**Eruption dynamics of CO₂-driven cold-water geysers: Crystal, Tenmile geysers in Utah
and Chimayó geyser in New Mexico**

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Abstract

The CO₂ bubble volume fraction, eruption velocity, flash depth and mass emission of CO₂ were determined from multiple wellbore CO₂-driven cold-water geysers (Crystal and Tenmile geysers, in Utah and Chimayó geyser in New Mexico). At shallow depths the bubble volume fraction ranges from 0 to 0.8, eruption velocities range from 2 – 20 m/s and flash depths are predominately shallow ranging from 5 - 40 meters below the surface. Annual emission of CO₂ is estimated to be $(4.77 \pm 1.92) \times 10^3$, $(6.17 \pm 1.73) \times 10^1$, $(6.54 \pm 0.57) \times 10^1$ tonnes/yr for Crystal, Tenmile and Chimayó geysers, respectively. These estimates are coherent with Burnside et al. (2013) showing that the rate of CO₂ leakage from wellbores is greater than fault-parallel or diffuse CO₂ leakage. The geyser plumbing geometry consists of a vertical wellbore which allows for the upward migration of CO₂-rich fluids due to artesian conditions. The positive feedback system of a CO₂-driven eruption occurs within the well. Active inflow of CO₂ into the regional aquifers through faulted bedrock allows geysering to persist for decades. Crystal geyser erupts for over 24 hours at a time, highlighting the potential for a wellbore in a natural environment to reach relatively steady-state high velocity discharge. Mitigating high velocity CO₂-driven discharge from wellbores will, however, be easier than mitigating diffuse leakage from faults or into groundwater systems.

Key word: Geyser, CO₂-driven eruptions, Faults, Carbon sequestration, Wellbore leakage

1. Introduction

Thermally driven geysers, like Old Faithful in Yellowstone, are characterized by periodic eruptions of liquid water and steam (Kieffer, 1989; Nicholl et al., 1994). Conventional subsurface structures are composed of a long conduit connected to a large chamber at the base (Hurwitz et al., 2012; Hutchinson et al., 1997; Kieffer, 1989; Rinehart, 1980; Vandemeulebrouck et al., 2013). Heating of liquid water in the chamber combined with the non-convective properties of the conduit provide the rapid feedback process of an eruption (Rinehart, 1980). Another potential subsurface structure capable of producing periodic thermally driven eruptions was recently revealed by Belousov et al. (2013). Large porous structures trap steam until the pressure of steam within the trap is greater than that of the liquid water pressure in the conduit. When the eruption is initiated, the steam immediately releases into the conduit and buoyantly accelerates producing an eruption at the surface. Like thermally driven geysers, CO₂-driven cold-water geysers also have conduits as a necessary part of their structure. The conduit in the case of CO₂-driven geysers is typically a manmade wellbore (Glennon and Pfaff, 2005). Furthermore, although both cold and hot water geysers are driven by a gas expansion process, gas evolves differently in cold water geysers. Temperatures within CO₂-driven cold-water geysers always remain below the boiling point of liquid water. In CO₂-driven geysers, CO_{2(g)} evolves by the pressure reduction (flashing) of CO₂-rich fluids (Lu et al., 2005), not by boiling. Once the internal pressure of CO_{2(aq)} becomes greater than that of the surrounding fluid ($P_{\text{CO}_2} > P_{\text{fluid}}$), CO₂ exsolves causing bubbles to nucleate, grow and coalesce. Reduction of hydrostatic pressure resulting from increasing CO₂ bubble volume fraction within the wellbore enhances expansion of CO₂ bubbles while the conduit walls constrict lateral growth leading to the surface eruption.

Growing interest in geologic carbon storage has brought attention to CO₂-driven cold-water geysers because of its similarity to high velocity wellbore leakage processes (Gouveia et al., 2005; Jordan and Benson, 2009; Oldenburg, 2011; Shipton et al., 2004). Most studies on carbon storage have focused on large scale **diffuse** leakage through faults or the near surface (Allis et al., 2005; Burnside et al., 2013; Jung et al., 2014; Lewicki et al., 2003; Shipton et al., 2004). However, many studies emphasized that the leakage rate of CO₂ from naturally leaking sites is greatest through geysering wellbores (Bickle and Kampman, 2013; Burnside et al., 2013; Shipton et al., 2004). The abundance of wellbores in proposed or current storage facilities and the uncertainties surrounding the potential for wellbores to develop into geysers demands an analysis of naturally occurring CO₂-driven geysers (Celia et al., 2004; Friedmann, 2007). Therefore, this study provides *in-situ* measurements of pressure and temperature from three CO₂-driven cold-water geysers (Crystal and Tenmile geysers in Utah and Chimayó geyser in New Mexico) and elucidates the sequential processes of in-well CO_{2(g)} occupation, eruption velocity, CO₂ flashing depths and annual CO₂ emission rate. Finally, **a conceptual model and numerical simulation of the CO₂-driven geysering process is presented with implications to leakage of geologic carbon storage.**

2. Field Sites of CO₂-Driven Cold-Water Geysers

The sedimentary basins of Green River, Utah and Chimayó, New Mexico have become prominent field laboratories for CO₂ sequestration analogue studies due to the naturally leaking CO₂ through faults, springs and wellbores (Han et al., 2013; Heath et al., 2009; Kampman et al., 2009; Kampman et al., 2014; Keating et al., 2010; Shipton et al., 2005). Both Crystal and Tenmile geysers lie in the northern extent of the Paradox Basin near Green River, Utah (Fig.

1A). Carbonate travertine deposits overlie ancient CO₂ leakage points. U-Th age dating of travertine deposits in this region indicate that CO₂ has been leaking for at least 400,000 years where rates increased during periods of climatic warming (Burnside et al., 2013; Kampman et al., 2012). The CO₂ originated from thermal decomposition of marine carbonates, specifically the Mississippian Leadville Limestone (Kampman et al., 2009; Shipton et al., 2004). Brine and CO₂ migrate upward along the fault systems to enter the shallow groundwater systems. The emitted gas exceeds 95% CO₂ for all Green River springs and geysers with the remaining percentage composed of atmospheric gases N₂, O₂ and Ar (Heath et al., 2009). The isotopic $\delta^{13}\text{C}$ values of CO_{2(g)} range from -6.61 to -7.55 per mil for the springs and geysers in the Green River region inferring a shared origin (Heath et al., 2009; Kampman et al., 2009).

Crystal geyser is an abandoned oil exploration well (Glen Ruby#1-X) drilled during the mid-1930's along the north side of the east-west striking Little Grand Wash fault (Fig. 1A). The total depth of the well is ~800 m, only cased at the surface with a height of 1.73 m above the ground surface and diameter of 0.39 m. Tenmile geyser, also an abandoned oil exploration well, is located south-east of Crystal geyser on the hanging wall of the Salt Wash Graben (Fig. 1A). The depth is unknown; a 1 m high and 0.23 m diameter casing rests at the surface. Hydrogeologic conditions are artesian for both of these wells (Hood and Patterson, 1984) fed by the Navajo Sandstone and potentially other aquifers such as the Entrada Sandstone (Kampman et al., 2014).

Chimayó Geyser is located in Chimayó, New Mexico within the Espanola Basin (Fig. 1B). The bedrock consists predominately of sandstones cut by north-south trending faults. Chimayó geyser lies near the Roberts Fault and may cut directly through it. The source of CO₂ is unknown for the region. The setting is similar to that of Green River, Utah where CO₂-rich

brines migrate upward along faults (Keating et al., 2010). The regional aquifer supplying Chimayó geyser is semi-confined. The well was originally drilled in 1972 for residential water use but ended up tapping into a CO₂-rich water source and has geysered ever since. It has a diameter of 0.10 m, depth of 85 m and is cased with PVC for the entire depth.

Each geysering well was instrumented with a pair of Solinst Levellogger Edge 3001 transducers to record the periodic changes in *in situ* pressure and temperature (Supplementary Table 1). The transducers were attached to multiple 1.27 cm diameter PVC pipes connected to each other to prevent excessive vibration from the eruption activities (Fig. 1C). The transducer depths were selectively chosen due to accessibility (e.g., blockage of rocks within the well), and the measurement intervals were chosen between 10 to 60 seconds. Pressure and temperature measurements recorded by the transducers have an accuracy of ± 0.05 kPa and ± 0.05 °C, respectively. Temperature measurements have a resolution of 0.003 °C.

3. Previous Research Activities

The first research project on Crystal geyser was conducted in the 1970's with aims of preventing the geyser's saline waters from entering the Green River (Baer and Rigby, 1978). The first recording of the eruption periodicity by surficial measurements of pressure and temperature was conducted by Gouveia and Friedmann (2006) showing that Crystal geyser averaged 100 minutes of eruptive time per day and estimated the CO₂ emission to be 1.1×10^4 tonnes per year. Then Han et al. (2013) provided the first in-well measurements of pressure and temperature (14 and 6.5 m depth) revealing a consistent 6-part eruption cycle composed of minor and major eruptions and recharge periods. Unlike Crystal geyser, Tenmile geyser has received little attention due to its infrequent eruptions and difficult accessibility (Doelling, 1994; Ross, 1997).

Water sampling of Tenmile geyser by Heath et al. (2009) and Kampman et al. (2009) revealed similarities to the water of Crystal geyser and surrounding Green River springs.

4. Periodicity and Eruption Characteristics

4.1. Crystal Geyser: Measurements made in 2013

Extensive eruption characterization of Crystal geyser in 2010 can be found in Han et al. (2013). The *in situ* measurements of pressure and temperature recorded in 2010 are provided in Fig. 2A and 2B for comparison to 2013. Instrumentation in 2013 revealed a new eruption periodicity of 4 parts; minor eruption period (mEP), major eruption period (MEP), aftershock eruptions (Ae) and recharge (R) (Fig. 2C and 2D). The total cycle is much longer, averaging a length of 102.9 ± 5.1 hours. The mEP had a mean length of 40.6 ± 6.4 hours. Unlike the mEP in 2010, the period now begins with ~15 small-scale bubbling events lasting 5.5 ± 0.6 hours (D1 in Fig. 2D); the pressure reduction of individual bubbling events was less than 5 kPa. The individual eruptions during the mEP in 2013 are similar to those in 2010 with a length of ~9 minutes although eruption intensity has diminished; the eruption height is now ~1 m. The water level rises and falls at the beginning and the end of the minor eruption, respectively. Because the area surrounding the well is impermeable travertine, a portion of this water directly reenters the well. Due to water pooling during an eruption and then reentering the well afterwards, it is slightly warmed or cooled due to the current atmospheric temperature; seen in Fig. 2C where in-well temperature oscillates ~ 0.2 °C during the mEP.

The major eruption period (MEP) consists of a continuous and more intense eruption. Prior to the MEP, the discharge of liquid water from the well increases without degassing. Then, suddenly, large eruptions driven by $\text{CO}_{2(g)}$ slugs occur. Oscillations of pressure within the MEP

show the surges of both CO_{2(g)} and water which appear as strong and weak eruptions at the surface (Fig. 2D). The first 20-30 minutes of the MEP produce the highest erupting jets reaching a maximum height of 5 m in 2013; this can be seen in Fig. 2C and 2D where pressure dropped to 0.04 MPa at 6 m depth. The eruption continues discharging liquid water and CO₂ at heights of 1-3 m above the surface. Like the mEP, the MEP has also seen a significant increase in length averaging 27.3±0.5 hours in 2013. Temperature fluctuations follow the same pattern seen in 2010 with a sharp decrease from 17.4°C to 16.8°C (Han et al., 2013).

After water drains back into the well following the end of MEP, the aftershock eruption (Ae) period begins (D2 in Fig. 2D). This new eruption period was not observed in 2010 and is, essentially, the recharge period accompanied by eruptions only during the first few hours. Water is initially a few meters below the surface developing the minimum hydrostatic pressure condition and suddenly rises driven by CO₂ bubbles reaching the top of the well casing. The eruption lasts less than a minute initially and increases in length later. The first few Ae are of significantly greater intensity where later Ae are mild and predominately consist of the water level rising accompanied by minor CO₂ bubbling. Once the final Ae ends, recharge continues until the mEP begins.

The duration and intervals separating eruptions at Crystal geyser have shown considerable change over the 35 years of documentation (Fig. 3A and B). Similarly, Daisy Geyser and Old Faithful Geyser in Yellowstone National Park have shown variations diurnally, seasonally and annually (Hurwitz et al., 2014). Following nearby earthquakes, the intervals separating eruptions at Old Faithful Geyser increased. At Crystal geyser, the ratio of quiet time to eruptive time was 42:1 in 1978, decreasing to 7.5:1 in 2005 and 3:1 in 2013 corresponding to a continually decreasing vigor in eruptions (Baer and Rigby, 1978; Gouveia et al., 2005; Han et al.,

2013). The reason for continuous changes in periodicity and intensity is unknown but could be due to reported dynamiting of the well (Shipton et al., 2004), growing rock obstructions and nearby seismic activity (Han et al., 2013), local drilling projects producing large quantities of CO₂-charged fluids, interactions between source aquifers and fault-controlled delivery rates of CO₂ to the aquifers (Kampman et al., 2014). Additionally, the geysering periods in 2013 were correlated with barometric pressure and earth tides revealing no connection during the measurement period.

4.2. Tenmile Geyser: Measurements made in 2011 and 2013

In total, 18 and 62 eruptions were recorded in 2011 and 2013, respectively (Fig. 4A and C). Tenmile geyser has a 4-part eruption cycle (Fig. 4B) which has a relatively consistent eruption length of 11.2 ± 0.67 minutes. The interval between eruptions is comparatively more variable, averaging 8.5 ± 2.6 hours (minimum and maximum intervals were 4.2 and 18 hours, respectively) (Fig. 3B). Increased bubbling of CO₂ from the well initiates the initial MEP (Fig. 4B) emitting jets up to 2-3 m high for ~2 minutes. Then the eruption suddenly ceases and water rapidly drains back into the well (D in Fig. 4B). After D, the water level begins to rise accompanied by vigorous CO₂ bubbling. During this time, ascending CO_{2(g)} and liquid water only reach the casing top (1 m). The mEP ends with bubbling ceasing and water remaining at surface elevation, slowly rising until the next eruption (R in Fig. 4B).

Analysis of the temperature data over a longer time-scale shows a daily temperature fluctuation regime (Fig. 4C and D). Typically, three eruptions (though 2 and 4 eruption cycles are seen) occur during this period. The first eruption of this cycle produces the largest increase in

temperature (0.45 °C) (D1 in Fig. 4D). Then temperature decreases ~0.3 °C until the second eruption which elevates temperature ~0.2 °C (D2), followed by a 0.3 °C drop. Finally the third eruption produces an increase in temperature of 0.15 °C (D3). Following the third eruption the temperature reaches its minimum value, typically ~15.2 – 15.3 °C. The cycle then restarts with a sharp temperature increase as noted above. D1 and D3 approximately correspond to the warmest and coldest atmospheric temperatures during the daily cycle (Fig. 4D). Other than the correlation with in-well water temperature and atmospheric temperature, no correlations between external forces exist at Tenmile geyser.

4.3. Chimayó Geyser: Measurements made in 2008

Chimayó geyser has a simple 2-part eruption cycle consisting of an MEP and long recharge period (Fig. 5A and B). Eruption duration averages 7.8 ± 1.2 minutes (Fig. 3B) with plumes reaching a maximum height of 20 m. The eruption heights are greatest for this geyser predominately due to its small cross sectional area (78.5 cm^2) which drives preferential vertical volume expansion and further upward acceleration. Furthermore the water supply is limited due to the well casing which causes a more gas-dominated eruption. The mean recharge length and interval separating eruptions are 10.9 ± 1.2 hours and 20.4 ± 5.6 hours, respectively (Fig. 3B and 5B). Minor temperature decreases of ~0.1°C occur during the eruption and are followed by a 0.7°C increase over the course of recharge. No correlations exist between Chimayó geyser periodicity and external forces.

5. Methodology and Analyses

The eruption mechanism of a CO₂-driven geyser is a strongly positive feedback system; CO₂ exsolution, pressure decrease, bubble growth, and buoyant migration are all interconnected parts of the eruption process (Lu et al., 2005; Zhang, 1996). Here we determine the bubble volume fraction, flash depth, flow rate during eruptions and the eruption/annual CO₂ emission at each geyser.

5.1. Bubble Volume Fraction

As CO_{2(aq)} exsolves, it begins a buoyant ascent as bubbles grow. Gas occupation increases towards the surface from the flash point within the wellbore. The fractional occupation of CO_{2(g)} in brine (α) is predicted from *in situ* temporal pressure and temperature data measured by two transducers at different depths (Lu et al., 2005).

$$\alpha = 1 - \frac{\rho_m}{\rho_l} \quad (1)$$

$$\rho_m = \frac{P_1 - P_2}{gh} \quad (2)$$

Where α is the bubble volume fraction, ρ_m is the mean mixture (CO_{2(g)} and brine) density, and ρ_l is the brine (H₂O-NaCl) density. ρ_m is determined by the pressure difference over depth where P is pressure ($P_1 > P_2$), g is gravitational acceleration, and h is the distance between two transducers. For example, the α obtained from Chimayó geyser refers to the bubble volume fraction between transducers at depths of 30.5 and 32 m. ρ_l was calculated with the algorithm by Batzle and Wang (1992) using the measured concentration of NaCl in 2010; the NaCl molality was 0.1, 0.17 and 0.03 for Crystal, Tenmile and Chimayó geysers, respectively. The calculated mean and ranges of α are listed in Table 1. The transition from diffuse bubbling to Taylor

bubbles or gas slugs occurs at $\alpha \approx 0.25$ -0.28 (Lu et al., 2005). α greater than 0.25, and hence the formation of slugs, is what produces vigorous eruptions. Crystal geyser's mEP(A) and mEP(C) predicted α to be 0.11 between two transducers (6.5 m and 14 m), suggesting that the formation of slugs is somewhere above these depths. The MEP(B) and MEP(D) reached a maximum α of 0.73 with both averaging 0.22 throughout the eruption period; therefore slugs predominately form between transducers. Tenmile geyser has a peak α of 0.64 and a mean of 0.11 (11.5 and 20.5 m). Chimayó geyser (30.5 m and 32 m) can reach α to be 0.75 with a mean eruption value of 0.52. It is interpreted that the wells with small cross sectional area (Tenmile: 415 cm² and Chimayó: 78.5 cm²) prevent horizontal expansion of the emitting CO_{2(g)}, and thus, allow relatively small amounts of CO_{2(g)} to occupy the well rapidly and enhance vertical acceleration.

5.2. Eruption Velocity

The change in enthalpy over a given depth has been used to determine the eruption velocity for hot water geysers and volcanoes (Karlstrom et al., 2013; Kieffer, 1989; Mastin, 1995). Even if temperature plays a large role in the solubility of CO₂ in water, the small change in observed temperature over depth at each of the geysers infers that it plays a minor role for the CO₂ degassing process during an eruption cycle (i.e. pressure change plays a much larger role). In this work, assuming that the CO₂ flow is compressible and soluble, Bernoulli's equation is most suitable for determining eruption velocities of CO₂-driven geysers. Assuming the Ostwald solubility coefficient of CO₂ (λ) is roughly independent of pressure, Zhang (1996) derived the equation of state for CO₂-liquid water mixtures ($\rho_f / \rho \approx 1 + \lambda P_f / P - \lambda$). Furthermore, using

Bernoulli's equation (eq. 3), Zhang (1996) predicted the erupting fluid velocity caused by degassing of CO₂-saturated lake bottom waters at Lake Nyos.

$$\int_{P_f}^{P_i} \frac{dP}{\rho} + \int_{v_f}^{v_i=0} v dv + \int_{z_f}^{z_i} g dh = 0. \quad (3)$$

Where P is pressure, ρ is the liquid density, v is the eruption velocity, g is gravitational acceleration, and h is a subsurface depth. Subscript *i* and *f* indicate the flash depth and surface conditions, respectively. The pressure gradient for application in Eq. 3 was developed by using the mean value over the eruption period. Fig. 6A shows the input parameters of temperature and pressure over depth. The temperature gradient for Crystal and Tenmile geysers (21.2 °C/km) was obtained from Heath et al. (2009) and the recorded temperature gradient (36 °C/km) between transducers was used for Chimayó geyser. The solubility of CO₂, shown in Fig. 6B, was then determined based upon the concentration of NaCl, mean pressure and temperature during eruptions using the algorithms developed by Duan and Sun (2003). Then the density profile of the NaCl-CO₂-H₂O fluid shown in Fig. 6B was determined using Duan et al. (2008). A second order polynomial equation showing the functional relationship between the density and pressure of each geyser is shown in Supplementary Table 2 for use in Eq. 3. By solving Eq. 3 with the predicted mixture density (ρ) profiles, the relationship between eruption velocity (v_f) at the surface and the depth (h) at which an eruption initiates was determined (Fig. 6C). The eruption velocity of each geyser is predicted from a visual estimate of eruption height (*H*) and the ballistic equation ($v_f = \sqrt{2gH}$). Karlstrom et al. (2013) utilized particle image velocimetry (PIV) along with the ballistic equation to determine the eruption velocity at Lone Star geyser, Yellowstone National Park. Comparison of these methods suggested that PIV and ballistic methods provided upper and lower bounds for the exit velocity, respectively. Only when the eruption was steam

dominated did the ballistic equation overestimate the velocity. Such gas dominated eruption periods do not exist for the geysers studied here. Finally, the flash depth (h) was predicted by constraining the exit velocity with the observed minimum and maximum eruption height (H); the observed H is shown in Table 1.

Estimates and ranges of the flash depth are shown in Fig. 6C. The mEP(A/C) at Crystal geyser reach mean heights of 1 m with a v of 4.4 m/s, revealing that eruptions initiate, on average, 9 m below the surface. Maximum eruption heights of 8 m occur during the MEP(B/D) equating to a maximum v of 12.5 m/s. In most cases, eruptions predominately reach heights of 2-5 m with a corresponding v of 6-10 m/s. Therefore the flash depth has a wide range (10 to 35 m) but typically initiates around a 20 m depth. The eruptions at Tenmile geyser reach a maximum height of 3 m resulting in a v of 7.7 m/s. The flash depth required to produce plumes that height would be 25 m below the surface while the mild eruption could initiate at 9 m. The eruptions at Chimayó geyser (16-20 m) initiate at a depth 31 to 40 m below the surface. We expect that imperfections in conduit geometry, fractures enhancing lateral expansion of $\text{CO}_{2(g)}$ and friction caused by well-filling rocks (except Chimayó geyser, which is cased with PVC) could cause an error in the estimation of the velocity over depth and, subsequently, the estimation of flash depth.

5.3. Mass Emission

Using the mean bubble volume fraction, eruption velocity and eruption period, the mass of $\text{CO}_{2(g)}$ emitted was determined with eq. 4.

$$m_{\text{CO}_2} = (\alpha A_w) \rho v \Delta t \quad (4)$$

322 where m_{CO_2} is the mass of CO_2 , α is the mean bubble volume fraction, v is mean eruption
 323 velocity, ρ is the density of $CO_{2(g)}$, A_w is the cross sectional area of the well and Δt is the mean
 324 time length of the eruption. Thus the equation is set to determine the net mass of $CO_{2(g)}$ that has
 325 passed between transducers and does not account for CO_2 exsolution shallower than this point.
 326 The density (ρ) of $CO_{2(g)}$ flowing through the measurement point (mid-point between
 327 transducers) was determined from the mean pressure and temperature during an eruption using
 328 Span and Wagner (1996). The times used are the mean eruption length (Δt); annual estimates are
 329 made with the subsequent mean amount of eruptions per year. The estimate for Crystal geyser is
 330 based on the eruption data recorded in 2010. As a whole, all eruptions from Crystal geyser are
 331 estimated to emit $(4.77 \pm 1.92) \times 10^3$ tonnes annually. The annual CO_2 emission determined by
 332 Gouveia et al. (2005) was 1.1×10^4 tonnes where they used a down-wind grid of Gray box
 333 samplers to measure the CO_2 concentration in the air. The estimate of CO_2 discharge rate during
 334 single minor eruptions are very similar at 1.7×10^{-1} kg/s and 1.9×10^{-1} kg/s for Gouveia et al.
 335 (2005) and this study, respectively (minor eruptions were referred to as “pre-eruptive events” in
 336 Gouveia et al. (2005)). The primary discrepancy between annual estimates is likely explained by
 337 the increase in eruption interval since the measurements by Gouveia and Friedmann (2006) (Fig.
 338 3A) and that CO_2 detected by their instruments will have come not only from the geyser but
 339 surrounding springs and diffuse flux from the ground. As revealed by Burnside et al. (2013) and
 340 Jung et al. (2014), significant amounts of diffuse CO_2 gas leaks through the Little Grand Wash
 341 fault traces. For example, Jung et al. (2014) measured $CO_{2(g)}$ flux of $36 \text{ kg/m}^2/\text{day}$ adjacent to
 342 Crystal geyser in 2013 which would accumulate in $1.3 \times 10^4 \text{ kg/m}^2/\text{yr}$. Furthermore, the growing
 343 blockages within the well presumably act in a manner to retard bubble growth and acceleration,
 344 diminishing the net release of $CO_{2(g)}$. Thus this estimate of CO_2 emitted is more accurate of

Crystal geyser's present state. Tenmile and Chimayó geysers emit $(5.63 \pm 1.58) \times 10^1$ kg and $(1.58 \pm 0.14) \times 10^2$ kg of CO₂ for an eruption accumulating in $(6.17 \pm 1.73) \times 10^1$ tonnes and $(6.54 \pm 0.57) \times 10^1$ tonnes annually, respectively. The reason for much higher estimates at Crystal geyser is that it not only discharges greater volumes of CO₂ per eruption but also the ratio of eruptive time to quiet time (Crystal: 0.33, Tenmile: 0.02, and Chimayó: 0.01) is 17-50 times larger (Fig. 3A).

6. Discussion and Conclusion

6.1. Geyser Eruption Mechanism

Based on the observation of three cold-water geysers, a further insight is obtained after the studies of Lu et al. (2006) and Han et al. (2013). A conceptual model is presented in Fig. 7 to illustrate the eruption mechanism that initiates by an in-well CO₂-degassing feedback process. Initially, the artesian condition ($P_{\text{formation}} > P_{\text{hydrostatic}}$) causes CO₂-rich fluids to continually migrate upwards from the bottom (T1 in Fig. 7). Such reasoning can be supported by field observations of continuously increasing water level in between eruptions. Additionally, Kampman et al. (2014) observed that the primary aquifers supplying Crystal and Tenmile geysers (e.g., Entrada and Navajo Sandstones) have formation overpressures ranging from 0–1.3 MPa, while Keating et al. (2013) observed that the aquifers supplying Chimayó geyser are also heterogeneously over-pressured. The simulations conducted by Lu et al. (2006), Pruess (2008) and Pan et al. (2011) for CO₂-H₂O leakage through a wellbore also revealed that eruptions are initiated by large pressure differences between the formation and well. Formation permeability will be one of the primary factors governing the supply rate of CO₂-rich water and subsequently the interval between two separate eruptions. Simulations by Ingebritsen and Rojstaczer (1993)

for geothermal geysers indicated that increasing formation permeability would reduce the duration of an interval as the recharging process to the conduit is faster. In contrast, Chimayó geyser has long eruption intervals (20.4 ± 5.6 hours) (Fig. 3B) because it's wellbore is fully cased and thus slows down the recharge process. The predicted flow rate of water into the well is denoted by the length of arrows in Fig. 7.

As shown in T1 of Fig. 7, prior to eruptions all of the geysers reach the overflow point of the well head. No eruptions or degassing will occur until CO_2 becomes supersaturated in the water. Pressure reduction due to the upward migration of CO_2 -rich fluids will initiate exsolution. The flash depth (FD) marks the point where $\text{CO}_{2(\text{aq})}$ initially begins to exsolve. Above the FD, the exsolved CO_2 bubbles migrate upwards due to buoyancy forces that depend on the density difference of liquid water and $\text{CO}_{2(\text{g})}$. Then the upwardly migrating CO_2 bubbles will reach terminal velocity (10-20 cm/s) when the drag and viscous forces are equal to the buoyant forces (Bozzano and Dente, 2001) (T2 in Fig. 7). The geyser eruptions take place as CO_2 bubbles continue to form by reducing the hydrostatic pressure, and consequently the FD deepens (from the surface) within the well. CO_2 bubble amalgamation will cause a rapid change in the internal pressure and shape of bubbles which subsequently alters the inertia, velocity and mass transfer in the bubbles (Lu et al., 2006). When the bubble volume fraction reaches ~ 0.25 gas slugs or Taylor bubbles will form due to bubble coalescence (Lu et al., 2005) (T3 in Fig. 7). Taylor bubbles are large cylindrical bubbles which occupy the entire cross section of the well with rounded heads and flat sterns (bullet-shaped) with respect to the direction of motion. Recirculation within slugs will enhance heat and mass transfer at the liquid-gas interface (Salman et al., 2006) (Arrows inside slug in T3). The slugs will effectively push parcels of water upwards, developing liquid “slugs” in between, and create vigorous eruptions as observed in the three geysers discussed in

this study. The development of $\text{CO}_{2(g)}$ or liquid slugs in the well is what causes the pulsing or surging eruptions seen. Once the eruption height reaches the maximum, the bubble volume fraction and flash depth will also reach their respective maximum accordingly (T3 in Fig. 7). Due to excessive degassing, eruptions will cease once the $\text{CO}_{2(aq)}$ concentration has reached a critical minimum, waiting for completion of another recharge (T4 in Fig. 7). Such combined processes of a CO_2 -driven eruption exhibit self-enhancing and self-limiting characteristics and result in the periodic eruption scenarios observed.

The MEP at Crystal geyser is a continuous eruption period (currently lasting ~27 hours) as shown in Fig. 2D. This type of eruption does not fit the proposed conceptual model addressed above because, if it is generated by an in-well degassing process, the supply of $\text{CO}_{2(aq)}$ takes a considerably longer time to deplete compared to the preceding minor eruptions. Postulating a scenario where the supply of CO_2 -rich water is suddenly much greater and continuous is difficult. Additionally, the revelations by Belousov et al. (2013) and Vandemeulebrouck et al. (2013) in hot water geysers have shown that periodic discharge of gas accumulations can drive eruptions. The discrepancy between the eruptions of the mEP and MEP at Crystal geyser therefore suggests that the MEP must be driven by an accumulation of compressible $\text{CO}_{2(g)}$ from the sourcing aquifers where the FD horizontally extends into the aquifer (T3' in Fig. 7). Periodic discharge of water and CO_2 during the mEP leads to a progressive decrease in the pressure of the supplying formations. Then, this decreasing pressure condition enables $\text{CO}_{2(g)}$ to form and accumulate within the aquifers. Fracture networks in damaged zones, which might cross the well of Crystal geyser, could provide highly permeable pockets for gas accumulation. Once the pressure of the $\text{CO}_{2(g)}$ accumulation has reached the critical threshold, it will begin to discharge into the well. Further evidence of a gas accumulation driving the MEP is provided by

observations just prior to the MEP where the discharge of liquid water (unaccompanied by $\text{CO}_{2(g)}$) rapidly increases for a few minutes followed by large gas bursts. Presumably, the discharging gas slugs from depth push a large column of water up and out of the well. Kampman et al. (2014) found that rapid changes in emanating fluid temperatures and chemistry coincide with the onset of the MEP, suggesting that accumulation of gas occurs somewhere within the Entrada Sandstone formation (0-150 meters below the surface), which is shallower than the Navajo formation considered as the source aquifer of mEP.

6.2. Numerical Simulation of CO_2 -Driven Cold-Water Geysers

In this section a 1-D non-isothermal multiphase pipe flow model is formulated to simulate the CO_2 -driven geyser eruptions. The simulations based on this model may provide, at least qualitatively, further details about geyser eruption scenarios and a better understanding of the proposed conceptual model presented in the previous section. As an example, the parameters for Chimayó Geyser are used (Table 2) since the fluid-flowing profile in the cased wellbore can typically be described by pipe flow. Exact replication of the eruption periodicity is beyond the scope of this model; more so it is utilized to demonstrate how the thermo-physical properties of CO_2 - H_2O mixtures affect the development of the flashing depth, CO_2 bubble volume fraction and eruption velocity. Details and discussions about this numerical model are given in Appendix A.

Fig. 8A presents the simulated relationships between the flash depth, CO_2 bubble volume fraction, and mixture velocity profiles with the inlet velocity at 100 m depth varying from 1 m/s to 2 m/s. The profiles can be considered as snapshots of the in-well dynamics during an eruption. The flash depth can be identified by the CO_2 bubble volume fraction when it deviates from 0.

Phase transition occurs at this depth where the pure liquid state of the mixture turns to two-phase with the presence of $\text{CO}_{2(g)}$. This transition causes a sharp increase in the mixture velocity where the acceleration is greatest immediately above the flash depth. It can be seen from Fig. 8A that lower inlet velocities result in shallower flash depths and lead to smaller gaseous CO_2 volume fraction and smaller exit velocities at the surface. We may take the profile with 1 m/s inlet velocity to be a representative of T2 in Fig. 7. With this, the hydrostatic pressure decreases constantly as the CO_2 continues to degas above the flashing depth. Beyond T2, the decreasing flash depth and increasing CO_2 bubble volume fraction enhance the velocity of both the mixture and inlet. Fig. 8A also shows that when the flash depth reaches the deepest level, the exit velocity reaches the highest, as illustrated in T3 in Fig. 7. It is noted that while the inlet velocity here is treated to be an input parameter, in a natural CO_2 -driven geyser it will be governed by the self-enhancing and limiting processes of an eruption such as bubble growth and pressure decrease.

The temperature profiles of the mixture ($\text{CO}_2\text{-H}_2\text{O}$) were investigated to understand the degree of thermal alteration resulting from the CO_2 degassing and thermal conduction effect (Fig. 8B). As a reference, Fig. 8B also presents the temperature profiles of pure liquid water where no degassing effect is involved. For this pure liquid water, the effect of thermal conduction on the water is greatest with the slowest flow rate (1 m/s). It is shown that when the water, initially at 15.85 °C, migrates from 100 m depth to the surface, its temperature would drop around 0.5°C. This is because the fluid is warmer than its geological surroundings (at the bottom the fluid was set to be at a thermal equilibrium state with its surroundings); when it moves upwards along the wellbore, the slower the fluid flows, the more heat it loses. In contrast, for the fastest moving liquid water (e.g., 2 m/s) the temperature only drops about 0.3°C because it loses

less heat to the surroundings. This trend is also retained for a mixture of H₂O and CO₂ before reaching the flashing depth, as shown in Fig. 8B. After the flash depth (10 to 15 m), rapid reduction of temperature occurs because generation and growth of CO₂ bubbles are accompanied by the endothermic effect of CO₂ exsolution and Joule-Thomson cooling. The range of temperature reduction was approximately 1-2°C in this example. Validation of the temperature changes simulated within a geysering wellbore by field measurements has yet to be conducted as it requires a multitude of measurement points during a single monitoring period. This warrants the merit of a further study as it could provide another relationship between the CO₂-driven eruptive behavior and its relevant thermal changes.

6.3. Geysering Wellbores in Carbon Capture and Storage Facilities

As proposed by the conceptual model in Fig. 7, a typical wellbore configuration would provide the conduit geometry required for eruptions. The hydrologic setting of the geysers studied here would be analogous to a Carbon Capture Storage (CCS) site where stored CO₂ has leaked into a shallow aquifer. At a CCS site, an intruding CO₂ plume could provide the overpressures required to drive CO₂-rich fluids upwards or cause supersaturation of CO₂ at the formation depth (Pruess, 2008). The historical accounts and analysis of the wellbore geysers show that eruptions can be fueled for decades and possibly centuries but whether the periodicity and intensity will change over time is difficult to discern (Fig. 3). The MEP at Crystal geyser highlights the potential for a wellbore to develop into continuous leakage. Though we propose that to sustain such a long eruption period, the proper geometry or traps must exist at depth to allow for the accumulation of CO_{2(g)}. Additionally, because Crystal geyser is not cased, it has a surface area of 289.8 m² in contact with CO₂-rich water bearing units (Entrada and Navajo

Sandstone) which help sustain discharge for over 24 hours. Chimayó geyser most accurately represents the eruptions that would be seen at a CCS site primarily due to having a casing which will limit the supply of H₂O-CO₂ and duration of eruptions.

As evidenced by the large difference in emission of CO₂ from the presented geysers, the degree of leakage will be dependent upon the casing condition, length and diameter of wells, the CO₂-saturation of fluids, sourcing aquifer conditions (pressure and temperature) and, especially, the ratio of eruptive to quiet time. Thus understanding the hydrologic properties of rock units in which wells are screened could provide valuable data for determining the risk for eruptions to occur and be sustained for long periods of time. The emission of CO₂ from Tenmile and Chimayó geysers ((6.17±1.73)×10¹ t/yr and (6.54±0.57)×10¹ t/yr) are comparable to that of slowly forming travertine deposits (Burnside et al., 2013). As determined by Burnside et al. (2013), travertine mounds along the Little Grand Wash and Salt Wash fault systems had deposition rates ranging (0.10-8.71)×10² t/yr and (0.20-8.00)×10¹ t/yr of CO₂, respectively. The rate of deposition (8.71×10² t/yr) from largest travertine mound analyzed by Burnside et al. (2013), L4, exceeds that of Tenmile and Chimayó geyser but is over a much larger area. Thus, even small CO₂-driven geysers like Tenmile or Chimayó geyser that have small eruptive to quiet period ratios present, on a spatial scale, the sources of most rapid leakage. While the discharge of CO₂ from geysering wells has been shown to reach significant rates, the conditions which allow geysering to occur are fleeting and will not be sustained like travertine deposition or fault zone CO_{2(g)} flux. Furthermore, CO₂-driven geysers are surficial expressions of leakage already occurring in the subsurface; a very difficult problem to mitigate. Thus, while wellbores which develop into CO₂-driven geysers have the potential to reach significant leakage rates, they still present a smaller risk due to being point specific and easily identifiable phenomena.

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Appendix. A Non-isothermal Flow Model for CO₂-Driven Cold-Water Geysers

1. Basic Assumptions

- a) It is assumed that the fluid in the cold geyser is a mixture of water and carbon dioxide. Namely, only water (H₂O) and carbon dioxide (CO₂) are present there and other fluid species (e.g., other gases), if any, are not considered.
- b) It is assumed that in this fluid mixture CO₂ can dissolve in water, but water does not dissolve in CO₂. This assumption can be justified because the latter process is significantly smaller in comparison with the former one in the range of temperature (10~20 °C) and pressure (0.1 ~ 2 MPa) concerned in this study.
- c) The content of CO₂ in this mixture is small, i.e., its mole (or mass) fraction is significantly less than 1 (while its volume fraction can be very large because the density of the gaseous CO₂ is much smaller than that of water).
- d) Flow is one-dimensional (in well).
- e) Strictly, when gaseous CO₂ is present in the mixture, the pertinent gas-phase velocity is distinct from its liquid-phase counterpart because of the buoyancy effect. However, in this study we will neglect the slip effect between the two velocities, and use the routine homogeneous model, which assumes that the two-phase mixture moves in the mean velocity without slip effect. A further discussion on this issue is given in “drift-flux model” in Section 4 of this Appendix.

2. Flow Equations

The general flow equations can be found in Malekzadeh et al (2012) and Lu and Connell (2014). The flow equations given below are expressed with the homogeneous model addressed-above [Assumption (e)]. It is noted that S.I. units are used throughout the text unless stated otherwise.

Mass balance equation

$$\frac{\partial \rho_m}{\partial t} + \frac{\partial}{\partial x}(\rho_m v_m) = 0 \quad (\text{A-1})$$

Momentum balance equation

$$\frac{\partial}{\partial t}(\rho_m v_m) + \frac{\partial}{\partial x}(\rho_m v_m^2) + \frac{\partial p}{\partial x} = -\rho_m g \sin \theta - f_m \frac{\rho_m v_m^2}{4R_w} \quad (\text{A-2})$$

In Eqs. (A-1) and (A-2), t represents time and x denotes the one-dimensional coordinate along the length or depth of the well, with upwards positive and the inlet (the bottom hole of the geyser) set to be the origin; ρ_m denote the density of the mixture, which can be further described by $\rho_m = f_L \rho_L + (1 - f_L) \rho_G$

, where f_L is the liquid volume fraction, ρ_L and ρ_G the density of water and CO₂, respectively. In Eqs. (A-1) and (A-2), v_m represents the average velocity of the mixture and p the pressure; f_m is the frictional coefficient of the fluid, θ the inclination angle of the well, and R_w the radius of the well.

Energy balance equation

$$\frac{\partial h_m}{\partial t} + v_m \frac{\partial h_m}{\partial x} + v_m \left(\frac{\partial v_m}{\partial t} + v_m \frac{\partial v_m}{\partial x} \right) - \frac{1}{\rho_m} \frac{\partial p}{\partial t} = -v_m \rho_m \sin \theta - \frac{q(T, x)}{\pi R_w^2 v_m}. \quad (\text{A-3})$$

Here, h_m denotes the specific enthalpy of the mixture, q characterizes the thermal exchange between the fluid and its surroundings, which will be further discussed in Section 4 of this Appendix.

To obtain the energy balance equation for this CO₂-H₂O system, one can formally let the enthalpy of the mixture h_m be expressed by

$$h_m = h_m(h_L, h_G; \lambda_d). \quad (\text{A-4})$$

Here, h_L and h_G is the specific enthalpy for H₂O and CO₂, respectively, λ_d is the mole fraction of CO₂ dissolved in the mixture.

Expanding Eq. (A-4) with respect to λ_d into a Taylor series, one finds

$$h_m = h_m(h_L, h_G; \lambda_d = 0) + \left. \frac{\partial h_m}{\partial \lambda_d} \right|_{\lambda_d=0} \lambda_d \quad (\text{A-5})$$

with a first order approximation, where $\lambda_d \ll 1$ (Assumption-c). Clearly, $h_m(h_L, h_G; \lambda_d = 0)$ means no dissolution of CO₂ into water, and in this case for the immiscible system it can be expressed by $h_m(h_L, h_G; \lambda_d = 0) = z_L h_L + z_G h_G$, where z_L and z_G stand for the mole fraction of water and carbon dioxide, respectively; Clearly, $z_L + z_G = 1$. $\partial h_m / \partial \lambda_d$ in Eq. (A-5), denoted by Δh_s here, is actually the dissolution heat of CO₂ in water. Then, Eq. (A-5) can be described by

$$h_m = z_L h_L + z_G h_G + \Delta h_s \cdot \lambda_d. \quad (\text{A-6})$$

Eq. (A-6) can also be expressed by the mass-based counterpart, and in that case, z_L , z_G and λ_d are the corresponding mass fractions.

Differentiating Eq. (A-6) one obtains $dh_m = z_L dh_L + z_G dh_G + \Delta h_s \cdot d\lambda_d + \lambda_d \cdot d\Delta h_s$, while $dh_k = C_{pk} dT - \eta_k C_{pk} dp$, ($k = L, G$). Here, C_{pk} ($k = L, G$) are the heat capacities at constant pressure for

water and carbon dioxide, respectively, and η_k ($k = L, G$) the pertinent Joule-Thomson coefficients of them. Substitution of these equations into Eq. (A-3) yields

$$\Gamma_m \frac{\partial T}{\partial t} + v_m \Gamma_m \frac{\partial T}{\partial x} - \Lambda_m \frac{\partial p}{\partial t} - v_m \Lambda_m \frac{\partial p}{\partial x} + v_m \frac{\partial v_m}{\partial t} + v_m^2 \frac{\partial v_m}{\partial x} = -v_m g \sin \theta \quad (\text{A-7})$$

Here, $\Gamma_m = C_{pm} + \lambda_d (\partial \Delta h_s / \partial T) + \Delta h_s (\partial \lambda_d / \partial T)$ and $\Lambda_m = \beta_m + \lambda_d (\partial \Delta h_s / \partial p) + \Delta h_s (\partial \lambda_d / \partial p)$,

while $C_{pm} = z_L C_{pL} + z_G C_{pG}$ and $\beta_m = z_L C_{pL} \eta_L + z_G C_{pG} \eta_G$.

It is noted that the dissolution (exsolution) heat, Δh_s , is usually determined by a single state argument, either by temperature or by pressure merely. Thus one has either $\partial \Delta h_s / \partial p = 0$ or $\partial \Delta h_s / \partial T = 0$ accordingly.

3. Equations of State (EoS)

a) *For water*

$$\frac{d\rho_L}{dp} = \chi_L (\rho_L - \rho_{L,0}). \quad (\text{A-8})$$

Here, χ_L is the compressibility of the water and $\rho_{L,0}$ represents the density of water at a reference state.

b) *For carbon dioxide*

We use the Peng-Robinson equation of state to describe the *PVT*-behavior of carbon dioxide. Details of this equation of state can be found in the original work of Peng and Robinson (1976) or Annamalai and Puri, (2002).

4. Supplementary Relationships

a) *Drift-flux model*

The flow equations described by Eqs. (A-1) to (A-3) are based on the homogeneous model [Assumption-(e) in Section 1 of this Appendix]. Theoretically, since the gas and liquid phase velocities are distinct, one needs to incorporate a drift-flux model (Zuber and Findlay, 1965) into the pertinent flow equations, where two velocities for gas and liquid phases are involved (e.g., Malekzadeh et al, 2012). However, as discussed in Lu and Connell (2014), introducing a drift flux model (e.g., Shi et al, 2005) would lead to mathematical discontinuity or singularity at transition borders of flow patterns or when the liquid volume fraction approaches zero. Therefore, a simplified, decoupled procedure is presented here to estimate the drift-flux effect, which is addressed below.

i) First, the flow equations described by Eqs. (A-1) to (A-3) [equivalently, by Eq. (A-7)] are solved, which allows one to obtain the average velocity of the bubbly flow and the liquid volume fraction.

ii) Then, the relationship between the superficial gas velocity (v_{sg}) and the average velocity v_m (e.g. Hasan and Kabir, 2002)

$$f_L = 1 - \frac{v_{sg}}{C_0 v_m + v_\infty} \quad (\text{A-9})$$

is used to evaluate the superficial gas velocity as f_L and v_m are known. Here, C_0 and v_∞ are two empirical constants.

b) *Dissolution (exsolution) heat of CO₂ in (from) water*

The equation given in Carroll et al (1991) is used, which is

$$\Delta_{\sin} H (\equiv \Delta h_s) = 106.56 - 6.2634 \times 10^4 \times \frac{1}{T} + 7.475 \times 10^6 \times \frac{1}{T^2} \quad (\text{A-10})$$

c) *Dissolution law of CO₂*

$$x_{CO_2} = H(T) p \quad \text{or} \quad x_{CO_2} = p / P_{CO_2}^{Sat}(T) \quad (\text{A-11})$$

Here, x_{CO_2} is the mole fraction of CO₂ dissolved in water, $H(T)$ the Henry coefficient, and $P_{CO_2}^{Sat}(T)$ denotes the saturation pressure curve of CO₂.

d) *Mass balance between components*

Let $n = n_L + n_G$, where n is the total mole number of the system, n_L the mole number of the liquid phase and n_G the mole number of gas phase; let $\lambda = n_L / (n_L + n_G)$ denote the mole fraction of liquid in the liquid-gas system. Then, from the mass balance of components one has

$$(1 - \lambda) y_{H_2O} + \lambda x_{H_2O} = z_L (= z_{H_2O}^0), \quad (\text{A-12})$$

$$(1 - \lambda) y_{CO_2} + \lambda x_{CO_2} = z_G (= z_{CO_2}^0). \quad (\text{A-13})$$

Here, x_{H_2O} and x_{CO_2} are the mole fraction of water and carbon dioxide in liquid phase, while y_{H_2O} and y_{CO_2} are their counterparts in gas phase, respectively. In Eqs. (A-12) and (A-13), $z_{H_2O}^0$ and $z_{CO_2}^0$ are the initial mole fraction of water and carbon dioxide, respectively.

e) *Determination of mole fraction of liquid λ*

According to *Assumption- b* addressed previously, one has

$$y_{H_2O} \equiv 0 \text{ (H}_2\text{O does not dissolve in CO}_2\text{)} \quad (\text{A-14})$$

and

$$y_{H_2O} \equiv 0 \text{ (gas phase is entirely composed of CO}_2\text{)} \quad (\text{A-15})$$

Substitution of Eqs. (A-14) and (A-15) into Eqs. (A-12) and (A-13) gives

$$\lambda x_{H_2O} = z_{H_2O}^0 \quad (\text{A-16})$$

and

$$(1-\lambda) + \lambda x_{CO_2} = z_{CO_2}^0 \quad (\text{A-17})$$

With Eq. (A-11) one finds

$$\lambda = \left(1 - z_{CO_2}^0\right) / \left\{1 - \left[p / P_{CO_2}^{Sat}(T)\right]\right\} \quad (\text{A-18})$$

Also, one can obtain

$$x_{H_2O} = z_{H_2O}^0 \left\{1 - \left[p / P_{CO_2}^{Sat}(T)\right]\right\} / \left(1 - z_{CO_2}^0\right) \quad (\text{A-19})$$

f) *Relationship between gas mass fraction x_{massG} and λ*

Let $m = m_L + m_G$, where m is the total mass of the system, m_L the mass of the liquid phase and m_G the mass of gas phase; let $x_{massG} = m_G / (m_L + m_G)$ denote the gas mass fraction in the liquid-gas system. One can then have

$$x_{massG} = \left[w_{CO_2}(1-\lambda)\right] / \left(z_{CO_2}^0 w_{CO_2} + z_{H_2O}^0 w_{H_2O}\right) \quad (\text{A-20})$$

Here, w_{CO_2} and w_{H_2O} is the molecular weight of carbon dioxide and water, respectively.

g) *Thermal exchange effect q*

The thermal exchange effect between a flowing fluid and its surroundings, namely, the heat flux term q in the relevant energy equation, may play a significant role in determining flow scenarios in wellbores. The simplest approach to its evaluation is based on the steady heat conduction model (e.g., Willhite, 1967; Hasan and Kabir, 2002), which can be expressed by $q = -2\pi R_{wto} U_{to} (T_f - T_{wb})$, where R_{wto} is the tubing outside radius, U_{to} is the overall heat transfer coefficient, T_f is the local temperature of the fluid,

and T_{wb} is the temperature at the wellbore formation interface (e.g., see Hasan and Kabir, 2002 for details).

5. Initial and Boundary Conditions

a) Initial Conditions

We use the solution for steady flow to be the initial condition. That is, simply letting $\partial(g)/\partial t \equiv 0$ in Eqs. (A-1), (A-2), and (A-7) and then solving the pertinent flow equations with a specific geothermal gradient, one may obtain the solution for the steady flow required.

b) Boundary Condition

The boundary flow condition is specified at the inlet of the well, i.e., at the bottomhole of the well. We assume that the fluid in the subsurface is approximately under an isenthalpic condition. Then, the variation of temperature of the fluid there can be related to pressure through

$$\left. \frac{dp}{dT} \right|_{\text{at bottomhole}} \equiv \frac{dp_{wb}}{dT_{wb}} = \frac{1}{\bar{\eta}_m} \quad (\text{A-21})$$

Here, $\bar{\eta}_m$ denotes the effective Joule-Thomson coefficient of the H₂O-CO₂ mixture.

Suppose that the temperature of the fluid in the subsurface is perturbed (e.g., a warmer fluid coming in from deeper places), so that

$$T_{wb} = T_{wb}^0 + \delta T_{wb}(t), \quad (\text{A-22})$$

Then pressure will also be perturbed accordingly. According to Eq. (A-21), we may (approximately) have

$$p_{wb}(t) \approx p_{wb}^0 + \frac{1}{\bar{\eta}_m} \delta T_{wb}(t) \quad (\text{A-23})$$

Here, p_{wb}^0 and T_{wb}^0 is the unperturbed pressure and temperature of the fluid, respectively.

Accordingly, the perturbed velocity of fluid can be estimated in terms of

$$v_{m,wb}(t) = v_{m,wb}^0 + \frac{1}{\pi R_w^2 \bar{\eta}_m} P_{idx} \cdot \delta T_{wb}(t) \quad (\text{A-24})$$

where $v_{m,wb}^0$ is the unperturbed velocity of fluid, and P_{idx} is the productivity index of the wellbore.

Figure Captions

Fig. 1. Map of Green River, Utah and Chimayó, New Mexico. (A) The location of Crystal and Tenmile geysers (red dots) in Utah and (B) the location of Chimayó geyser in New Mexico. Faults are shown as red lines. Utah and New Mexico maps are modified from Kampman et al. (2009) and Keating et al. (2010), respectively. (C) Schematic diagram of well configuration and transducer installation.

Fig. 2. Variations of in situ pressure and temperature at Crystal geyser in (A) 2010 and (C) 2013. (B) and (D) Variations of pressure and temperature during a single eruption cycle from the blue highlighted region in (A) and (C), respectively. The yellow, green, orange and red bars bracket the times of mEP, MEP, Ae and R, respectively. Air temperature, shown in green in (C), at Crystal geyser. The selected period of B1 in (B) highlights the pressure change during a minor eruption and B2 highlights the pressure change during the MEP(B). The selected period of D1 in (D) denotes the minor bubbling event which initiates the mEP and D2 represents the Ae, which occur at the onset of the recharge period during observation in 2013.

Fig. 3. Comparison of interval to eruption length. (A) Eruption intervals and durations of Crystal, Tenmile, and Chimayó geysers with their trend (dashed) lines. (B) The magnified view of short eruption intervals and durations shown in (A). The 2010, 2012, and 2013 eruption interval and lengths at Crystal geyser are from Han et al. (2013), Kampman et al. (2014), and this study, respectively.

Fig. 4. Periodicity of Tenmile geyser. Variations of pressure and temperature within the well of Tenmile geyser in (A) 2011 and (C) 2013, respectively. Air temperature at the nearby Crystal geyser is shown in green in (C). (B) Variations of pressure and temperature during a single eruption cycle from the blue-highlighted region in (C). The green, blue, red and yellow bars bracket the times of the MEP, D, mEP and R, respectively. (D) Long term temperature fluctuations from the yellow-highlighted region in (C). D1, D2 and D3 refer to the three temperature spikes which make up the long term temperature fluctuation.

Fig. 5. Periodicity of Chimayó geyser. (A) Variations of pressure and temperature within the well of Chimayó geyser in 2008. (B) Variations of pressure and temperature during a single eruption cycle from the blue highlighted region in (A). The green and red bars bracket the times of the major eruption period (MEP) and recharge (R), respectively.

Fig. 6. (A) Interpolated eruption pressure (dashed lines) and temperature gradients (solid lines) based on the measured pressure and temperature at two transducers. (B) CO₂ solubility profiles (dashed lines) calculated from Duan and Sun (2003) and density of the CO₂-NaCl-H₂O mixture (solid lines) over depth calculated from Duan et al. (2008). (C) Calculated relationship between exit velocity and flash depth. Stars and error bars represent predicted flash depths of Crystal, Tenmile, and Chimayó geysers.

842 Fig. 7. Conceptual model of the eruptive process. Green and blue colors are representative of
843 CO₂ saturated and undersaturated waters, respectively. CO_{2(g)} bubbles are shown in white and the
844 flash depth (FD) is marked by the red dashed line. Plots showing the pressure (red line), flash
845 depth (horizontal black dashed line) and bubble volume fraction (blue dashed line) over depth
846 during the respective periods below.

847 Fig. 8. Simulation results of (A) mixture velocity (liquid water and CO_{2(g)}) and CO₂ bubble
848 volume fraction and (B) temperature over depth.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1. CO₂ Emission variables and results.

	Eruption height (m): Mean (Min.-Max)	Well Area (m²)	Bubble Volume Fraction: Mean (Min.- Max)	Exit velocity (m/s): Mean (Min.-Max)	Eruption duration (min): Mean	CO₂ emission per eruption period (kg)	Annual CO₂ emission (tonnes)
Crystal mEP(A/C)	1 (0.5-2)	0.119	0.11 (0-0.16)	4.4 (3.2-6.2)	9	$(1.02 \pm 0.42) \times 10^2$	$(8.05 \pm 3.31) \times 10^2$
Crystal MEP(B)	5 (2-8)	0.119	0.22 (0-0.70)	10 (6-12.5)	72	$(3.08 \pm 1.23) \times 10^3$	$(6.75 \pm 2.70) \times 10^2$
Crystal MEP(D)	5 (2-8)	0.119	0.22 (0-0.73)	10 (6-12.5)	348	$(1.50 \pm 0.60) \times 10^4$	$(3.29 \pm 1.32) \times 10^3$
Tenmile	2 (1-3)	0.042	0.11 (0-0.64)	6.25 (4.5-8)	11.2	$(5.63 \pm 1.58) \times 10^1$	$(6.17 \pm 1.73) \times 10^1$
Chimayó	18 (16-20)	0.008	0.52 (0-0.75)	18.5 (17-20)	7.8	$(1.58 \pm 0.14) \times 10^2$	$(6.54 \pm 0.57) \times 10^1$

Table 2. Numerical Simulation Parameters.

Model Parameter	Value
Length of Well, (L)	100 m
Radius of Well, (R_w)	0.05 m
Deviation angle of Well, (θ)	0°
Overall heat transfer coefficient (U_{to})	1.0 J/ms°C
Surface Temperature ($T _{x=L}$) and Surface Pressure ($p _{x=L}$)	11.85°C 0.101 MPa
Bottomhole Temperature ($T _{x=0}$) and Bottomhole Pressure ($p _{x=0}$)	15.85°C 1.101 MPa
H ₂ O and CO ₂ Mole Fraction ($z_{H_2O}^0$ and $z_{CO_2}^0$)	0.96, 0.04
Joule-Thomson Coefficient (H ₂ O, CO ₂) ($\eta_{L(H_2O)}$ and $\eta_{G(CO_2)}$)	-0.22, 11.2 °C/MPa
Heat Capacity (H ₂ O, CO ₂) ($C_{pL(H_2O)}$ and $C_{pG(CO_2)}$)	4.18, 0.84 J/g°C
Inlet Velocity ($v_m _{x=0}$)	1, 1.25, 1.5, 1.75, 2 m/s