a drastic change in Na^+/H^+ and K^+/H^+ activity ratios in the pore fluid because the hydrogen ions that were predominantly dissociated species in the brine become predominantly associated species in steam. The net result is the stabilization of alkali feldspars in contact with steam that may contain appreciable HCl° that is produced by the reaction of precipitated salt with the steam.

INTRODUCTION

In 1973 we initiated an experimental study of the partitioning of sodium and potassium between brine and steam and between solid salts and steam in the system NaCl–KCl–H_2O, with the aim of obtaining a better understanding of conditions controlling base exchange reactions involving alkali feldspars and hydrothermal fluids in volcanic and subvolcanic environments. We soon found that our experiments also were providing information about the generation of HCl by hydrolysis of the salt, and the focus of the experiments was shifted somewhat to include a study of this phenomenon. Unfortunately, that work ended prematurely because we were diverted to other activities that had, at the time, higher priority. Although the initial results were very interesting, they were not published then because we considered them very preliminary. It is now evident that we will not resume this experimental study and have decided to publish our results because of increasing concern within the geothermal energy industry about the conditions at which HCl is generated in hydrothermal systems (e.g., Anderson, 1989; Haizlip and Truesdell, 1988; 1989). Although our results are for much higher temperatures than are encountered in the production of geothermal resources they have implications with respect to natural hydrothermal systems at lower temperatures.

The solubility of NaCl in superheated steam at temperatures in excess of 400°C has been investigated by several researchers, including Olander and Liander (1950), Styrikovich *et al.* (1955), Sourirajan and Kennedy (1962), Martynova and Samoilov (1962), Martynova (1964), Galobardes *et al.* (1981), and Armellini and Tester (submitted). The formation of HCl by the hydrolysis of sodium chloride in dry steam was specifically addressed by Galobardes *et al.* (1981) at 350–550°C, by Armellini and Tester (submitted) at 450–550°C, and by Hanf and Sole (1970) at 600–950°C. All of the hydrolyses studies were carried out in a similar manner; dry steam or nitrogen containing steam at a controlled humidity were flowed at constant temperature and pressure through long, pipe-like

reaction vessels packed with sodium chloride. In these dynamic flow-through experiments a given quantity of steam was in contact with salt for a relatively short period of time (a few seconds to a few minutes, depending on flow rate). However, the above investigators concluded that equilibrium solubilities of NaCl in steam are attained very quickly at high temperatures because similar results were obtained at different rates of flow, and in experiments using reaction chambers in which flow paths were of different lengths.

Pitzer and Pabalan (1986) carried out a thermodynamic analysis of the solubility of NaCl in steam and, based on the results of Hanf and Sole (1970) and Galobardes *et al.* (1981), concluded that the effect of hydrolysis on NaCl properties at high temperatures is probably very small. Recently Anderko and Pitzer (in press) formulated an equation of state representation of phase equilibria in the system NaCl–H_2O, and Sterner *et al.* (1992) have reported the results of a thermodynamic analysis of solid-liquid equilibria at high temperatures and pressures in the system NaCl–KCl–H_2O. It is noteworthy that Sourirajan and Kennedy (1962), who investigated the system NaCl–H_2O over widely ranging temperatures and pressures, and with reaction times of a few hours, reported significantly higher solubilities of NaCl in dry steam than those reported by other investigators, except for Alekhin and Vakulenko (1988). Alekhin and Vakulenko (1988) measured solubilities *in-situ* using a radioactive tracer and reported even greater solubilities than those reported by Sourirajan and Kennedy (1962). However, Armellini and Tester (submitted) point out that the Alekhin and Vakulenko (1988) results possibly may be in error due to absorbed NaCl molecules on the inner walls of the reaction vessel.

APPARATUS AND EXPERIMENTAL PROCEDURE

The experiments were carried out using a reaction vessel made of Inconel X with an internal capacity of 68 cm^3. Fluid could be injected into or withdrawn from the vessel through a stainless-steel capillary tube that was inserted into the chamber through the closure plunger, using a high-pressure fitting. The vessel, charged with solid reactants (Table 1), was placed vertically in a doubly wound furnace with one winding heating just the ends of the furnace and a second winding heating the middle portion.

The reaction vessel was heated to about 600°C with the sampling port open to allow escape of air as the internal temperature increased. After attaining a stable temperature of 600°C, measured at the top of the reaction vessel, the sampling port was closed and then known amounts of water were slowly injected into the hot vessel until a desired maximum internal pressure was attained. The water and salt were allowed to equilibrate at about 600°C overnight and then sampling was initiated. At this time the temperature external to the sample chamber at the bottom of the vessel generally was about 10°C hotter than at the top, but the gradient within the sample chamber probably was much less owing to convection of the fluid.

TABLE 1. *Starting materials used in experiment (in grams).*

Experiment No.	NaCl (g)	KCl (g)	Quartz (g)	H_2O (g)	NaCl:KCl (by wt.)	m soln.	NaCl/KCl mole ratio
P42	4.0	---	---	21	---	3.26	---
P23	1.5	0.5	---	14.4	3:1	2.60	3.83
P26	1.5	0.5	---	27	3:1	1.20	3.83
P45	45.0	15.0	---	18	3:1	53.95	3.83
P30	3.0	1.0	1.0	21	3:1	3.08	3.83

Samples were extracted from the top of the vessel; thus the temperature closest to the point of sampling was taken as the experimental temperature, 600 ± 3°C. Generally about every 45 to 60 minutes during the day three separate steam condensate samples were quickly extracted for chemical analyses. However, a few intervals between sampling episodes were more than 16 hours overnight. At the time of sampling, a portion of the capillary tube was placed in an ice bath to quench the sampled fluid to less than about 20°C. It generally took about 5 minutes to extract the three samples. At each sampling episode the first of the three samples generally weighed about 0.6 to 0.8 g and was discarded because it was contaminated with a small amount of condensate that filled the capillary and valve prior to sampling. The next sample also generally weighed about 0.6 to 0.8 g and the last about 0.2 to 0.3 g. The pressure decreased as a consequence of withdrawal of each sample.

The samples were diluted with about 10 g distilled water and analyzed for Na and K by atomic absorption. Cl was determined by potentiometric titration using silver nitrate and a silver reference electrode. Less than 0.5 ppm Ni was found in the samples, indicating that there was no significant attack by the hot brine or steam upon the Inconel X reaction vessel at the conditions of the experiment.

In some experiments the fluid pressure was sufficiently high at the start of an experiment for brine (or brine plus quartz) to fill the reaction chamber. As a result of fluid extraction, pressure declined and a steam cap formed above the brine. Thereafter, only steam was sampled. Continued extraction of steam resulted in the precipitation of salt, and the brine evaporated to dryness so that only steam and solid salt (or salt plus quartz) occupied the reaction chamber during the last few sampling events at low pressures. In the illustrations that follow, the data are plotted at the average pressure during the time that an individual sample was collected.

RESULTS

Figure 1 shows our experimentally determined molal concentrations of Cl (circles) and Na (squares) dissolved in steam in the system NaCl–H_2O (P42, Table 1), compared with experimental results reported by Sourirajan and Kennedy (1962) and by Martynova (1964), and with calculated solubilities of NaCl according to the models of Pitzer and Pabalan (1986) and Anderko and Pitzer (in press). All of the experimental and modeled solubilities are in general agreement at a pressure of about 30 MPa. At

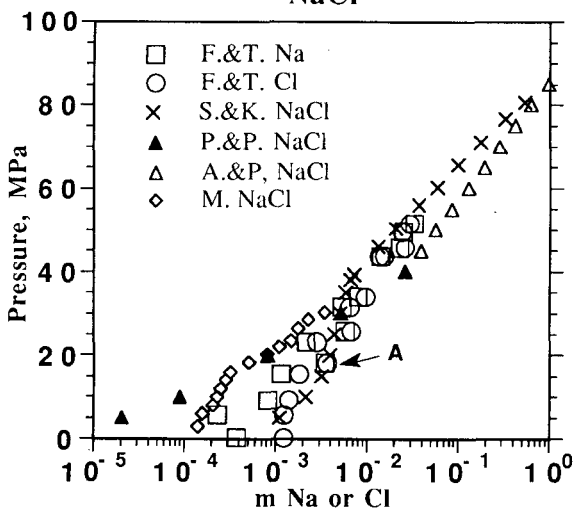

FIG. 1. Experimental results in the system NaCl–H_2O (run P42, Table 1) showing molal Cl or Na dissolved in steam coexisting with brine or halite at 600°C, plotted versus the average vapor pressure during sampling. In the legend F.&T. indicates results of the present investigation; S.&K. indicates results reported by Sourirajan and Kennedy (1962); P.&P. indicate solubilities according to the model of Pitzer and Pabalan (1986); A.&P. indicates solubilities according to the model of Anderko and Pitzer (submitted); and M. indicates results reported by Martynova (1964).

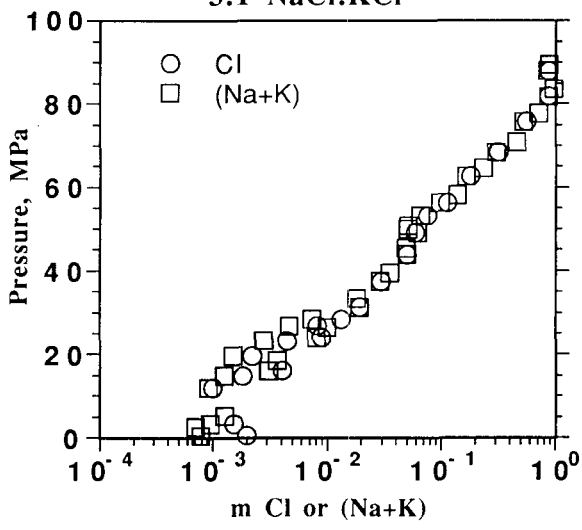

FIG. 2. Experimental results in the system NaCl–KCl–H_2O, starting with a 3:1 mixture of NaCl:KCl by weight (runs P23 and P26, Table 1), showing molal Cl or total alkalies (Na+K) dissolved in steam coexisting with brine and/or halite at 600°C, plotted versus the average vapor pressure during sampling.

other pressures our results generally plot closer to those of Sourirajan and Kennedy (1962) than to those of Martynova (1964), particularly at pressures less than about 25 MPa. Above 30 MPa our measured solubilities are less than the solubilities indicated by the Anderko and Pitzer (in press) model, and below 30 MPa our measured solubilities are considerably greater than the modeled solubilities of Pitzer and Pabalan (1986).

In the system NaCl–H_2O there is an invariant point at a pressure of 39.8 MPa at 600°C where the reactants consist of coexisting gas plus brine plus solid salt (halite). Salt may not exist at higher fluid pressures where only gas plus brine are stable, and brine may not exist at lower pressures where only gas and solid salt are stable. At pressures above 39.8 MPa, where steam coexists with brine, within the analytical uncertainty steam contains molal concentrations of Cl equal to the molal concentration of dissolved Na. At lower pressures where solid salt is a reactant, significantly more Cl generally was found dissolved in steam than Na indicating the presence of HCl°(*g*).

Figure 2 shows our results for Cl and (Na+K) dissolved in steam (at pressures below 80 MPa) in the system NaCl–KCl–H_2O, starting with 3:1 mixtures by weight of NaCl and KCl (P23 and P26, Table 1). At pressures above 80 MPa only one phase (liquid) was present. In the three-component system NaCl–KCl–H_2O at constant temperature, there is still one degree of freedom when brine plus steam plus halite coexist. Therefore, halite (containing KCl in solid solution) may coexist with brine and steam of varying compositions over a range of pressures. The system becomes invariant at a constant temperature and pressure when sylvite precipitates along with halite. However, sylvite did not precipitate in our experiments because there is complete solid solution between halite and sylvite at 600°C. The formation of NaOH and HCl° by hydrolysis reactions is a complicating factor because residual NaOH will impart an extra degree of freedom to the system when HCl° is preferentially removed during sampling of steam. Also, like KCl, NaOH forms a solid solution with halite, and its presence effects the amount of salt that may dissolve in a coexisting gas (discussed later).

Figure 3 shows the results of adding quartz to a 3:1 mixture by weight of NaCl and KCl (P30, Table 1). At pressures below about 30 MPa, addition of quartz to the system NaCl–KCl–H_2O greatly increases the Cl dissolved in steam (Figs. 3 and 4), but has very little, if any, effect on dissolved Na (Fig. 5). Figures 6 and 7 show contrasting concentrations of Cl and Na dissolved in steam starting with 3:1 NaCl:KCl mixtures by weight in which the reaction vessel in one run (P45, Table 1) initially contained 60 g salt (≈54 m Cl) and in two other runs (P23 and P26, Table 1) it initially contained only 2 g salt (<3 m Cl). An important observation is that increased concentrations of both Na and Cl were attained in steam in experiments when initially there was less NaCl present relative to water. In the P23 and P26 experiments (1.5 g NaCl) the initial NaCl/H_2O weight ratios were 0.10 and 0.06 respectively, while in the P45 experiment (45 g NaCl) the initial NaCl/H_2O weight ratio was 2.5.

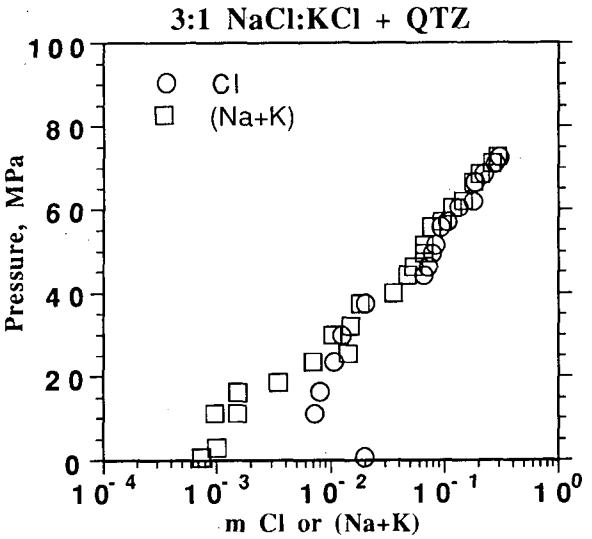

FIG. 3. Experimental results in the system NaCl–KCl–H_2O-quartz, starting with a 3:1 mixture of NaCl:KCl by weight (run P30, Table 1), showing molal Cl or total alkalies (Na+K) dissolved in steam coexisting with brine and/or halite at 600°C, plotted versus the average vapor pressure during sampling.

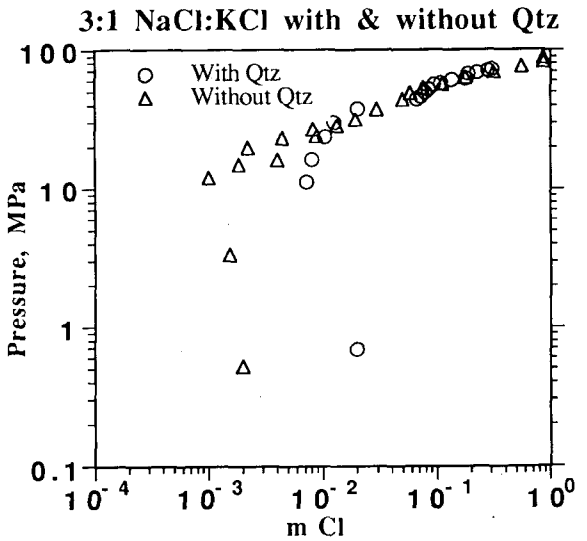

FIG. 4. Comparison of molal concentrations of Cl dissolved in steam starting with 3:1 mixtures by weight of NaCl:KCl with quartz and without quartz.

DISCUSSION

The smaller concentrations of both Na and Cl found dissolved in steam in experiments starting with more salt relative to water indicate that these variations are not likely to be due mainly to kinetic factors. If kinetic factors were dominant, one would expect those systems with the largest surface areas of salt relative to the amount of water present

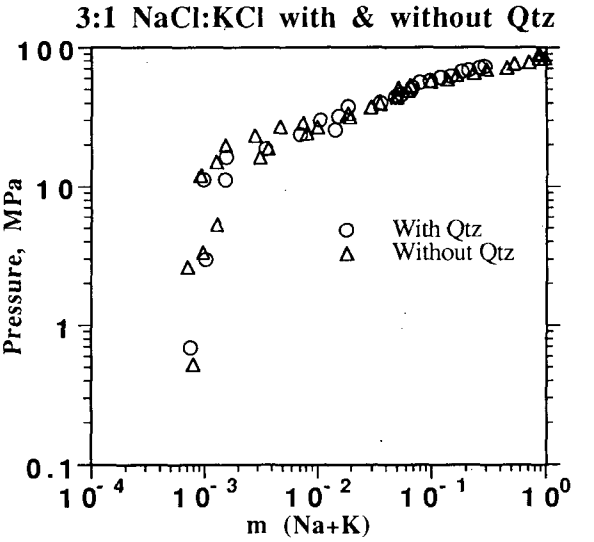

FIG. 5. Comparison of molal concentrations of Na dissolved in steam starting with 3:1 mixtures by weight of NaCl:KCl with quartz and without quartz.

to attain the highest concentrations of dissolved salt most quickly, assuming that higher concentrations of dissolved salt represent a closer approximation to equilibrium conditions. Such was not the case, and below we suggest a model in which equilibrium conditions were approached in most or all of the experiments, with different solubility results mostly caused (1) by variations in the amount of NaOH produced by hydrolysis reactions and (2) by variations in the mole fraction of NaOH(*s*) in solid solution within halite. The following discussion of the solubility results and hydrolysis effects is based mainly on reactions within the system NaCl–H_2O. The addition of KCl to the system is a complicating factor, but this does not appear to change drastically the general conclusions.

In their flow-through experiments in the temperature range 450–550°C both Styrikovich *et al.* (1955) and Martynova and Samoilov (1962) measured Cl^- ion concentrations and calculated NaCl solubilities, assuming that Na^+ and Cl^- ions were present in quenched steam in about equal molal concentrations. Their respective results are in good agreement, but at pressures less than 10 MPa their reported solubilities are significantly higher than those of Galobardes *et al.* (1981). Galobardes *et al.* (1981) calculated NaCl solubilities using measured Na^+ ion concentrations even though they found the ratio of molal chloride to sodium about equal to 1.2 at 450°C and extracted a highly basic solution (pH ~11) when they pumped cold water (as opposed to dry steam) through a salt-packed column that previously had been used for several weeks in their dry steam experiments at 450°C. This clearly shows that solid NaOH(*s*) formed and remained in the column of packed salt during their dry steam flow-through experiments. Also, in flow-through experiments in the same temperature-pressure range as the above experiments, Armellini and Tester (submitted) measured both Na^+ and Cl^- ion concentrations and their

Cl^- results are in agreement with those of Styrikovich *et al.* (1955) and Martynova (1964), and their Na^+ results are in agreement with those of Galobardes *et al.* (1981). The larger molal concentrations of Cl in steam relative to Na in these experiments clearly show the importance of hydrolysis of NaCl at high temperatures and low pressures according to the reaction,

$$NaCl(s) + H_2O(g) = NaOH(s) + HCl°(g). \quad (1)$$

It is not surprising that our results show considerably greater solubilities at comparable temperatures and pressures than the modeled solubilities of Pitzer and Pabalan (1986) because they calibrated their model using experimental results reported by Galobardes *et al.* (1981), who, as noted above, measured dissolved Na and then calculated NaCl solubilities with the assumption that stoichiometric quantities of dissolved Cl were present in solution. Therefore, the Pitzer and Pabalan (1986) model is likely to yield lower than measured solubilities to the extent that NaOH and HCl form by the hydrolysis of NaCl.

In the flow-through experiments of Hanf and Sole (1970), Galobardes *et al.* (1981), and Armellini and Tester (submitted), in which the mass ratio of salt to steam was very large and the transient steam was in contact with solid salt for only a few seconds to a few minutes, equilibrium was attained by dissolving salt, starting with pure steam. Our experimental technique, in which samples of fluids were extracted from a reaction chamber at successively lower pressures, was similar to the technique employed by Sourirajan and Kennedy (1962). In these experiments a maximum amount of salt was dissolved in steam at high pressure at the start of an experiment. During and after each sampling episode a new equilibrium condition was approached from supersaturation toward saturation. Because the concentration of (Na+K) in the third sample collected generally was less than the concentration of (Na+K) dissolved in the second sample that was collected at higher pressures not more than 3 or 4 minutes previously, we conclude that both condensation of brine and precipitation of salt from steam occur rapidly as pressure declines. The 45 to 60 minute (or longer) interval between the start of individual sampling episodes is likely to have been sufficient to achieve equilibrium with respect to the partitioning of Na and K between brine and steam and to attain equilibrium solubilities of salt in dry steam. However, the NaOH(s) that is produced according to equation (1) forms a limited solid solution with the remaining NaCl(s), and the interval between samplings may not have been sufficient for solid state diffusion to result in a uniform mole fraction of NaOH(s) in solid solution within halite. In this regard it is noteworthy that the data point labeled A in Fig. 1, which has about equal amounts of dissolved Na and Cl, and which plots on the Sourirajan and Kennedy (1962) solubility curve, is for a fluid that equilibrated with salt for about 16 hours between sampling episodes. All the other data points shown in Fig. 1 are for fluids that equilibrated with salt for about 30 minutes to 1 hour between sampling episodes and for as little as 2 or 3 minutes between individual sample extractions. It is possible that equilibrium of NaOH in solid solution in halite was attained by diffusion within 16 hours, but not in the runs of shorter duration. This is an important consideration because NaOH° as well as NaCl° dissolve into the steam phase, and the equilibrium concentration of NaOH° dissolved in steam will depend on the mole fraction of NaOH(s) in solid solution in the halite (Hanf and Sole, 1970; Armellini and Tester, submitted). In particular, Armellini and Tester (submitted) noted that limitations imposed by diffusion rates of NaOH(s) into halite "could lead to unsteady behavior and hydrolysis levels which depend on experimental parameters such as salt particle sizes and previous history of the salt bed."

A factor that may be important in explaining the difference in experimental results using flow-through techniques compared to quasi-static experiments is the much larger H_2O/NaCl mass ratio in the latter experiments. When steam is in contact with halite, hydrolysis reactions will proceed until sufficient HCl° is generated to attain equilibrium. The amount of HCl° generated is independent of the amount of halite present, but, as noted above, apparently is highly dependent on the amount of NaOH(s) in solid solution in halite. Figure 8 is a schematic phase diagram for the system NaCl–NaOH–H_2O at a temperature and pressure such that only gas plus solid salt exist. It is drawn to be compatible with the experimental observations and assumes limited solid solution of NaOH(s) within halite. The positions of tie lines show in a general way how solubilities of both Na and Cl in gas may increase as the mole fraction of NaOH(s) in solid solution in halite becomes greater. Furthermore, the mole fraction of NaOH(s) that is attained within halite depends on the mass of NaOH(s) generated by the hydrolysis reaction, the mass of halite remaining after that reaction, and the rate of diffusion of NaOH(s) into the halite. For the same amount of NaOH(s) generated, the resulting mole fraction of NaOH(s) in halite will be smaller when larger amounts of halite are present initially. In our experiments it is likely that diffusion of NaOH(s) into halite generally did not achieve a uniform, equilibrium distribution, but some diffusion appears to have occurred. We suggest that the effective mole fraction of NaOH(s) in halite, as a controlling factor with respect to the gas phase, was much larger in the quasi-static experiments (larger initial H_2O/NaCl mass ratios) than in the flow-through experiments (smaller initial H_2O/NaCl mass ratios).

In our experiments the effects of variations in the initial H_2O/NaCl mass ratio on the amounts of Na and Cl dissolved in steam can be seen in Figs. 6 and 7 that compare the results for experiment P45 (45 g NaCl), in which the initial H_2O/NaCl mass ratio was 0.4, with those for P23 and P26 (both 1.5 g NaCl) in which this ratio was 9.6 and 18, respectively. Clearly, smaller initial H_2O/NaCl mass ratios result in less Na and Cl dissolved in steam. Thus, the equilibrium constant for the hydrolysis reaction shown by equation (1) must take into account the departure of the solid salt from unit activity resulting from the solid solution of NaOH(s) in halite and of the NaCl° and NaOH° that enter the gas phase.

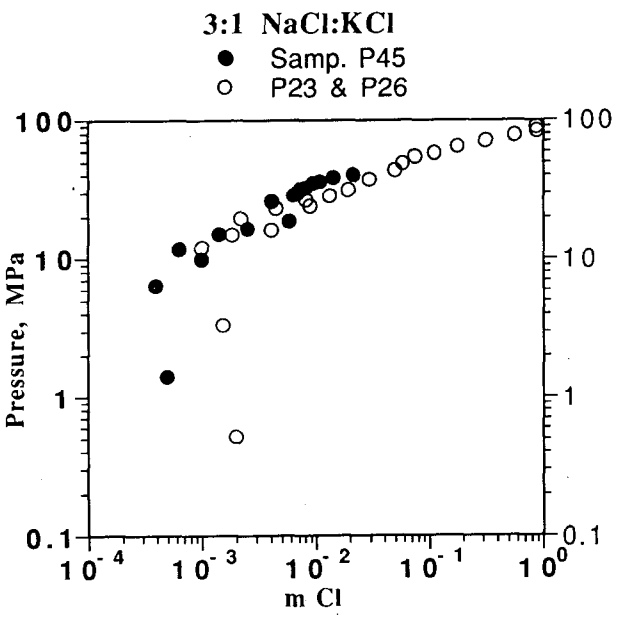

FIG. 6. Molal Cl dissolved in steam as a function of pressure for run P45, starting with 45 g NaCl, compared to runs P23 and P26, each starting with 1.5 g NaCl.

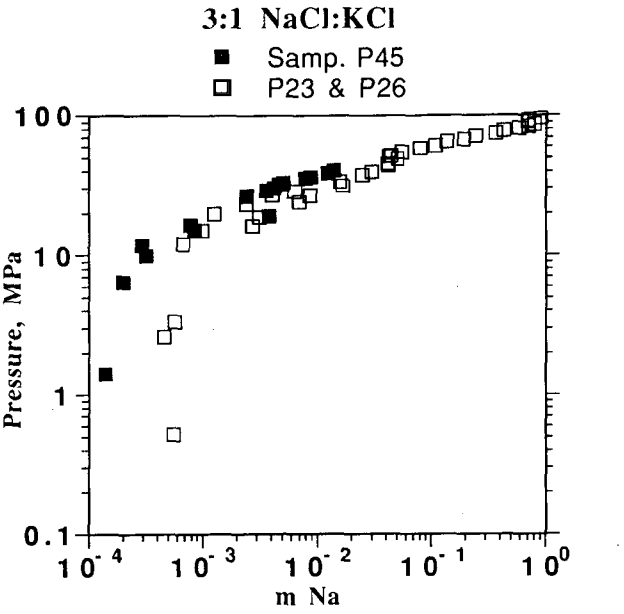

FIG. 7 Molal Na dissolved in steam as a function of pressure for run P45, starting with 45 g NaCl, compared to runs P23 and P26, each starting with 1.5 g NaCl.

To investigate the likely effects of salt hydrolysis reactions in natural systems, we added quartz to a 3:1 mixed salt system, expecting the yield of HCl° to increase because quartz reacts with NaOH to form sparingly soluble sodium disilicate that has a retrograde solubility at high tempera-

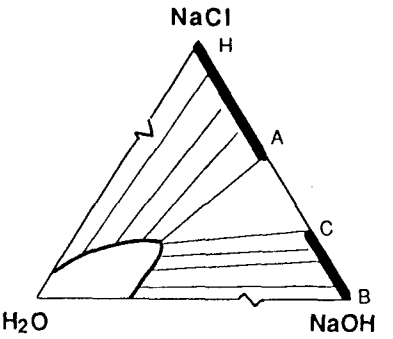

FIG. 8. Triangular diagram showing schematically how gas compositions apparently are affected by solid solution compositions in the system NaCl–NaOH–H_2O at a temperature and pressure such that gas plus solid salt coexist in the absence of brine. Limited solubility of NaOH(s) in halite (H to A) and limited solubility of NaCl(s) in solid NaOH (B to C) is assumed. The heavy curved lines show compositions of the gas phase and the light straight lines show compositions of coexisting gas and solids.

tures (Rowe *et al.*, 1967, and references therein). The reaction is

$$2NaOH(s, l) + 2SiO_2(s) = Na_2Si_2O_5(s) + H_2O(g). \quad (2)$$

Combining equations (1) and (2),

$$2NaCl(s) + 2SiO_2(s) + H_2O(g) = Na_2Si_2O_5(s) + 2HCl(g). \quad (3)$$

Figures 4 and 5 indeed show that at 600°C and pressures below about 40 MPa the addition of quartz to the system NaCl–KCl–H_2O markedly increases dissolved Cl as HCl° in steam with no apparent change in the total dissolved Na.

IMPLICATIONS REGARDING NATURAL SYSTEMS

In natural hydrothermal systems Na^+/K^+ activity ratios in fluids usually are fixed by base exchange reactions involving alkali feldspars (Orville, 1963; Fournier, 1976), while Na^+/H^+ and K^+/H^+ activity ratios are fixed by hydrolysis reactions involving various silicates, including amphiboles, pyroxenes, and especially feldspars and mica (Hemley and Jones, 1964; Hemley and Hunt, 1992). Where micas are present, pH values generally are near neutral or only slightly acidic. Where feldspars have been completely altered to micas, Na^+/H^+ and K^+/H^+ activity ratios are likely to be fixed by hydrolysis reactions involving mica and kaolinite below about 250°C, or mica and pyrophyllite above about 250°C (Hemley and Jones, 1964). In this situation pH values may become moderately acidic. However, extreme acidity can occur only where all feldspars and micas have been altered to pyrophyllite, kaolinite, or alunite.

Pore fluids that evaporate in response to a pressure drop or by boiling in place with escape of steam become ever more saline, and the alkali metal activities in the residual brines increase, thereby increasing Na^+/H^+ and K^+/H^+ activity ratios if compensating reactions do not occur. However, in natural systems compensating reactions are likely to occur. For example, clays and mica are likely to be converted to feldspars by base exchange with release of hydrogen ions, so that an increase in salinity by boiling (implying an increase in Na^+ and K^+ activities) is accompanied by an increase in hydrogen ion activity in order to maintain constant Na^+/H^+ and K^+/H^+ activity ratios. To the extent that the pore fluid initially contained chloride ions, the residual brine becomes slightly richer in hydrochloric acid as boiling progresses, mainly as a result of conversion of mica to feldspar. The evolving steam carries away only a small amount of gaseous HCl° because most hydrochloric acid remains dissolved in the brine. However, exceedingly acid brines generally are not generated by this process because acidity is buffered by rock-water interactions (Hemley and Hunt, 1992), and the rock/water ratio is large where there is sufficient thermal energy to allow large increases in salinity of brine by boiling in place in the formation.

The situation changes drastically when a brine boils dry; the precipitated salts react with steam and silicates with release of gaseous HCl° that is an associated, relatively unreactive, neutral species. The NaCl° and KCl° dissolved in dry steam, however, are appreciably reactive and dissociate to a somewhat greater extent, as shown by fast rates of reaction observed in base exchange experiments involving alkali feldspars at 400–700°C and low pressure (Fournier, 1976). Because hydrogen chloride is present in dry steam mainly as HCl° at high temperatures, its formation by hydrolysis reactions is not likely to significantly decrease Na^+/H^+ and K^+/H^+ activity ratios in the steam. Therefore, alkali feldspars in contact with evaporating brines and dry steam remain stable. In experiments in which only Na- and K-feldspars were in contact with steam plus brine plus alkali metal salt, Na-feldspar was converted to K-feldspar as a consequence of brine and steam becoming relatively enriched in potassium owing to precipitation of NaCl(*s*) (Fournier, 1976).

In a natural system instead of forming sodium disilicate as a reaction product, as in equations (2) and (3), it is likely that salt and quartz would react with various aluminum-rich silicates, forming alkali feldspars and other common hydrothermal alteration products, with release of HCl°. For example, a net reaction might involve NaCl, quartz and calcium feldspar, forming albite and epidote, or NaCl, quartz and muscovite, forming K-feldspar and albite. These net reactions are:

$$4CaAl_2Si_2O_8 + 4SiO_2 + 2NaCl + 2H_2O = 2NaAlSi_3O_8 + 2Ca_2Al_3Si_3O_{12}(OH) + 2HCl°, \quad (4)$$

and

$$2KAl_2(AlSiO_{10})(0H)2 + 12SiO_2 + 4NaCl = 2KAlSi_3O_8 + 4NaAlSi_3O_8 + 2HCl°. \quad (5)$$

When chloride-rich brine boils to dryness, the HCl° that forms by reactions involving salt and silicates, such as (4) and (5), is carried along with steam that escapes from the system. At higher and cooler levels in the system where steam condenses, HCl° is highly fractionated into the liquid condensate where the HCl° dissociates, becoming very reactive and corrosive at these conditions.

An unexpected result shown by the experimental work is that the amount of NaCl° and NaOH° dissolved in steam is inversely proportional to the initial salinity of a Cl-rich brine. This is because of the greater mole fraction of NaOH(*s*) that is attained in solid solution within halite when the initial salt/water ratio is lower. Thus, in a natural system where Cl-rich saline water initially fills all pore spaces, subsequent depressurization that allows steam to form and eventually salt to precipitate may result in higher concentrations of NaCl° and NaOH° dissolved in steam where there are lower initial salinities of pore fluid, provided that all NaOH(*s*) that is generated by hydrolysis reactions is not removed from the system by reaction with silicates.

CONCLUSIONS

At 600°C in the simple system NaCl–H_2O, steam in equilibrium with chloride-rich brine in the absence of halite at high pressures dissolves alkali metals and chloride in approximately stoichiometric quantities. In contrast, at lower pressures excess chloride as HCl° is found dissolved in dry steam in contact with halite. The hydrolysis reaction that produces the HCl° also produces NaOH(*s*) that diffuses into halite, forming a solid solution. Both NaCl° and NaOH° are found dissolved in steam, and the solubility of each is increased as the mole fraction of NaOH(*s*) in halite increases. In the quasi-static experiments, compared to dynamic flow-through experiments, higher initial ratios of H_2O/NaCl have resulted in higher mole fractions of NaOH(*s*) in solid solution in halite and, accordingly, higher reported solubilities of NaCl dissolved in steam. Addition of KCl to the system is a complicating factor, but it does not appear to change these conclusions significantly. In contrast, addition of quartz to the system NaCl–KCl–H_2O greatly increases the amount of HCl° produced by the hydrolysis of NaCl.

In natural systems at lower temperatures, brines generally are not likely to become very acid because their pH values are buffered by mineral reactions involving feldspars and micas. Hydrolysis reactions, that produce HCl° dissolved in steam, are likely to occur only where halite has precipitated as a result of boiling accompanying depressurization. However, the system need not have boiled dry to produce HCl in significant concentrations in steam because halite may coexist with brine of varying composition over a finite pressure range at a constant temperature. Most NaOH, that forms as a byproduct of the hydrolysis of NaCl, is likely to react quickly with quartz and other minerals, forming sparingly soluble alteration products (particularly alkali feldspars), and resulting in increased amounts of HCl° dissolved in steam. Thus, in natural systems NaOH° generally is not likely to

be available for transport along with HCl° in steam, and steam condensates may be very acidic.

The experimental results reported here are in agreement with empirical observations that HCl corrosion problems seem to become greater for steam produced from the hottest parts of The Geysers geothermal field where pressures are well below the boiling-point curve for pure water. Although there is general agreement that HCl is an important gas evolved from cooling magmas, a magmatic source is not required for the attainment of significant quantities of HCl° in steam. All that is required is that steam come in contact with precipitated chloride-rich salt within hot rock that contains reactive silicates.

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