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Estimation of Long-Term CO_2 and H_2S Release During Operation of Geothermal Power Plants

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ABSTRACT

The concentrations of CO_2 and H_2S in undisturbed liquid-dominated high-temperature geothermal reservoir waters are generally controlled by temperature dependent equilibria with various mineral buffers. These equilibria cause the concentrations of these gases to increase with temperature. The presence of equilibrium steam in the reservoir (two phase reservoir) will cause the gaseous concentrations in the fluid to be higher than the aqueous equilibrium concentrations at any particular temperature. In the range of about 230-300°C, the CO_2 buffer is considered to be clinozoisite + prehnite + quartz + calcite. In high-temperature waters of low salt content, which are strongly reducing, the H_2S buffer is considered to be pyrite + pyrrhotite + epidote + prehnite. In waters of higher salinity, the respective H_2S mineral buffer may consist of pyrite + magnetite + hematite. The concentrations of CO_2 and H_2S in steam of wet-steam wells producing from liquid-dominated reservoirs are higher than those of the parent fluid, frequently in the range 50-300 and 2-20 mmoles/kg of steam, respectively. However, values as high as 1000 mmoles/kg for CO_2 and 50 mmoles/kg for H_2S are not uncommon. The concentrations of these gases in steam from wet-steam wells depend on 1) their concentration in the parent geothermal water, 2) the steam fraction, which has formed by depressurization boiling, 3) the reservoir steam fraction, if present, 4) the steam separation pressure, and 5) the boiling processes, which lead to the steam formation.

Long-term utilisation of geothermal reservoirs may lead to decline in the concentrations of CO_2 and H_2S in the steam. The decline can be caused by recharge of cooler water into producing aquifers and/or progressive boiling of water retained in the aquifer rock by capillary forces. Further, enhanced boiling, which is a consequence of reservoir pressure draw down, and steam separation during lateral flow into production wells may cause the well discharge to become depleted in gas. The separated steam may form a steam cap over the liquid reservoir and/or enhance fumarolic activity.

Although gas emissions from geothermal power plants may be enhanced much during the early years of production relative to natural discharge, in the long run, the integrated gas emission may not exceed that of the natural gas flux. A steady state may be reached between the flux of gases from the magma heat source into the geothermal system and from the geothermal system into producing wells and fumaroles.

The source of noble gases, apart from He, in geothermal fluids is air saturated meteoric water. The relative abundance of noble gases in geothermal steam may aid assessment of which processes are responsible for changes in the concentrations of the environmentally important CO_2 and H_2S.

1. INTRODUCTION

Compared to other renewable energy resources, geothermal energy has the disadvantage to release gases (CO_2, H_2S and CH_4) into the atmosphere in the emitted steam that have adverse environmental effects. Carbon dioxide and CH_4 are greenhouse gases and H_2S is poisonous besides its unpleasant smell, even at very low concentrations. For power generation, geothermal energy is, however, much more favourable environmentally than combustion of fossil fuel. As an example, the CO_2 emission from the Krafla power plant in Iceland is 841 tons per MW-year (MWy), which is about 10% of that of a classical coal fired power plant (8760 tons per MWy) (Ármannsson and Kristmannsdóttir, 1992). The total sulfur emission of a standard coal or oil plant is about 96 tons per MWy whereas the emissions from Krafla are about 53 tons/MWy.

Attempts have not been made to remove CO_2, and CH_4 from geothermal steam. By contrast, various methods are available to remove H_2S from geothermal steam and some of them have been applied at some geothermal power plants. In other plants, the H_2S is released into the atmosphere. Once in the atmosphere, the H_2S may be oxidized into SO_2 and in this way contribute to the global emission of SO_2. Studies in Iceland indicate, however, that oxidation of H_2S into SO_2 is limited. The oxidation does not apparently extend beyond native sulfur and due to the frequent rain in Iceland the sulfur is likely to precipitate in the vicinity of the emission areas (Kristmannsdóttir et al., 2000). The limited oxidation of geothermal H_2S in Iceland may be the consequence of cold climate and short residence time due to frequent rainfall.

In this study we focus on two environmentally important geothermal gases, CO_2 and H_2S. Their concentrations in high-temperature reservoir waters have been considered to be controlled by close approach to temperature dependent equilibria with various mineral buffers (Arnórsson and Gunnlaugsson, 1985; Arnórsson et al., 2000) although this may not be the case for all geothermal systems, at least for CO_2, in which case it is externally fixed, i.e. is by its supply to the geothermal fluid. In general, the concentrations of CO_2 and H_2S in steam discharged from wet-steam wells and geothermal power plants depend on

1. their concentrations in the parent geothermal fluid
2. the steam fraction in the discharge which has formed by depressurization boiling
3. the reservoir steam fraction, if present
4. the steam separation pressure
5. the steam fraction that formed by heat transfer from the aquifer rock to the boiled geothermal water in the depressurization zone around producing wells.

In this study we present temperature equations for equilibrium aqueous CO_2 and H_2S concentrations, in geothermal waters according to three mineral buffers using the most recently published thermodynamic data, one for CO_2 and two for H_2S. Special discussion is given to possible changes in the CO_2 and H_2S content of geothermal steam from wet-steam wells upon long-term production. This issue is relevant for the long-term release of gases from geothermal power plants. Ideas are given with respect to geochemical monitoring of geothermal reservoirs under utilisation with the purpose of predicting possible decline in gas emissions. Further it is pointed out that gas emissions may technically be reduced to insignificant levels by specific power plant design and extraction of the gases as useful industrial and fuel products.

2. MINERAL BUFFERS

Various studies indicate that CO_2 and H_2S concentrations in the aquifer water of high-temperature geothermal systems are governed by close approach to equilibrium with specific mineral buffers, at least prior to utilisation. Various buffers may be involved depending on the geothermal system host rock composition and the salinity of the fluid (Arnórsson and Gunnlaugsson, 1985; Arnórsson et al., 2000). Upon utilisation, the CO_2 and H_2S concentrations in the aquifer fluid may change, and consequently also in the fluid discharged from wells. The cause may be recharge of cooler water into producing aquifers, recharge of injected waste fluid or various boiling processes in the zone of depressurization of a wellfield. The source of the gases to the geothermal fluid is mostly thought to be the magma heat source. Some of the CO_2 and H_2S, may be derived from the carbon and sulfur in the rock undergoing alteration at depth. During the lifetime of geothermal systems, a fraction of the carbon and sulfur brought into the system at deep levels may accumulate in the hydrothermally altered rock in the upper part of the geothermal system, as carbonate and sulfide minerals. Dissolution of these minerals upon enhanced recharge of cooler water, as a consequence of utilisation, may contribute to the CO_2 and H_2S content of the geothermal fluid discharged from wells.

2.1 Source of thermodynamic data to retrieve equilibrium constants for gas-mineral buffers

Below temperature equations are presented which describe the equilibrium constants for selected gas-mineral reactions. The equilibrium constant equals the respective gas concentration in the aqueous phase.

The data used to derive these equations are from Holland and Powell (1998) for the minerals except for pyrite and pyrrhotite, which are from Helgeson et al. (1978), the standard Gibbs energy of formation of aqueous CO_2 and H_2S have been calculated from the solubility constants after Fernandez-Prini et al. (2003), and that for liquid water from Helgeson and Kirkham (1974).

2.2 Carbon dioxide

The mineral buffer controlling the carbon dioxide content of the aquifer water is clinozoisite + prehnite + quartz + calcite. The reaction is:

$$\text{clinozoisite + calcite + 3/2 quartz + water} = \text{3/2 prehnite} + CO_2(aq) \tag{1}$$

and:

$$K_{CO_2} = \frac{a_{pre}^{3/2} \cdot a_{CO_2(aq)}}{a_{czo} \cdot a_{cal} \cdot a_{qtz}^{3/2} \cdot a_{H_2O}} \tag{2}$$

where K_{CO2}, a_{pre}, a_{CO2}, a_{czo}, a_{cal}, a_{qtz}, and a_{H2O} are the equilibrium constant of reaction (1), and the activities of prehnite, aqueous carbon dioxide, clinozoisite, calcite, quartz, and pure water, respectively.

One can obtain the value of the equilibrium constant for this reaction from the following equation:

$$\log(K_{CO_2}) = \log(a_{czo}) + 5.30 - \frac{1686.82}{T} + 0.01008 \cdot T - 3.192 \cdot \log(T) \tag{3}$$

where a_{czo}, and T are the activity of clinozoisite, and the temperature in Kelvin, respectively. The activities of the other minerals are taken to be unity. The equilibrium constant is in this case equal to the activity of carbon dioxide as can be derived from equation (2), and, since the gas is taken to behave ideally, to the concentration of CO_2 in the aquifer water in mol/kg.

2.3 Hydrogen sulfide

The case of the H_2S is different in the way that the buffer depends on the water oxidation-reduction potential. We have chosen to consider two buffers; the first corresponds to strongly reducing conditions:

$$\text{1/3 pyrite + 1/3 pyrrhotite + 2/3 prehnite + 2/3 water} = \text{2/3 epidote} + H_2S(aq) \tag{4}$$

The second one involves an oxidising environment:

$$\text{1/2 pyrite + 1/2 magnetite + water} = \text{hematite} + H_2S(aq) \tag{5}$$

The equilibrium constants of the reactions are

$$K_{H_2S,pyrr} = \frac{a_{epi}^{2/3} \cdot a_{H_2S(aq)}}{a_{pyr}^{1/3} \cdot a_{pyrr}^{1/3} \cdot a_{pre}^{2/3} \cdot a_{H_2O}^{2/3}} \tag{6}$$

and

$$K_{H_2S,hem} = \frac{a_{hem} \cdot a_{H_2S(aq)}}{a_{pyr}^{1/2} \cdot a_{mag}^{1/2} \cdot a_{H_2O}} \tag{7}$$

where $K_{H2S,pyrr}$, $K_{H2S,hem}$, a_{epi}, $a_{H2S(aq)}$, a_{pyr}, a_{pyrr}, a_{pre}, a_{H2O}, a_{hem}, and a_{mag} are the equilibrium constants of reactions (4) and (5) and the activities of epidote, aqueous hydrogen sulfide, pyrite, pyrrhotite, prehnite, pure water, hematite, and magnetite, respectively.

The following equations describe the temperature dependence of the equilibrium constants for reactions (4) and (5), respectively:

$$\log(K_{H_2S,pyrr}) = \log(a_{epi}) + 13.47 - \frac{3375.53}{T} + 0.01299 \cdot T - 5.958 \cdot \log(T) \tag{8}$$

and:

$$\log(K_{H_2S,hem}) = 28.308 - \frac{4271.94}{T} + 0.011888 \cdot T - 10.751 \cdot \log(T) \qquad (9)$$

In deriving these equations, the activity of liquid water and all minerals, except epidote were taken to be equal to unity. The composition of the epidote may vary considerably and hence the activity of the $Ca_2FeAl_2Si_3O_{12}(OH)$ component is the epidote solid solution.

3. RESULTS

Data from several fields worldwide have been selected to study how the aqueous CO_2 and H_2S concentrations in the reservoir water conform to equilibrium control with the mineral buffers selected. The areas include Svartsengi and Krafla, Iceland (unpublished data of Iceland Geosurvey; Gudmundsson and Arnórsson, 2002), Olkaria, Kenya (Karingithi, 2002), Cerro Prieto, Mexico (Nehring and D´Amore, 1984) and Kawerau and Broadlands, New Zealand (see Arnórsson and Gunnlaugsson, 1985). The aqueous reservoir concentrations of the respective gases were calculated with the aid of the WATCH speciation program (Arnórsson et al., 1982), version 2.1 (Bjarnason, 1994). However, in the case of Svartsengi the reservoir CO_2 and H_2S concentrations represent total carbonate carbon and total sulfide sulfur. This is a reasonable approximation since practically all the carbonate carbon and sulfide sulfur in >200°C reservoir waters occurs as CO_2 and H_2S, respectively (Arnórsson and Gunnlaugsson, 1985). The concentrations of bicarbonate and other carbonate bearing species are insignificant as wells as bisulfide and other sulfide bearing species. In all cases, initial aquifer steam fractions were taken to be zero.

3.1 Carbon dioxide

The results for CO_2 are shown in Fig. 1. The curves in this figure represent unit activity of clinozoisite and an activity equal to 0.3. The latter number corresponds with the average mole fraction (activity) of clinozoisite in epidote in high-temperature geothermal fields in Iceland but all these fields are located in basaltic rocks. At Olkaria the reservoir rock is largely trachyte although minor basalt is also present. The Cerro Prieto reservoir is hosted by intermediate volcanic and clastic sediments. At Broadlands and Kawerau the reservoir rock is andesitic to rhyolitic. It is thought that the activity of clinozoisite in hydrothermal epidote may increase with increasing silica content of common volcanic rocks. Accordingly, one would expect that the aqueous CO_2 concentrations for the geothermal fields selected would lie between the two curves drawn in Fig. 1, if equilibrium was closely approached with the mineral buffer in question. This is indeed the case for the majority of the data points. Yet, some points have too low values for aqueous CO_2 concentrations and a few display too high values.

It is not a straight forward procedure to calculate the chemical composition of the aquifer water of liquid-dominated high-temperature geothermal fields from analysis of samples collected at the wellhead as well as individual species concentrations, including those of CO_2 and H_2S (see Arnórsson et al., 2005a, 2005b). The calculation procedure used here assumes that no equilibrium steam is present in the reservoir. If it was, the calculated CO_2 aquifer water concentrations are too high. The choice of aquifer temperature is also important for the calculation of aqueous gas concentrations in the reservoir. For all the geothermal fields considered for the present study, except Cerro Prieto, the selected aquifer temperature is based on evaluation of the results for solute geothermometers and measured temperature down-hole in thermally stabilized wells. At Cerro Prieto the selected aquifer temperature is the Na-K-Ca geothermometer temperature. Selection of a too high aquifer temperature leads to too low calculated aquifer water gas concentrations.

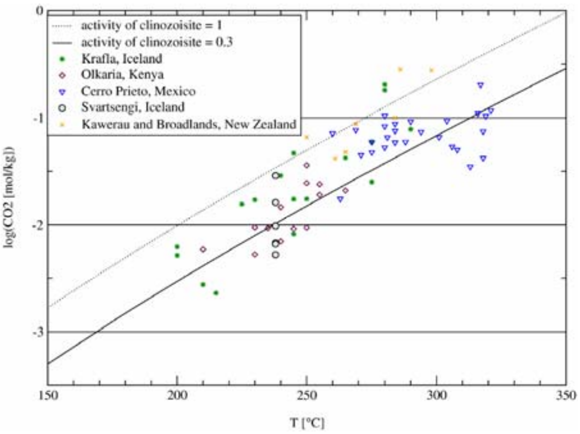

Figure 1: Calculated concentrations of CO_2 in the aquifer water of various geothermal fields.

Overall, the results for CO_2 presented in Fig. 1 conform reasonably well with control of the gas by equilibrium with the mineral buffer clinozoisite + prehnite + calcite + quartz in the temperature range considered (200-320°C). The data presented in Fig. 1 are based on samples collected at various periods after production started. They do not indicate any rapid decline in CO_2 with time of production over a period of a few decades. To detect such decline, accurate monitoring data are required over an extended period of time.

3.2 Hydrogen sulfide

Figure 2 shows the result for H_2S for the two different mineral buffers. The continuous and the doted line represent the buffers pyrite + magnetite + hematite and pyrite + pyrrhotite + epidote + prehnite, respectively. All the minerals are assumed to be pure (unit activity), except epidote, for which an activity of 0.7 is taken as average value for the Icelandic basaltic rocks.

The Krafla data plot very close to equilibrium with the mineral buffer pyrite + pyrrhotite + epidote + prehnite. The calculated H_2S aquifer water compositions for all the other fields considered are similar or lower than that corresponding to equilibrium with the mineral buffer. Some of the samples from Svartsengi are relatively far below the equilibrium curve of the pyrite + magnetite + hematite buffer. The samples from Olkaria in Kenya seem to be close to equilibrium with or slightly depleted in H_2S compared to this mineral buffer. The interpretation of the values of Cerro Prieto depends, as for CO_2, on the accuracy of the temperature calculated with the Na-K-Ca geothermometer and the apparent low values of some of the wells could also be explained by an overestimation of the aquifer temperature. Most of the Kawerau and Broadlands samples plot close to equilibrium with pyrite + magnetite + hematite buffer, while two concentrations are more than 0.5 lower on the log scale.

A lower activity of epidote for the buffer pyrite + pyrrhotite + epidote + prehnite would shift the equilibrium curve down and make it closer to the buffer pyrite + magnetite + hematite. The control of the H_2S concentration by those mineral buffers depends therefore as much on the mineral activities as on the choice of the mineral buffer.

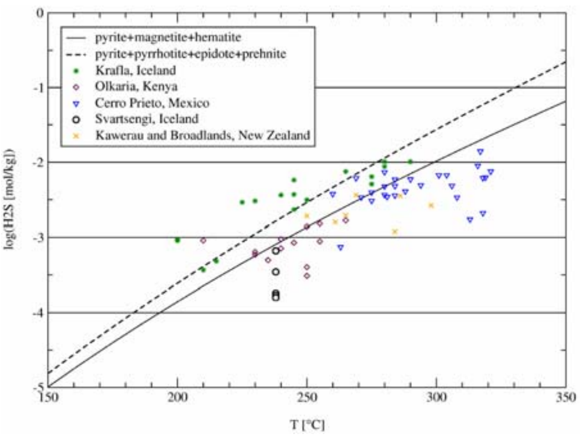

Figure 2: Calculated concentrations of H_2S in the aquifer water of various geothermal fields.

3.3 The Krafla geothermal field

The aquifer water for some of the Krafla wells have CO_2 concentrations equal to that corresponding to equilibrium with the mineral buffer considered. Other wells have higher CO_2 concentrations. These high concentrations are considered to be the consequence of relatively high flux of this gas from the magma heat source but the presence of reservoir steam may also contribute to these relatively high CO_2 levels. A new magma was intruded into the roots of the Krafla geothermal system during a volcanic rifting episode, which started at the end of 1975 and lasted for 9 years (Einarsson, 1978, Björnsson, 1985). At the beginning of this episode, the gas content of fumaroles rose strongly, particularly that of CO_2, as well as in the only productive well in the area at that time (Ármannsson et al., 1989).Many wells were drilled in the period 1976-1984. When initially discharged, the gas content of many of these wells was high but it has decreased with time (Gudmundsson and Arnórsson, 2002; Ping and Ármannsson, 1996) and for CO_2 it was much higher than that expected, if the mineral buffer clinozoisite + prehnite + quartz + calcite controlled aqueous CO_2 mobility. It is considered that these high concentrations were determined by high flux of CO_2 from the new magma that was intruded into the roots of the geothermal system and that reactions with the reservoir rock were not sufficiently fast to cope with the flux to maintain the geothermal fluid close to equilibrium with a mineral buffer. For many of the wells drilled into the Krafla geothermal reservoir, CO_2 concentrations have decreased to a level corresponding to equilibrium with the mineral buffer considered here (Fig. 1) but other wells are still high. The experience at Krafla indicates that magmatic processes can cause fluctuations in the gas content of geothermal reservoir fluids which are in no way related to utilisation.

Power production at Krafla started around 1980. Decreasing Cl in the water discharged from many of the wells indicative enhanced recharge of cooler water into productive aquifers (Gudmundsson and Arnórsson, 2002). The cooler water component may be as much as 40% of the total fluid discharged from individual wells after production over 15 years. Despite this recharge, CO_2 levels have not fallen below those corresponding to equilibrium with the mineral buffer under consideration. This is taken to indicate that supply of CO_2 to the geothermal fluid is sufficient to maintain equilibrium with the mineral buffer.

The H_2S aquifer water compositions at Krafla are quite similar to those expected at equilibrium with the mineral buffer pyrite + pyrrhotite + epidote + prehnite (Fig. 2). Of the 16 data points for this area, 7 deviate from the equilibrium curve by less than 0.1 SI units and altogether 11 are within 0.3 SI units. The remaining 5 data points have higher H_2S concentrations than those corresponding to equilibrium. These data points include 50% of those with aquifer temperatures below 250°C. These relatively “cool” and shallow aquifers may have received H_2S from rising steam from deeper aquifers. Alternatively, the cause may that the selection of mineral buffer is not valid. Epidote is not stable below about 230°C. Another buffer could be involved. Despite this, the overall results indicate that H_2S aquifer water concentrations are controlled by close approach to equilibrium with a mineral buffer and above about 230°C this buffer is pyrite + pyrrhotite + epidote + prehnite.

3.4 The Svartsengi geothermal field

The Svartsengi geothermal reservoir is very homogeneous in terms of temperature and water composition because of high vertical permeability. The reservoir is 70% recharged with seawater and 30% with meteoric water. Production has led to the formation of a steam cap over the liquid dominated reservoir. The top of the liquid dominated reservoir is two-phase but below it is sub-boiling.

The CO_2 reservoir water concentrations vary by almost one order of magnitude despite the constant temperature. For individual wells, monitoring data indicate that they are relatively stable with respect to their CO_2 content (Bjarnason, 1996). The difference is between wells. Hydrogen sulphide behaves very similarly to CO_2. The calculated CO_2 concentrations in the aquifer water at Svartsengi are both above and below the equilibrium curve (Fig. 1). High concentrations, i.e. higher than those corresponding to equilibrium with the mineral buffer considered, are taken to be due to contribution to the well flow from the steam cap. Concentrations below those corresponding with the respective mineral buffer equilibrium are considered to be due to inflow of degassed water just under the steam cap.

The concentrations of H_2S are always below that expected at equilibrium with the minerals buffers considered. However, because of the rather constant CO_2/H_2S ratios in all well discharges, the variation in H_2S concentrations can be explained in the same way as the variation in the CO_2 concentrations. It has not been defined which mineral buffer may control aqueous H_2S in the reservoir.

4. NOBLE GASES

It is envisaged that the concentrations of noble gases in the discharge of wet-steam wells may provide important information on boiling processes in high-temperature liquid-dominated geothermal reservoirs and in this way help understanding the behaviour of the reactive and environmentally important CO_2 and H_2S. Monitoring data over a long utilisation period are, however, lacking to demonstrate this. Except for He, the source of the noble gases to geothermal fluids is air dissolved in the parent meteoric or seawater. This water is expected to be air-saturated so the initial noble gas content of the geothermal water is known from the solubility of these gases in water. It is, however, possible that the initial noble gas concentrations may be higher than predicted from solubility constants, due to entrapment of air bubbles in the source water.

Boiling in producing aquifers of liquid-dominated geothermal reservoirs occurs principally by two processes, depressurization and heat transfer from the aquifer rock to the cooled fluid (the fluid cools by depressurization boiling) in the depressurization zone around producing wells (see e.g. Arnórsson et al., 2005b). In the long run some of the steam discharged from wells may have formed by progressive boiling of water held as film by capillary forces on the surface of mineral grains. This steam would be expected to become progressively depleted in noble gases. Upon prolonged utilisation of the geothermal reservoir, enhanced cooler water recharge would bring in air-saturated water and heating of this water through contact with the aquifer rock and subsequent depressurization boiling would yield steam with maximum possible content of noble gases. The reactive gases, CO_2 and H_2S would, on the other hand, be expected to decline in concentration in the steam, whether generated by progressive boiling of capillary water or recharging air-saturated water. The relative changes in the reactive and noble gas concentrations would accordingly be expected to provide information on the nature of the source water to the steam discharged from wells.

Pressure drawdown in geothermal reservoirs, which occurs as a consequence of long-term utilisation, is known to have enhanced fumarolic activity and led to the formation of steam caps over liquid-dominated reservoirs, such as Wairakei, New Zealand (Clotworthy, 2000) and Svartsengi, Iceland (Ármannsson, 2003). When this occurs the steam separates from the boiling water by gravity. The boiled water becomes depleted in gas in the process, which either escapes into the atmosphere through fumaroles or the gas is retained underground with the steam forming the steam cap.

The only noble gas monitoring data from exploited high-temperature geothermal fields are those on Ar from Svartsengi. The Ar concentrations in the Svartsengi reservoir water are at present around 10% of that of air-saturated water, except for wells receiving fluid from the steam cap which are higher in Ar. These low concentrations cannot be explained by boiling and degassing in deep aquifers because they are sub-boiling. It is considered to be either due to direct flow into wells of boiled and degassed water at the top of the liquid reservoir or recharge of this water into deeper productive aquifers. This interpretation is consistent with the interpretation given above for CO_2 and H_2S.

5. CONCLUSIONS

The CO_2 and H_2S concentrations in the aquifer water of different geothermal high-temperature fields, and therefore the concentrations in the steam of the producing wet-steam wells, are largely controlled by close approach to chemical equilibrium between these gases and hydrothermal mineral buffers.

The mineral buffer clinozoisite + prehnite + quartz + calcite is considered to control aquifer water CO_2 concentrations. At any particular temperature the equilibrium CO_2 concentrations show some variation due to variations in the chemical composition of clinozoisite, one of the mineral phases in the buffer controlling aqueous CO_2 concentrations. Higher activity (mole fraction) of clinozoisite in the epidote solid solution yields higher concentration of aqueous CO_2 at equilibrium.

It is not clear which mineral buffer may control H_2S aquifer water concentrations in some of the fields considered for the present study. For relatively dilute waters (Krafla), the controlling buffer is considered to be pyrite + pyrrhotite + prehnite + epidote. For waters of higher salinity (other areas considered), it may be the same buffer but having epidote of lower iron content or a mineral buffer reflecting a higher oxidation state, such as pyrite +magnetite + hematite. In the range 200-300°C, the equilibrium constants for the two buffers, just mentioned, are almost identical if an epidote activity of 0.25 is assumed for the epidote-bearing buffer. Both of them match reasonably well the data from Olkaria and Cerro Prieto but not so well those from Svartsengi, Kawerau and Broadlands.

The data on CO_2 and H_2S considered for the present study are based on samples taken at various times in the utilisation history of the geothermal fields in question. They do not reflect drastic deviation from equilibrium concentrations that could be caused by a long-term decline as a consequence of utilisation.

Carefully produced monitoring data are needed to map changes CO_2 and H_2S concentrations in producing aquifers of wet-steam wells. These data, together with data on the noble gases, are considered important for gaining understanding of the causes of possible changes, or constant values, in the reactive gas (CO_2 and H_2S) concentrations.

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